

DEVELOPMENT OF INEXPENSIVE CELLULOSE-BASED SORBENTS FOR CARBON DIOXIDE

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Abstract - Aqueous amine solutions are benchmark solvents for CO₂ capture and their operational drawbacks are well-known. In order to overcome these problems, the support of amines on solid materials appears as an option for CO₂ capture. Cellulose is a versatile and low-cost material that can be used as a support. This study reports chemical modification of cellulose fibers extracted from rice husk with different amines and their potential for CO₂ capture. The obtained compounds were characterized by different techniques. The CO₂ sorption capacity was gravimetrically assessed in a Magnetic Suspension Balance. Quantum mechanical simulations and experimental results revealed that -NH- and -NH₂ represent major working sites of the employed compounds. The best result for CO₂ sorption was attained for the amine-modified cellulose CL-D-400 with a sorption capacity of 409 μmol CO₂/g at 1 bar and 1091 μmol CO₂/g at 10 bar with amine concentrations as low as 2 × 10⁻⁶ mol/mg. **Keywords:** Cellulose; Rice husk; CO₂ capture; Amines; Simulation.

INTRODUCTION

The CO₂ concentration in the atmosphere is increasing every year, as well as global warming and its effect on climate change (Barbosa et al., 2016; Chan et al., 2016; Hussain et al., 2015; Nouri and Ebrahim, 2016; IPCC, 2013; Seo et al., 2014). Preventing the growth of carbon dioxide emissions in the atmosphere is essential for achieving the global warming reduction target (Dutcher et al., 2015). Different strategies have been considered and adopted by several countries aiming to reduce the CO₂ emissions, such as the improvement of energy efficiency, increasing the use of low carbon fuels or nuclear energy, renewable energy development, geo-engineering approaches and CO₂ capture and storage (CCS)(Garcés et al., 2013; Leung et al., 2014). Among these different strategies, CCS is considered crucial because it reduces the CO₂

emission from large emission sources (Arias et al., 2016; Gardarsdóttir et al., 2015; Kamarudin and Alias, 2013; Leung et al., 2014).

Chemical absorption using amine aqueous solutions is a benchmark technology for CO₂ capture (Arias et al., 2016; Bachelor and Too-chinda, 2012; Kamarudin and Alias, 2013). However, it has some operational drawbacks, such as high power consumption required for solvent regeneration, equipment corrosion (Gray et al., 2005; Kamarudin and Alias, 2013), degradation/evaporation of amines, the need of a large-volume absorber (Yu et al., 2012), besides additional operating costs due to substitution of solvents (Seo et al., 2014).

To overcome the drawbacks of chemical absorption, the impregnation and grafting of amines on solids have been suggested in the literature (Bachelor and Too-chinda, 2012; Gray et al., 2005; Knowles et al., 2005; Lima et al., 2015; Yu et al., 2012). Unfortunately, many

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of these commercial sorbents remain prohibitively expensive (Bachelor and Toochinda, 2012). This generates the necessity of developing inexpensive sorbents for CO₂ capture. As alternatives for obtaining low-cost sorbents, impregnation of agricultural wastes with amines has been suggested. Some examples are bagasse, rice straw, industrial residues, such as mullite, fly ash and other oxygen rich sorbents (Bachelor and Toochinda, 2012; Gray et al., 2004). Strategies to use residues for CO₂ capture will foster emergence of green technologies and sustainable development.

Brazil is among the ten largest rice producers in the world. By 2017, it produced about 11 759 096 tons of rice. Rice husk (RH) is a major agricultural waste generated as a byproduct during the rice milling stage (Rosa et al., 2012), while cellulose constitutes about 33% of rice husk (Johar et al., 2012).

Cellulose is the most abundant natural polymer (Zhang et al., 2016). It is a low-cost versatile material, thermodynamically stable, presenting crystalline structure and numerous hydrogen bonds (Shukla et al., 2013). Cellulose undergoes functionalization primarily through the hydroxyl groups (Cuadro et al., 2015; Shukla et al., 2013).

Previous studies have been conducted on nanofibrillated cellulose modification using aminosilanes for CO₂ capture from the air (Gebald et al., 2011, 2013). Commercially fibrillated cellulose suspension was used in that work. Herein, we investigated chemical modification of cellulose fibers, extracted from rice husk, with different amines. The potential of the newly developed compounds for CO₂ capture was characterized. Quantum mechanical simulations were employed to elucidate the impact of different functional groups on CO₂ sorption.

EXPERIMENTAL SECTION

Materials

The rice husks were donated by Cooperativa Arrozeira Extremo Sul Ltda. The material was washed with distilled water and dried in an oven at 100°C for 8h. The dried husk was ground in a knife mill. The fraction that passed through the 20 mesh sieve (0.841 mm) was collected. Anhydrous citric acid (CA, 99.5% Synth), sodium hydroxide (NaOH, 97% Vetec), hydrogen peroxide (H₂O₂, 35%, Neon), N,N-dimethylformamide (DMF, 99.5%, Merck), ethanol (CH₃CH₂OH, 99%, Vetec), hydrazine (32.04 g/mol, HYD, aqueous solution 65%), ethylenediamine (60.10 g/mol, EDA, 99%, Vetec), Jeffamine® M-2005 (Mn = 2000 g/mol, Huntsman), Jeffamine® D-4000 (Mn = 4000 g/mol, Huntsman), Jeffamine® D-400 (Mn = 430 g/mol Huntsman), Jeffamine® EDR-148 (Mn = 148 g/mol, Huntsman) were used as purchased.

