CO$_2$ adsorption by cryogels produced from poultry litter wastes

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Abstract

Poultry litter waste (PLW) is the main by-product generated by the Brazilian poultry industry. A sustainable approach for reusing this waste is the production of biochar to be further used aiming CO$_2$ adsorption. In this work, biochars were produced by varying the N$_2$ flow along the pyrolysis process of 150 (PLW-150) and 1000 (PLW-1000) mL min^{-1}. PLW and biochars were characterized for their morphology, porosity, specific surface area, and CO$_2$ adsorption capacity. From the biochars, carbon cryogels (CC) were produced aiming their use as CO$_2$ adsorbents. The results of the cryogel adsorption test showed a CO$_2$ adsorption capacity of 13.1±2.9 and 33.8±3.3 mg g^{-1} for the CC-PLW.150 and CC-PLW.1000 cryogels, respectively. Therefore, reusing this residue for cryogels production and its use in the CO$_2$ adsorption signifies an attractive perspective to minimize the environmental damage caused by CO$_2$ emissions.

Keywords: *biochar, carbon cryogels, CO$_2$ adsorption, porous materials, poultry litter wastes.*

1. Introduction

According to Brazilian Agricultural Research Corporation (EMBRAPA), Brazil had a 3% increase in national chicken production in 2019, holding third place in the world ranking. Considering other poultry species in addition to chickens rearing, there is an excessive waste generation, mostly made up of poultry litter.

Poultry litter waste is the material spread out on the aviaries' floor to provide bedding for the birds. This material is usually composed of wood chips, sawdust, wheat, straw, peanut husks, rice husks, among others, and cellulose as its main component. Using this residue as fertilizer seems to be economically attractive, since it represents an internal resource in the crop, as it contains a great concentration of nutrients. Nevertheless, there are great environmental restrictions regarding its application, which may cause environmental damage, such as antibiotics leaching and the spread of pathogens towards ecosystems. A sustainable approach for these wastes' reuse is thermochemical conversion since the by-products generated have greater economic value and can also be converted into energy[1].

Pyrolysis is known as the thermal degradation process of organic matter in the total or partial absence of oxygen, in solid (char), liquid, and gaseous compounds. The solid portion is rich in carbon and consists of a large part of the inorganic compounds present in the biomass. Maximum char yields and moderate amounts of tar might be achieved with low heating rates and long residence times[1,2].

Cryogels are three-dimensionally structured solid materials with high porosity, which provides them excellent physical and thermal properties. They are extensively studied in thermal and acoustic insulation areas, adsorption of organic fluids, dyes, and gases[3]. Cellulose-derived cryogels present the advantage of being derived from plant biomass, without the need for synthetic modifications[4].

The main contribution to CO$_2$ emissions into the atmosphere is the use of fossil fuels[5]. Recently, great efforts have been made to reduce the problems generated by CO$_2$ emissions, within technologies for capturing, storing, and using carbon. The most developed techniques currently used are liquid amine absorption and membrane separation. Nevertheless, these technologies display limitations, such as equipment corrosion, high energy consumption, and harmful products generation. Due to the high levels of CO$_2$ emission, it is necessary to develop efficient low-cost technologies in CO$_2$ separation and purification from flue gases[6,7]. Porous solid materials such as zeolites, activated carbons, and polymer-based aerogels can minimize the aforementioned issues[8,9]. Among these materials, polymeric

natural-based aerogels, especially those derived from cellulose, are considered the most promising candidates for CO_2 adsorption, as they are materials with three-dimensional networks, with low densities, high specific surface areas, thermal stability, and mechanics, and good sorption properties[8,10]. Therefore, the goal of the present work was to produce carbon aerogels, from the pyrolysis of poultry litter waste, for use as a CO_2 adsorbent. Additionally, the scientific contribution of this work, when compared to other works that report CO_2 adsorption in biochars, is its incorporation into the cryogel, which presents a different structure from the powder, facilitating its use. It can also be highlighted that the reuse of agro-industrial waste as a carbon source is being proposed.

2. Materials and Methods

2.1 Materials

Poultry litter waste (PLW) was used as biomass. The sample was collected in an aviary in the city of Antônio Prado – Brazil. It consists of wood chips and sawdust. Polyethylene glycol (PEG) and carboxymethyl cellulose (CMC) reagents were purchased from Sigma-Aldrich S.A. and used as received.