Cellulose extraction

The cellulose extraction was adapted from literature procedures (Johar et al., 2012; Teodoro et al., 2011). The rice husk was treated with 4 wt% NaOH at 90°C for 2h to remove the lignin and hemicellulose of the rice husk fibers. The acid hydrolysis treatment was conducted on the fibers after alkali treatment using 10.0 mol/L H₂SO₄ at 50°C for 40 min under continuous stirring. Afterwards, bleaching was carried out by addition of 16% (v/v) H₂O₂ and 5 wt% NaOH solution in a 1:1 proportion (v/v) at 55°C for 2h to remove the remaining lignin. The rice husk: solution ratio was 0.05 g/mL. Each step was repeated for five times. The solid was filtered and washed with distilled water until neutral pH was achieved and dried at 50°C in the oven after each treatment.

Cellulose chemical modification

Cellulose chemical modification was performed in two stages. The first was modification with citric acid (Figure 1). The second step was functionalization with amines (Figure 2). The modification with citric acid was performed by a similar procedure described elsewhere (Rodrigues et al., 2006; Zhu et al., 2008). The cellulose was poured into a flask containing 1.2 mol/L aqueous solution of citric acid to obtain 100g/L cellulose solution. This solution was stirred for 0.5h at room temperature. The temperature was increased up to 120°C and kept constant 1.5h under stirring. After cooling, the cellulose was washed with distilled water in the proportion of 200 mL/g for several times to remove any excess of citric acid and dried at 55°C for 24h. The concentration of carboxylic groups (mol/mg) introduced into the modified cellulose was determined by back titration (Gurgel et al., 2008; Karnitz et al., 2007; Shang et al., 2016), by treating the material (0.1 g) with 100 mL of an aqueous solution of NaOH (0.02 mol/L) for 1h under constant stirring. The materials were separated by filtration and the solution was titrated with HCl (0.02 mol/L).

The amine functionalization reaction is described elsewhere (Bernard et al., 2016; Magalhaes et al., 2014). In a Schlenk flask, under N₂ atmosphere 1g of citric acid modified cellulose was added to the amine (molar ratio COOH/AMINE = 1:1) dissolved in 15 mL of dimethylformamide (DMF). The mixture was stirred at 40°C for 2h. The materials were separated by filtration, washed repeatedly with distilled water and ethanol and dried at 55°C for 24h. The concentration of amine (mol/mg) introduced into the modified cellulose was determined by back titration, by treating the material (0.1 g) with 100 mL of an aqueous HCl solution (0.02 mol/L) for 1 hour under constant stirring. The materials were separated by filtration and the solution was titrated with NaOH (0.02 mol/L) (Gurgel et al., 2008; Karnitz et al., 2007) (see Figure 2).

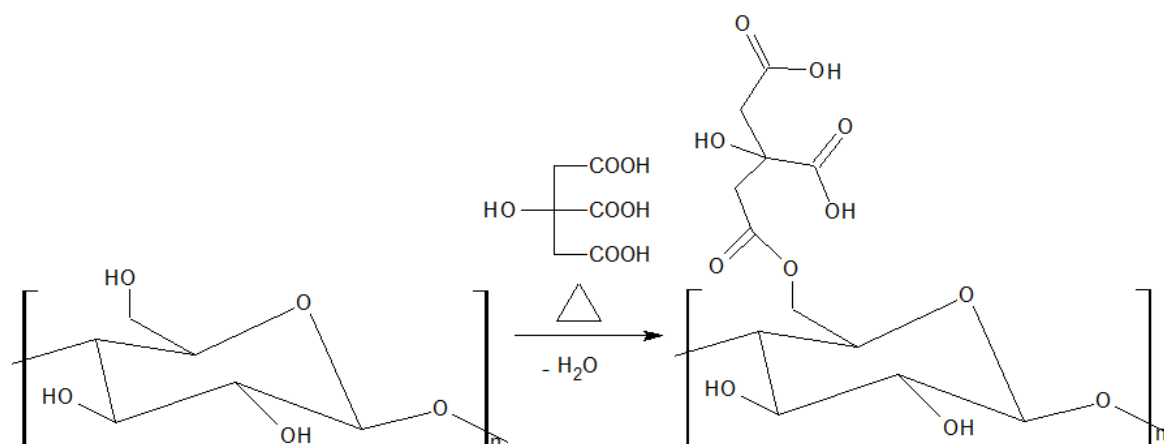


Figure 1. Schematic representation of the carboxylic acid functions introduced on the cellulose surface.

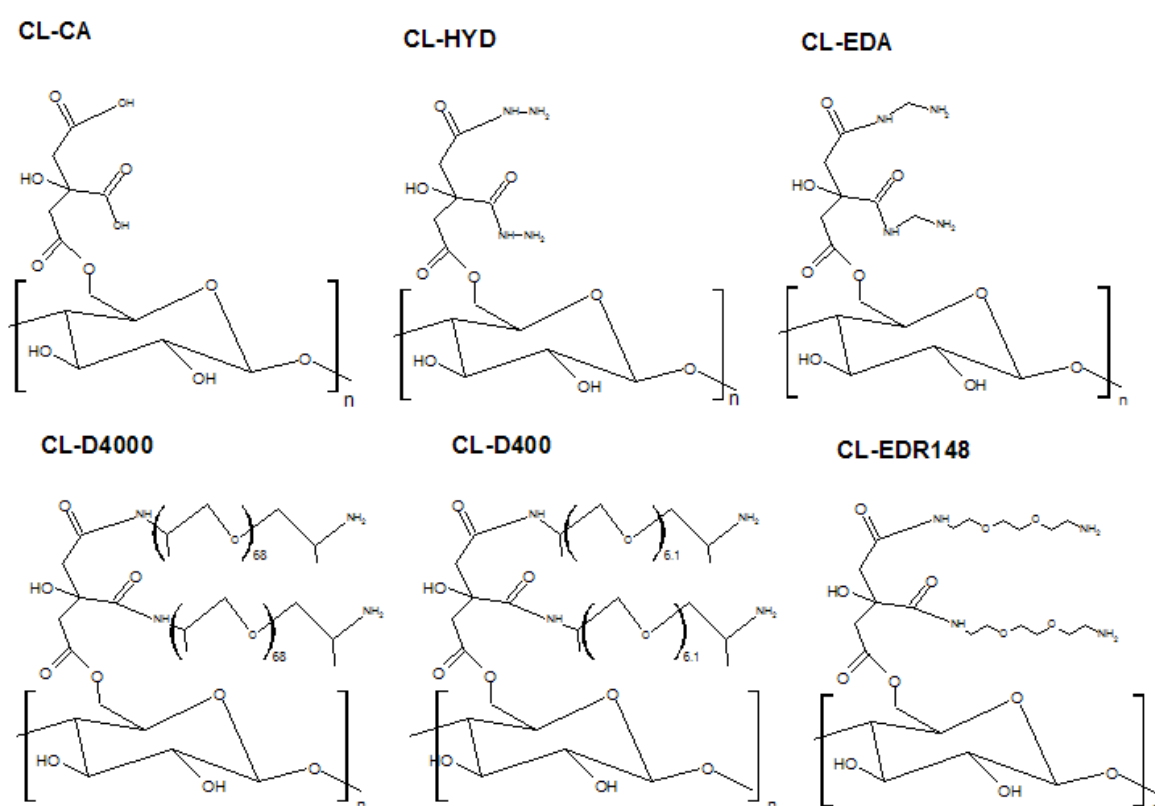


Figure 2. Schematic representation of amine-modified cellulose.

Characterization

The synthesized materials were characterized with a Universal Attenuated Total Reflectance sensor (UATR-FTIR) using a Perkin-Elmer Model 100 FTIR Spectrum, in the range 4000–650 cm^{-1} . Field emission scanning electron microscopy (FESEM) analyses were performed in a FEI Inspect F50 equipment in secondary electrons (SE) mode. Thermogravimetric Analysis (TGA) was performed using a TA Instruments SDT-Q600 between 25°C and 600°C with a heating rate of 10°C/min in nitrogen atmosphere. Specific surface area and pore size were calculated from nitrogen sorption data using Brunauer-Emmett-Teller (BET) at -196°C (Micromeritics, ASAP 2420). Powder X-ray

diffraction (XRD) pattern was recorded on Bruker-AXS D8 ADVANCE diffractometer operated at 40 kV and 20 mA using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the range 3–40° with a step of 0.02° and scanning time of 1.0 min. The Segal method (Eq. 1) was used to calculate the sample crystallinity index (CrI) of the samples (Segal et al., 1959).

$$\text{CrI} = \frac{I_{002} - I_{\text{AM}}}{I_{002}} 100 \quad (1)$$

where I_{002} is the maximum intensity of the 002 peak and I_{AM} is the intensity scattered by the amorphous part

of the sample. The diffraction peak for plane (002) is located at diffraction angle around $2\theta = 22^\circ$ and the intensity scattered by the amorphous part is measured as the lowest intensity at a diffraction angle around $2\theta = 18^\circ$ (Johar et al., 2012).

Ab Initio Calculations

Thermodynamics of the reactions was estimated using molecular partition functions obtained from the numerical *ab initio* calculations and subsequent vibrational frequency analysis. The Gaussian-X composite schemes proposed by Curtiss and coworkers (Curtiss et al., 1998; Curtiss et al., 2007) were used. For an interested reader, we compared G-3 with its simplified modification G-3-MP2, as well as a newer method, G-4-MP2. The term 'MP2' in the method designation means that the MP4 stage in the original composite method (G-3, G-4) was substituted by the MP2 stage (Curtiss et al., 1999). The reported results correspond to an ideal gas approximation. Gibbs free energy, enthalpy and entropy of each process, computed at given external conditions, are based on the Hess law of constant heat summation and known relations between these thermodynamic quantities.

Binding energies were computed using the Becke-3-LYP hybrid density functional (Becke, 1988; Lee et al., 1988) with the 6-311+G* atom-centered split-valence triple-zeta basis set. Both polarization and diffuse functions are included in this basis set for higher accuracy of the theoretical results. The basis set superposition error was excluded through the counterpoise approach. The geometries of the molecules were appropriately optimized prior to computing binding energies at the requested level of theory.