2.2 Poultry litter waste (PLW)

2.2.1 Poultry litter waste pyrolysis

Biomass pyrolysis experiments were firstly performed. Approximately 100 g of poultry litter waste was placed into a bench reactor. The cylindrical quartz reactor operated under a nitrogen gas (N_2) atmosphere using two different flow rates: 150 (PLW.150) and 1000 (PLW.1000) mL min^{-1}. The oven temperature was then increased at a speed of 5 °C min[1] until reaching 800 °C. The reactor was kept at this temperature for 60 minutes (holding time) and then cooled, still with a N_2 flow, to room temperature. The total cooling time was approximately 10 h. After pyrolysis, the biochar formed was then macerated to be later used in powder form.

2.2.2 Biochar characterization

The poultry litter waste was characterized regarding its morphology through field emission scanning electron microscopy, using a FEG Mira 3 - Tescan equipment (Czech Republic); thermogravimetry using a TGA-50 - Shimadzu® thermobalance (Japan) at a heating rate of 10 ºC min^{-1} over a temperature range from 23 to 800 ºC in a N_2 atmosphere. Biochars were characterized for their specific mass; specific surface area by the Brunauer, Emmet, and Teller (BET) method using the Quantachrome Instruments equipment (model 1200e), managing the nitrogen adsorption/desorption process at -196 ºC. The samples went through a degassing process conducted under vacuum and at 380ºC, for a period of 20 h; ultimate analysis following the following technical standards: ASTM D5373/02 (carbon, hydrogen and nitrogen) and ASTM D4239-14e2 (sulfur), using ELEMENTAR instruments, Vario Macro model.

2.3 Carbon Cryogels (CC)

2.3.1 Carbon Cryogels (CC) production

For cryogels production, 7 g of biochar, 90 mL of deionized water, 2.5 g of PEG and 1.0 g of CMC were used. PEG was previously solubilized in water at 60°C for 30 minutes with constant agitation. Afterward, the CMC was added and stirred till the system homogenization. Finally, the biochar was manually mixed. The formed gel was placed into cylindrical molds and then frozen at -80°C for 24 hours and afterward dried in a Liobrás lyophilizer – model LioTop L101 (Brazil) for approximately 72 hours. The cryogels were named CC-PLW.150 and CC-PLW.1000 about the nitrogen flow used, 150 and 1000 mL min^{-1} respectively.

2.3.2 Cabon Cryogels (CC) characterization

The CO_2 adsorption capacity of the cryogels was determined in a Netzsch STA 449 F3 Jupiter® thermobalance. Approximately 10 mg of cryogel was used for each run. The test started with a flow of 50 mL min^{-1} of N_2 and a temperature of 120ºC for 60 minutes, to eliminate possible volatile compounds present in the biochar. Then, the temperature was decreased to 25°C and the CO_2 replaced the N_2 (flow of 50 mL min^{-1}). The experiment was maintained for 30 minutes with CO_2 flow. The values corresponding to the CO_2 adsorption mass were collected every 1.5 seconds and the result was expressed in mg of CO_2 per g of cryogels. To evaluate the adsorption cycles, the procedure was repeated five times.

3 Results and Discussion

3.1 Raw-material and biochars characterization

The poultry litter waste, received in the form of sawdust, was pyrolyzed as described above and was used as the carbon source to produce the carbon cryogels. PLW presents the chemical composition of 37.38%wt of cellulose, 7.34%wt of hemicellulose and 20.23%wt of lignin.

Figure 1 shows the photographs and micrographs of the poultry litter waste before and after pyrolysis. As it can be seen in the photographs, the PLW.150 and PLW.1000 samples present different size particles, and the N_2 flow did not modify their characteristics visually. By electron microscopy images, it is possible to verify the appearance of cavities in biochars. The fibrous structure of the material remained, even after the fibers were broken and weakened during the pyrolysis process. During the material devolatilization process, there is a gradual release of different volatile compounds as the temperature increases at a low heating rate. As a result, cracks occur on the surface of the fibers, which cause them to break. The carbonized particles formed by PLW devolatilization contain complex pore structures.

The EDS spectra (Figure 2) showed that in biochars there was an increase in carbon, and consequently, a decrease in the oxygen level due to the pyrolysis process. This behavior is corroborated by the results found in the ultimate analysis presented in Table 1, where there was an increase above 30% in the amount of carbon in biochars concerning PLW.

The biochars yield was similar, around 44% to the raw materials mass was converted into biochar. The main
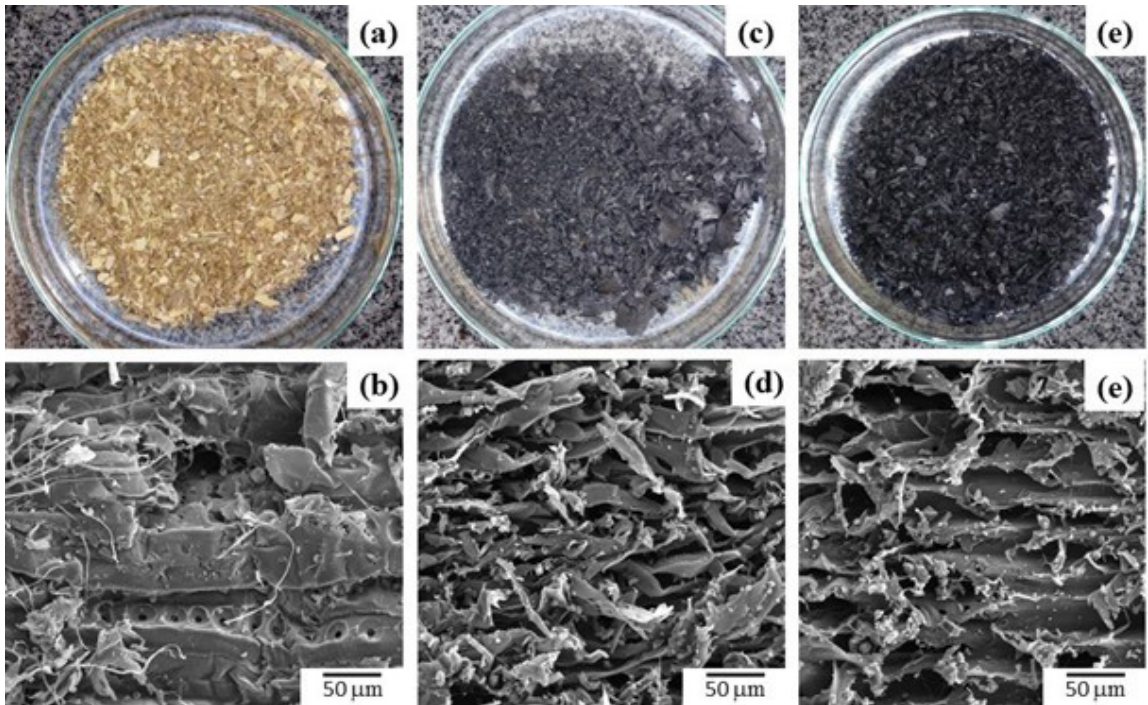
Figure 1. Photographies; (a) PLW; (d) PLW.150 and (g) PLW.1000. Micrographs: (b) PLW; (e) PLW.150 and (h) PLW.1000.
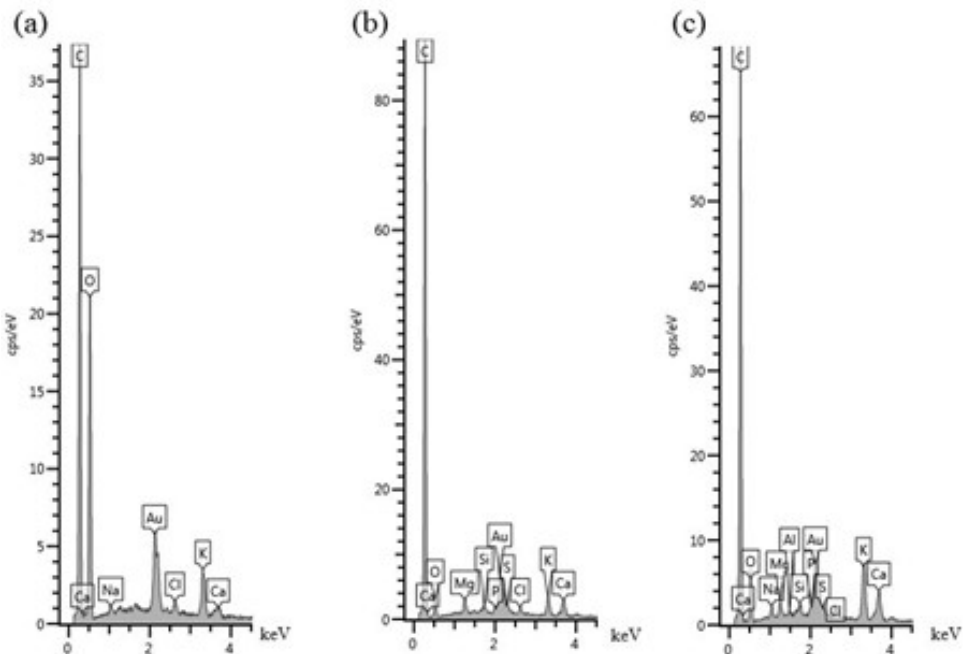
Figure 2. EDS: (a) PLW; (b) PLW.150 and (c) PLW.1000.