Gas adsorption measurements

Pure gas sorption (CO_2) in the samples was gravimetrically assessed in a Magnetic Suspension Balance (MSB), (Rubotherm Prazisionsmesstechnik GmbH, 35MPa and 400°C) equipped with a single sinker device for absorbate density determination and thermostated with an oil bath (Julabo F25/ $\pm 0.1^\circ\text{C}$). The apparatus details are described elsewhere (Blasig et al., 2007; Dreisbach and Lösch, 2000). When compared to other gravimetric sorption methods, the MSB device has the advantage of allowing high-pressure sorption measurements since the sample can be potted into a closed chamber coupled to an external precise accurate balance (accuracy of $\pm 10 \mu\text{g}$). The samples (0.06 to 0.09 g) were weighed and transferred to the MSB sample container, and the system was subjected to 10^{-7} MPa vacuum at the temperature of the sorption measurement, 25°C , for 24 hours (constant weight was achieved in this time). The gas (CO_2 , Air Liquide / 99.998 %) was admitted into the MSB

pressure chamber up to the desired pressure, 0.1-3 MPa. In this study, a pressure gauge with an accuracy of 10^{-3} MPa was used to control the system pressure. The gas solubility in the samples for each isotherm and pressure considered was measured during 3-4 hours until no more weight increase for gas sorption was observed. At this step of gas solubility in the samples, the weight reading from the microbalance at pressure P and temperature T is recorded as $W_t(P,T)$. The mass of the adsorbed gas in the sample (W) was calculated using the following equation (2):

$$W = [W_t(P,T) - W_{sc}(P,T) + \rho_g(P,T) \cdot (V_{sc}(T) + V_s(T))] - W_s(\text{vac},T) \quad (2)$$

where $W_{sc}(P,T)$ is the weight of the sample container, $\rho_g(P,T)$ stands for gas density, directly measured with the MSB coupled single-sinker device, dismissing the application of any equation of state to calculate the gas sorption, $V_{sc}(T)$ is the volume of the sample container, determined from a buoyancy experiment when no sample is charged into the sample container, $V_s(T)$ the specific solid sample volume, $W_s(\text{vac},T)$ is the weight of samples under vacuum and the term $\rho_g(P,T) \cdot (V_{sc}(T) + V_s(T))$ represents the buoyancy force. In this work, the solubility in the sample was treated as the excess solubility.

RESULTS AND DISCUSSION

Specific surface area, amine load and crystallinity

Table 1 shows amine loading and crystallinity for each sample. The specific surface area was insignificant and close to the experimental error, indicating this material does not show porosity. The concentration determined of carboxylic functions of the CL-CA sample was 2.15×10^{-6} (mol/mg). This result is close to the previously known investigations (Gellersted and Gatenholm, 1999). The concentration of the loaded amines ranged from 2.00×10^{-6} to 2.04×10^{-6} (mol/mg), indicating that almost all supplied carboxyl groups were reacted. The corresponding crystallinity values are discussed below.

Table 1. Specific surface area, amine loading and crystallinity.

Sample	Amine loading (mol/mg)	Crystallinity (%)
CELLULOSE	-	87
CL-CA	-	84
CL-HYD	2.00×10^{-6}	91
CL-EDA	2.04×10^{-6}	88
CL-M2005	2.02×10^{-6}	-
CL-D400	2.03×10^{-6}	63
CL-D4000	2.01×10^{-6}	-
CL-EDR 148	2.03×10^{-6}	86

X-ray diffraction (XRD)

Figure 3 shows the X-ray diffraction profile of the extracted cellulose and modified cellulose samples.

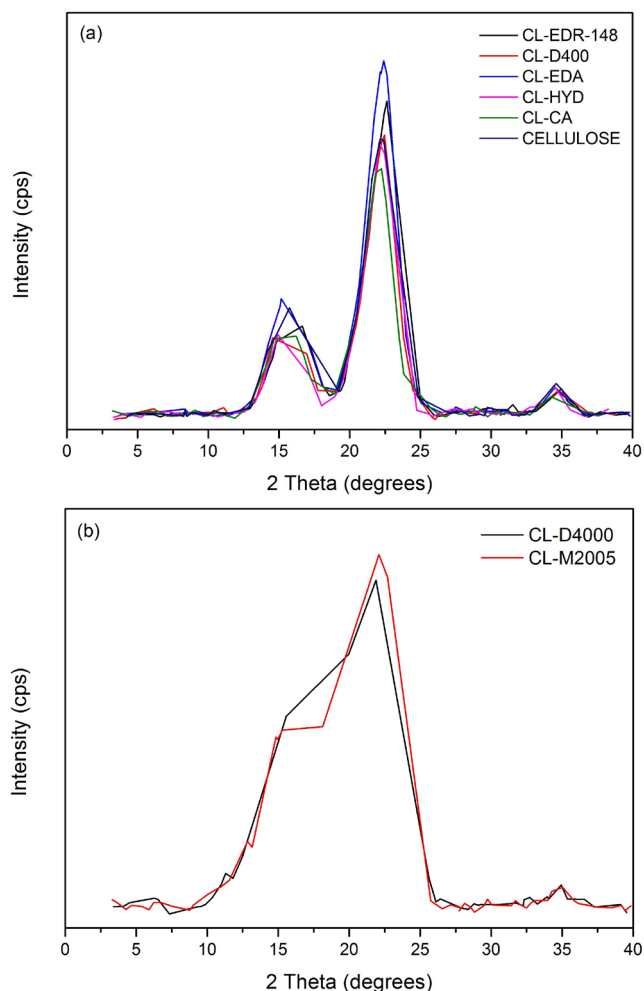


Figure 3. XRD pattern of cellulose and modified celluloses samples.