variation was in the bio-oil formation, where the increase in nitrogen flow (from 150 to 1000 mL min⁻¹) increased the liquid fraction yield (from 25.75 to 32.64% wt). This might be due to the shorter residence time of the vapors into the reactor. Longer times promote cracking reactions and secondary char formation[3,11].

The (inert) gas flow rate in pyrolysis processes plays an important role in the formation of products. With the increase in the inert gas flow, there is a significant reduction in the residence time of the pyrolysis vapors in the bed, and, consequently, a reduction in the occurrence of secondary reactions. The increase in bio-oil yield of 25.75%wt. (experiment conducted

Table 1. Yield, ultimate analysis and specific surface area of poultry litter waste and biochars.

	PLW	PLW.150	PLW.1000
Biochar (%wt.)	-	43.26	44.07
Oil (%wt.)	-	25.75	32.64
Gases (%wt.)	-	30.99	23.29
N (%wt.)	2.35 ± 0.09	1.15 ± 0.02	1.04 ± 0.08
C (%wt.)	30.72 ± 1.37	44.08 ± 0.28	40.00 ± 2.28
H (%wt.)	5.36 ± 0.20	1.29 ± 0.02	1.21 ± 0.08
S (%wt.)	0.19 ± 0.02	0.35 ± 0.02	0.45 ± 0.02
O* (%wt.)	61.39 ± 1.49	53.14 ± 0.31	57.30 ± 2.46
Specific surface area ($m^2 \, g^{-1}$)	-	161.896	141.800
Total pore volume ($cm^3 \, g^{-1}$)	-	0.102	0.089

*Calculated by difference.

Table 2. Pore volume of carbon cryogels.

	Mesopore ($cc \, g^{-1}$)	Micropore ($cc \, g^{-1}$)	Total Volume (mesopore+micropore) ($cc \, g^{-1}$)	% micropores (micropore volume/volume total*100)
CC.PLW-1000	0.02348	0.06547	0.08895	73.6
CC.PLW-150	0.031	0.07119	0.10219	69.7

with a flow of 150 mL/min) to 32.64%wt (experiment conducted with a flow of 1000 mL/min), is associated with the shorter residence time of pyrolysis vapors in the gas phase in the experiment with higher flow, minimizing the secondary cracking reactions. Long residence times of pyrolysis vapors allow volatile species formed during primary pyrolysis to undergo secondary decomposition reactions in the gas phase to form non-condensable gases ($CO/CO_2/CH_4$). The highest content of non-condensable gases was observed for the experiment carried out with the lowest inert gas flow (30.99%wt), that is, longer residence time of the pyrolysis vapors, when compared to the experiment carried out with a flow of 1000 mL/ min, which presented 23.29%wt. of non-condensable gases.

The carbon, nitrogen, hydrogen, sulfur, and oxygen yields, obtained by ultimate analysis, are shown in Table 1 and it is possible to verify that the carbon content increases considerably when compared the biochar with the raw material. This takes place because during the pyrolysis there is a decrease in the hydrogen and oxygen concentrations, due to dehydration, decarboxylation and condensation reactions. The PLW carbon concentrations was 30.72%wt. and 44.08 and 40.00%wt for PLW-150 and PLW-1000 biochars, respectively.

Regarding to the total pore volume and the specific surface area, the increase in the inert gas flow caused the reduction in total pore volume and, consequently, in the specific surface area. According to Mortari et al.[12] fast release of volatiles produces substantial internal overpressure and coalescence of the smaller pores, which also justifies the smaller volume of micropores and larger volume of mesopores for the experiment with higher flow. The specific surface area found for both biochars is representative of cellulose-based biochars, such as the values found by Zazycki et al.[13] for 93 $m^2 \, g^{-1}$ pecan nutshell and by Yu et al.[14] for hinoki cypress of 143 $m^2 \, g^{-1}$.

The adsorbent-used materials are classified based on their pore size, microporous (pore diameter < 20 Å); mesoporous (20 Å < pore diameter < 500 Å), and macroporous (mean diameter > 500 Å). Microporous materials are extensively applied for gases and vapors adsorption[15]. Table 2 presents the volumes of micropores and mesopores of biochars, as well as the percentage of micropores calculated considering the total pore volume. The micropores fraction in biochars is 69.8% and 73.6% (to the total pore volume in each biochar) for PLW.1000 and PLW.150, respectively. Due to their high micropores fraction, biochars present great potential to be applied in CO_2 adsorption, and therefore used for the cryogels production.

Figure 3a displays the poultry litter waste thermogravimetry before and after pyrolysis process. The total poultry litter mass lost was 67%. The results show two mass loss events, the first between 19 and 200ºC, caused by the initial of hemicellulose thermal degradation phenomenon, related to the low molecular weight components evaporation, including moisture. The second mass loss event starts at 200ºC and it might be associated to several degradation phenomena of the PLW different components, mainly cellulose and lignin, which are the major components present in this organic matter[1,16]. Biochars behaved as expected, where there was only one mass loss event related to the sample moisture. Due to the pyrolysis process having been carried out at 800ºC, the organic matter present in the PLW suffered degradation, causing the produced biochars to be considered thermally stable materials.

Figure 3b shows the weight loss curves of cryogels, where it is possible to note two mass-loss events. The first, referring to the degradation of CMC molecules starting at 250ºC and the second event referring to the degradation of PEG, starting at 350ºC, as can be seen in Figure S.1 – Supplementary Material. Due to the addition of these two components, had an increase in the initial degradation temperature of cryogels (T = 220°C) over PLW (T = 177°C). The CC-PLW.150 cryogel showed a residual mass of 37%, whereas the CC-PLW.1000 of 34%.
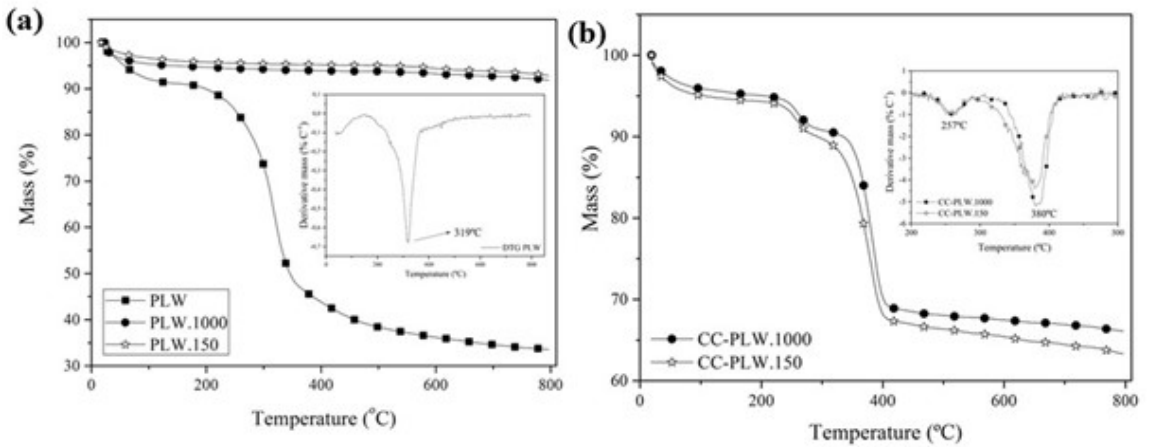
Figure 3. Thermogravimetry: (a) poultry litter waste (PLW) before and after pyrolysis with Nitrogen rate of 150 (PLW.150) and 1000 (PLW.1000) mL.min-1 and (b) cryogels CC-PLW.1000 and CC-PLW.150.
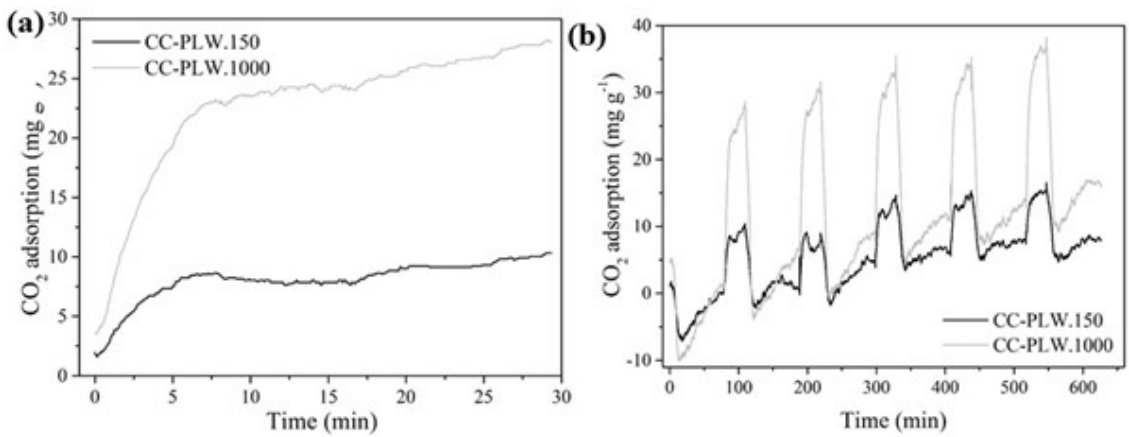
Figure 4. CO_2 adsorption capability of the CC-PLW.150 and CC-PLW.1000 cryogels: (a) 30 min and (b) for 5 cycles.