All samples exhibit typical cellulose peaks around $2\theta = 16^\circ$, 22.6° and 35° (Johar et al., 2012; Zhang et al., 2016). The patterns indicated that the obtained cellulose presented a typical form of cellulose I since there was no doublet in the main peak at $2\theta = 22.6^\circ$ (Li et al., 2009). One can also observe a change in the profile of the x-ray diffraction patterns after the chemical modification. The samples that were modified with amines containing higher molecular weight side chain presented less defined peaks, indicating a lower organization when compared with cellulose and the samples obtained with amines containing lower molecular weight side chains. The crystallinity index values (Table 1) highlight that cellulose modified with low-molecular-weight amines (CL-HYD; CL-EDA, CL-EDR-148) present higher crystallinity values. The compound CL-D-400 functionalized with Jeffamine® D-400 ($M_n = 430$ g/mol) showed considerable decrease in crystallinity. The samples synthesized with higher-molecular-weight amines (CL-M-2005 and CL-D-4000) exhibited skewed peaks, which indicate that a new assembly is formed

via the inserted side chain. These results indicate that the bigger the size of the inserted side chain the smaller the crystallinity of the sample, probably due to the reduction in the packing degree of cellulose molecules caused by side chains.

Spectroscopic characterization

The infrared spectra of cellulose in all samples (Figure 4-a, b and c) showed a broad band located at $3330 - 3340$ cm^{-1} , attributed to the stretching of the OH groups, band near 2920 cm^{-1} related to C-H stretching, band at 1160 cm^{-1} corresponding to C-O-C asymmetrical bridge stretching, broad bands around 1050 cm^{-1} and 890 cm^{-1} related to the C-H and C-O stretching vibration of the cellulose structure (Johar et al., 2012; Rosa et al., 2012). Having compared spectra for cellulose (Figure 4a) and citric acid modified cellulose (Figure 4b), we identified a strong band at 1740 cm^{-1} attributed to the carboxylic acid (X-COOH). This evidences introduction of citric acid into the cellulose chain (Cuadro et al., 2015). Figure 4c presents the FTIR for CL-400 sample. A reduction in intensity of the carboxyl group absorption band (1740 cm^{-1}) due to the chemical modification with amines was observed. A new band at 1454 cm^{-1} , characteristic of the symmetric bending of primary amines (NH_2) and at 2869 cm^{-1} relative to the CH_2 stretching modes of the amine chains (Yu et al., 2012). A shoulder at 3286 cm^{-1} is evidenced which may be attributed to amide N-H stretching vibrations (Yu et al., 2012).

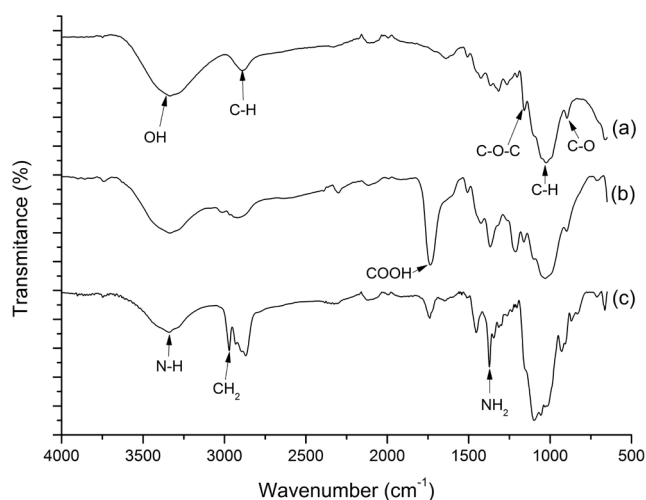


Figure 4. FTIR spectra of: (a) cellulose, (b) citric acid modified cellulose and (c) CL-D400.

Thermogravimetric Analysis (TGA)

Figure 5 presents TG and DTG curves obtained for all materials. All samples showed two thermal events. The earlier weight loss was ca. 4% and t_{onset} below 100°C , attributed to water vaporization. The later weight loss attributed to cellulose degradation (t_{onset} of 289°C and T_{max} of 324°C) being 71%. The

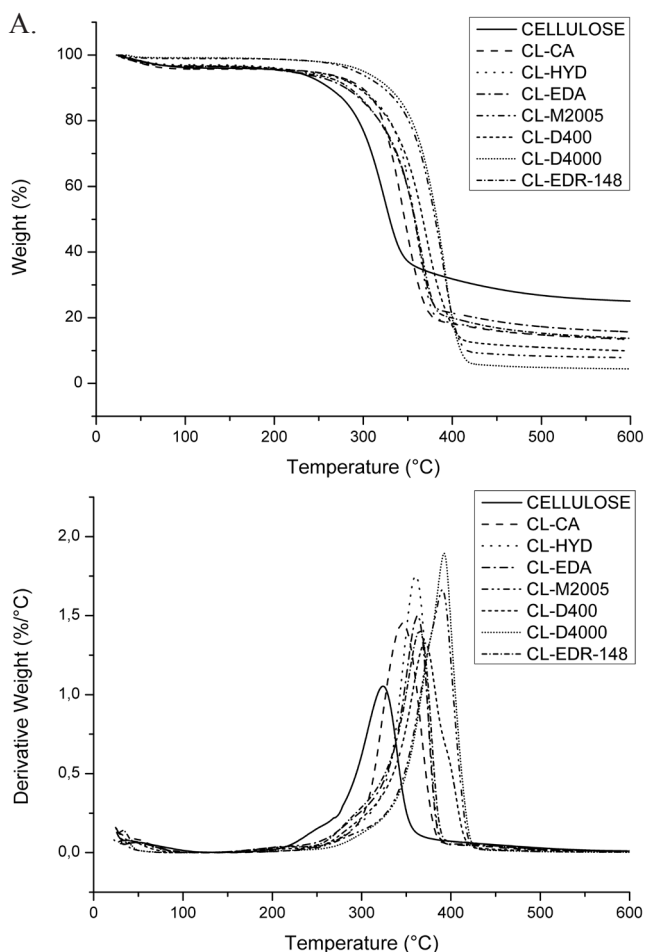


Figure 5. TG (a) and DTG (b) curves for cellulose and modified celluloses samples.

modified samples presented a higher thermal stability than cellulose. Degradation temperatures varied from $t_{\text{onset}} = 318^{\circ}\text{C}$ to 360°C and $T_{\text{max}} = 346^{\circ}\text{C}$ to 392°C with a weight loss around 83%.

Field emission scanning electron microscopy (FESEM)

Figure 6 exemplifies different effects on the rice husk surface after cellulose extraction as well as chemical modification. The cellulose extraction in the form of bundles of fiber (Figure 6b) can be highlighted by comparing with the smooth compact surface of the untreated rice husk (Figure 6a). Citric acid modified cellulose (Figure 6c) showed similar morphology to that shown by the sample after bleaching treatment (Figure 6b). Amine modification of cellulose samples led to a separation of fiber bundles, especially sample CL-D-400 (Figure 6g). This may contribute to the increase of contact surface area and, consecutively, to CO_2 sorption.

Gas sorption measurements

Table 2 presents the experimental results for CO_2 sorption at 1 bar and 10 bar for the synthesized materials. Note that at both pressures all amine-functionalized samples presented higher sorption values when compared with the citric acid modified cellulose (CL-CA).

The experimental results corroborate the thermodynamic potentials obtained by simulation (see section 3.7), which indicated that for CL-

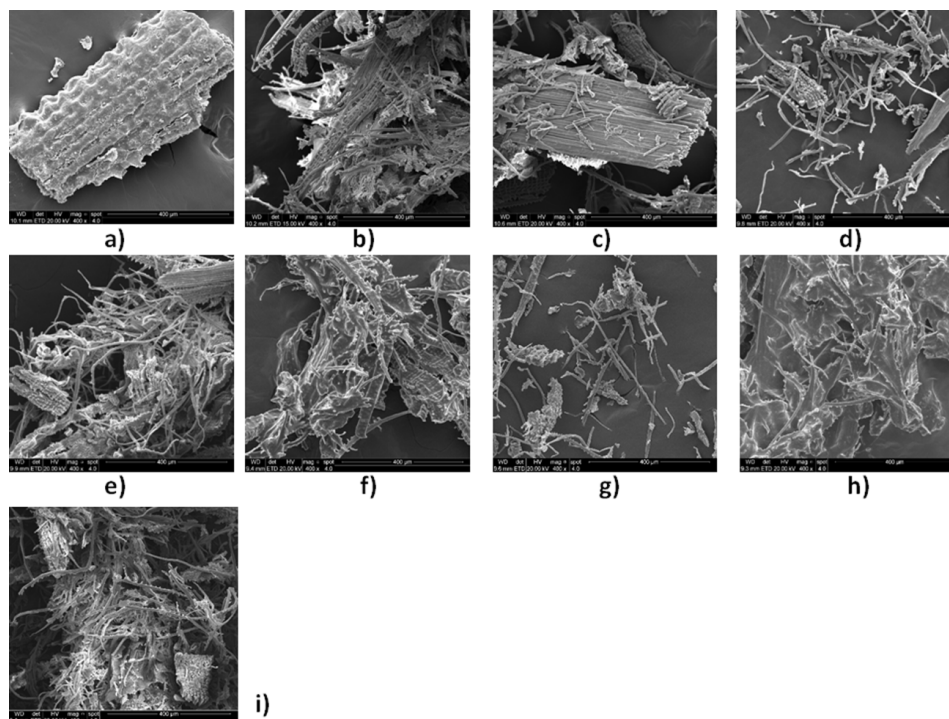


Figure 6. Micrographs of the materials: (a) rice husk fibers, (b) cellulose, (c) CL-CA, (d) CL-HYD, (e) CL-EDA, (f) CL-M2005, (g) CL-D-400, (h) CL-D-4000, (i) CL-EDR-148.