3.2 Carbon Cryogels (CC)

Table 3 shows cryogels CC-PLW.150 and CC-PLW.1000 photographs beyond the apparent density of both. As it is seen, they present the same physical appearance and three-dimensional structure besides having an apparent density very close due to their same amount of solid particles.

The cryogels CO_2 adsorption capability was tested at 25ºC and atmospheric pressure. The cyogels behavior is shown in Figure 4. As seen in Figure 4a CO_2 adsorption capacity was stable for up to 5 cycles. This shows the cryogels effectiveness does not drop after the desorption process, which is an important feature in selecting adsorbents. The previously described behavior was also found by Leung et al.[7] for cellulose aerogels synthesized from old corrugated containers. The maximum CO_2 adsorption capacity (Figure 4b) was 13.1±2.9 and 33.8±3.3 mg g^{-1} to CC.PLW.150 cryogels and CC-PLW.1000 respectively. This CO_2 adso

The different micropore volumes of biochars used to produce cryogels, seen in Table 2, are the possible inferences for the difference in adsorption capacity between

Table 3. Specific mass of carbon cryogels.

Photography	Cryogels	Apparent density (g cm⁻³)
	CC-PLW.150	0.118 ± 0.014
	CC-PLW1000	0.121 ± 0.016

the materials. According to Zhang et al.[17], the large CO_2 capture capacity is exclusively due to their high volume of narrow micropores and not to the high surface areas or pore volumes, neither to the presence of heteroatoms. The biochar microporosity plays a fundamental role in the adsorption capacity of CO_2 and is the main subject for the increase in the CO_2 adsorption capacity in the CC-PLW.1000 cryogel.

Table 4 shows the CO_2 adsorption capacity of aerogels produced with different raw materials[8]. summarized a series of CO_2 adsorption capacity data for different aerogels, and

Table 4. CO_2 adsorption capacity of aerogels produced with different raw materials.

Aerogels	CO_2 adsorption capacity (mg g^{-1})	BET surface área (m² g^{-1})
Amino functionalised Silica-Aerogels[9]	23.01	633
Chitosan grafted graphene oxide aerogel[10]	11.31	33
Carbon nanotube/PVA aerogels[16]	145.2	59

highlighted that silica aerogels had an average of 23.03 - 347.60 mg g^{-1} at 1 bar; carbon aerogels synthesized by different organic precursors have CO_2 adsorption capacity in the range of 14.52 - 651.20 mg g, and hybrid aerogels have a capacity in the range of 49.28 - 293.04 mg g. Several factors influence the adsorption of CO_2, including the texture and chemical properties of the surface of the adsorbents, whether or not chemical modifications are carried out. Furthermore, temperature and partial pressure of CO_2 are important parameters regarding the adsorption kinetics that strongly influence the CO_2 rate.

4. Conclusions

Carbon cryogels were synthesized with biochars produced from the pyrolysis of poultry litter waste and evaluated for their performance for CO_2 adsorption. The major presence of micropores into the biochar porous structure provided the cryogels great CO_2 adsorption capacity, as well as stability in their adsorption capacity for 5 cycles. These results demonstrate that cryogels are promising candidates for CO_2 adsorption at room temperature.

5. Acknowledgements

6. References

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Supplementary Material

Supplementary material accompanies this paper.

Figure S.1 – TGA of PEG and CMC.

This material is available as part of the online article from https://www.scielo.br/j/po