Table 2. Sorption values for cellulose and amine modified cellulose samples at 25°C.

Sample	10 bar	1 bar
	$\mu\text{molCO}_2/\text{g}$	
CL-CA	243	0.227
CL-HYD	864	287
CL-EDA	1045	346
CL-EDR-148	961	330
CL-D-400	1091	409
CL-D-4000	777	264
CL-M-2005	961	334

CA sample only via physisorption occurs; CO_2 is adsorbed due to electrostatic interactions. However, for samples functionalized with NH and NH_2 groups, chemisorption occurs. It is well-known that the interaction between the basic surface and acidic CO_2 molecules results in the formation of surface ammonium carbamates under anhydrous conditions (Yu et al., 2012). Among the amine-modified cellulose samples, the best CO_2 sorption result was obtained for the sample functionalized with CL-D-400, whereas the worst result was recorded in the case of CL-D-4000. The micrograph images (Figure 6g) showed a better separation of fiber bundles for the sample CL-D-400. This can improve the interaction of CO_2 with the cellulose chain groups. For the CL-D-4000 sample, (Figure 6h) a higher compaction of the fibers is observed, which can hinder the interaction with CO_2 . More detailed discussion regarding the interaction of the compounds with CO_2 is available below.

The CO_2 sorption capacity of the amine modified cellulose described in this study was lower when compared with commercial solid adsorbents (1800-2000 $\mu\text{mol}/\text{g}$) of surface areas of 1000 to 1700 m^2/g (Gray et al., 2004). However, the cellulose used in this study originates from an agricultural residue and presents a low amount of amine (2×10^{-6} mol/mg) when compared to the literature (concentrations of 10-20% (w/w)) (Bachelor and Toochinda, 2012). For example, the sorption results at 1 bar and 30°C were 351 $\mu\text{mol CO}_2/\text{g}$ (for bagasse enriched with 20% of DEA) and 329 $\mu\text{mol CO}_2/\text{g}$ (for rice chaff). These results are similar to that obtained for CL-EDA (346 $\mu\text{mol CO}_2/\text{g}$) and lower than the sorption values obtained for the sample CL-D-400 (409 $\mu\text{mol CO}_2/\text{g}$) using lower amine concentrations of around 2×10^{-6} (mol/mg).

In order to examine the reusability of the best material, CL-D-400 was subjected to five additional runs. The sorption was carried out at 25°C under 1 bar of CO_2 pressure. The CO_2 desorption was carried out at 100 °C. At the end, a loss of 5% in the sorption capacity was observed. We believe the sorption capacity loss is related to ammonium carbamate formation as evidenced in the proposed mechanism described in the literature (Aboudi and Vafaezadeh, 2015).

Quantum mechanical simulations

Our experimental results (Table 2 with gas-capture results) indicate that all employed compounds, except CL-CA, exhibit a similar performance. Pressure increase leads to better CO_2 capture, while the order of the compound efficacies persists. A poor performance of CL-CA is due to the absence of chemisorption in this case and weak attraction of the CO_2 molecule to the protonated acetate group. Indeed, the computed binding energy for this case amounts to just 7 kJ mol^{-1} . The other results can be rationalized via computation of thermodynamic potentials for chemisorption of the molecular fragments (Figure 7), which represent the major working sites, $-\text{NH}-$ and $-\text{NH}_2$, of the employed compounds.

Thermodynamic potentials (Figure 8) were used to rationalize the experimentally observed performances of the cellulose-based compounds. The depicted potentials correspond to the chemisorption reactions, but omitting subsequent solvation and ionization in aqueous media. This is done for simplicity of discussion and straightforward comparison. For instance, a total free energy of ethylamine is 20 kJ mol^{-1} , due to hydrogen bonds between the products of chemisorption and media. Johnson and coworkers (Xie et al., 2010) thoroughly investigated the mechanism of CO_2 chemisorption by the primary amine and presented extensive evidence that the two-step pathway via a zwitterion intermediate is most energetically favorable and, thus, most expected under the working conditions.

The trend of enthalpy completely repeats the trend of free energy (Figure 8). The entropic contribution is similar in all cases. Therefore, the chemical environment (in particular, non-covalent binding energy) is responsible for the difference between the considered molecular fragments. The best performance was found for CL-D-400 and CL-EDA. This is confirmed theoretically by the thermodynamics of

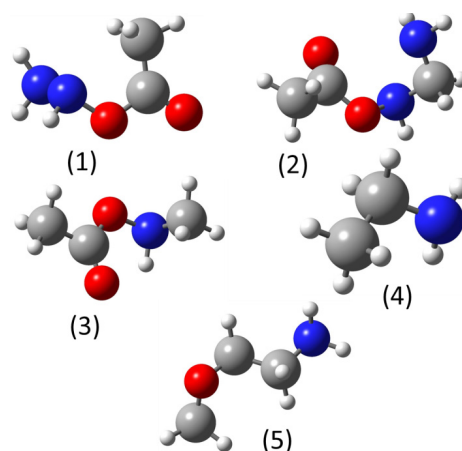


Figure 7. Optimized structures of the molecular fragments which are responsible for CO_2 capture in the modified cellulose species.

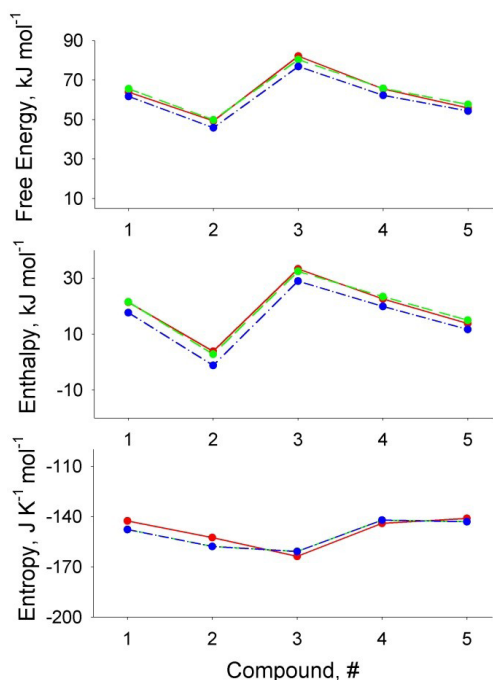


Figure 8. Free energy (top), enthalpy (center) and entropy (bottom) for CO₂ capture through chemisorption at -NH₂ by the molecular fragments depicted in Figure 7. The results from the G-4-MP2 method are red solid lines, from the G-3-MP2 method are green dashed lines, from the G-3 method are blue dash-dotted lines.

fragment 2, whose free energy and enthalpy are lowest. The chemisorption is conducted both through the amide and amine groups and their high concentrations in the compounds. The performance of CL-D-4000 is worse, since that compound contains lots of ether groups, which are not efficient for CO₂ fixation. The ether group itself attracts CO₂ weakly. The binding energy corresponding to this process is 8 kJ mol⁻¹. The impact of a few available carboxylate groups is even smaller, 4 kJ mol⁻¹ in terms of binding energy. The performance of CL-HYD is inferior to that of CL-EDA, because the amide group cannot bind CO₂ in the -NH-NH₂ configuration. The resulting compound is unstable (according to the stationary-point-search simulations) and, therefore, is never formed. In turn, separating -NH- and -NH₂ by one or two methylene groups allows to achieve a more decent CO₂ capture.

It is noteworthy that the gas-phase thermodynamics provides a correct account of the reactions occurring in the condensed phase allowing one to rate large molecules with multiple binding sites. This fact also suggests that intra-molecular interactions are more important than inter-molecular ones upon chemical adsorption. All methods, G-3, G-3-MP2, G-4-MP2, for thermodynamic potentials provide very similar results.

Since a total number of molecules decreases upon chemisorption, a pressure increase shifts this reaction

rightwards. Figure 9 depicts an effect of pressure up to 1000 MPa. The latter brings the 34 kJ mol⁻¹ free energy increase. An approximate shift of the chemisorption equilibrium constant can be estimated from the following relationship: $K^i = \exp(-G^i/R \times T)$, where T is temperature, R is the gas constant, Gⁱ is the free energy at the given conditions. These calculations allow to determine to which extent it is economically feasible to invest in the high-pressure apparatus. The calculated effect of pressure is in concordance with our experimental results. In all systems, higher pressure results in a significantly better CO₂ fixation.

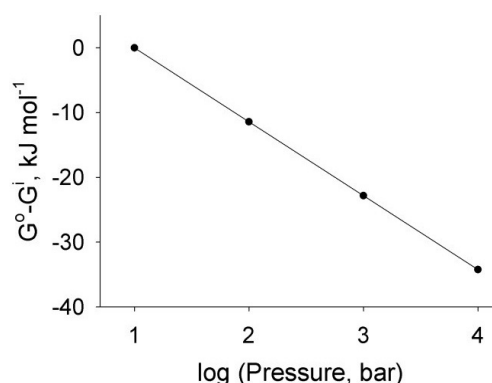


Figure 9. Free energy decrease due to elevation of external pressure. The thermodynamics of the CO₂ capture reaction by ethyl amine were considered for an example.

CONCLUSION

The chemical modification of cellulose fibers, extracted from rice husk, with different amines was performed. The potential of the obtained compounds for use as sorbents for CO₂ capture was evaluated. The quantum mechanical simulations and the experimental results revealed the role of each moiety of the new compounds in the gas capture process. A poor performance of CL-CA was due to the absence of chemisorption in this case and a relatively weak attraction of the CO₂ molecule to the protonated acetate group. The best performance was found in CL-D-400 (409 μmol CO₂/g at 1 bar). This result is confirmed theoretically by the thermodynamics of fragment 2, whose free energy and enthalpy are lowest. The chemisorption is conducted both through the amide and amine groups, therefore, their high concentrations in the compounds are important. On the other hand, when a higher-molecular-weight amine was used (CL-D-4000) the performance was worse, since that compound contained lots of ether groups, which are not efficient for CO₂ fixation. The performance of CL-HYD is inferior to that of CL-EDA, because the amide group cannot chemically bind CO₂ in the -NH-NH₂ configuration. In turn, separating -NH- and -NH₂ by one or two methylene groups results in a more decent

CO₂ capture. Higher pressure results in a significantly better CO₂ fixation. The use of an industrial residue, cellulose, is a low-cost option material for CO₂ capture.

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