CO₂ adsorption in biochars obtained from soursop (*Anonna muricata*) seeds by chemical activation with metallic salts

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Abstract

Environment remediation is one of the primary goals of sustainable development and anthropogenic activities, and the use of fuels in various industrial processes through combustion has led to an increase in CO_2 as well as big damage to the atmosphere by the greenhouse effect. Biochar has been used for the capture of carbon dioxide due to its high surface area. In this study, we obtained biochar from soursop seeds. The materials were synthesized by pyrolysis of precursor materials and chemical activation with chlorides of Ca and Mg at a concentration of 5% w/v. The effect of the defatting process of the soursop seeds on the obtained carbon was also researched. The absorbed solids were characterized through thermogravimetric analysis, X-ray diffraction, and CO_2 adsorption, followed by infrared spectroscopy, N₂-physisorption, CO_2 -physisorption, CO_2 , XPS, DRIFTS and TPD of NH₃. The type of activating agent and pretreatment conditions used were more favorable than the defatted process at obtaining carbons with N₂ surface areas between 26 and 220 m²g⁻¹. The biochars were analyzed by CO_2 surface area to describe the microporous framework, and the solid with the best CO_2 surface area was the one with the highest CO_2 adsorption. According to the statistical analyses conducted, the evaluated models Langmuir, Freundlich, and Redlich-Peterson presented good fits to the experimental data. However, the Redlich-Peterson model showed the lowest values for the residual variance, which were of the order of 0.001 or less in all cases based on the CO_2 adsorption isotherms on the studied activated carbons. However, the carbons obtained by defatting showed favorable hydrophilic behavior along with adsorption capacities in the bioremediation process and affinity towards of this GHG.

Keywords Biochar · Soursop seeds · Environment remediation · Chemical activation · Carbon dioxide

1 Introduction

The carbon footprint is related to the amount of greenhouse gases produced by anthropogenic activities and emitted by a country dependent on economic growth and currently calculated in tons of CO_2 [1]. In Colombia, the carbon footprint does not exceed 4 tons per year, however, an increase

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of 1.45 to 1.53 tons per capita between 2020 and 2011[2] indicates a minor environmental efficiency for this country. Some efforts to decrease the carbon footprint have been made through the development of adsorbent materials. Thus, an economically and environmentally viable way is to use residual biomass to obtain adsorbent biochar for storage and subsequent use of CO_2 .

Biochar (BC) is generally employed in the adsorption of various contaminants [3], due to its low synthesis costs and less expensive regeneration energies than other adsorbents [4]. Some recent reviews on AC from biomass-based sources for CO_2 capture have shown the current potential and trends in the last few years. Biochar is easily obtained by the carbonization of residual biomass with a high lignocellulose content [5]. Its porous structure can be manipulated by distinct methods, and different chemical functional groups are set up into the surface by various treatments using physical and chemical reagents [6], with the aim of increasing CO_2 affinity. Soursop seeds



are a good precursor of adsorbent materials. This tropical fruit contains 30% of its total weight in seeds, which are considered waste [7]. An alternative to the valorization of these seeds is the production of low-cost animal feed, but it isn't possible because of the high content of antinutritional factors and toxic metabolites [8]. Soursop seeds have the potential to be used as a precursor to produce biochar for CO_2 adsorption.

The method of preparation of biochar from seeds that is most known is pyrolysis, however, the conditions of pyrolysis and the presence of the activating agent are the principal variables that improve the CO₂ adsorption on biochar obtained from biomass [9]. The pyrolysis is carried out using a precursor previously impregnated with a solution of H₃PO₄, KOH, NaOH, or ZnCl₂, which produces carbon with a high surface area and microporous framework [10]. These activating agents are efficient, but the byproducts resulting from washing are too harmful to be discarded. Chemical activation using CaCl₂ or MgCl₂ has been recently explored to obtain mesoporous solids, improving CO_2 adsorption [11]. These salts act as dehydrating agents and serve as pore shaper [12]. CaCl₂ forms symmetric pores after the washing process, and the action of MgCl₂ could be similar. In addition, a high heating ramp rate favours the loss of volatile matter, avoiding blockages in the porous framework and decreasing the superficial groups on the surface of carbon.

Different samples of biochar from soursop seeds were obtained, and it has been tested if the oils in the precursor materials interfere with or contribute to CO₂ adsorption and its interaction with activating agents [13]. So, the synthesis of biochars using seeds with high oil content produces bio-oils in the pyrolytic process. In some cases, these byproducts generate interference in the pore frameworks, which makes the pollutants adsorption difficult. Some authors have performed a defatting process with the final purpose of obtaining a cleaning surface and improving the entry of adsorbate molecules [13]. This process was realized on a part of the seeds before the activated process, expecting to improve the adsorption of CO₂. Although the defatted process does not improve the surface area, the methodology activation with CaCl₂ produced a homogenous surface with intermedium acid sites, which increased the CO₂ adsorption in these samples. Besides with MgCl₂ activating process improve the surface area without defatting, the acidity of the samples increases too, affecting CO₂ adsorption. This precursor is chemically activated with dehydrating agents of low use in the literature regarding the production of this type of adsorbents generating contribution and innovation in the state of the art, after its preparation and characterization, the CO₂ adsorption capacity was evaluated with a view to the future of industrial use.

2 Materials and methods

2.1 Soursop seeds characterization

Bromatological characterization was conducted in triplicate and included the content of ash, moisture, fiber with acid detergent fiber (ADF)—neutral detergent fiber (NDF), ethereal extract, and amount of protein [14]. The analysis of ADF is related to the percentage of cellulose and lignin in the sample, while the analysis of NDF is related to the content of ADF and hemicellulose. Thermogravimetric analysis was performed in equipment Setaram 1600 using a temperature ramp of 5 °C.min⁻¹ to 1000 °C in an N₂ atmosphere of 20 mLmin⁻¹. The soursop seed samples were pulverized and measured in an alumina crucible of 90 µL; a mass of soursop seed and degreased seeds at 39.4 and 31.2 mg, respectively.

The samples of soursop seeds were washed and crushed to a 1:2 ratio of chemical activation, using $CaCl_2$ and MgCl₂ to activate agents in magnetic stirring for 6 h; the degreased soursop seeds were taken to Soxhelt extraction with n-hexane in a refluxed system for 4 h, and this was activated in the same form and dried for 12 h at 100 °C.

2.2 Preparation of the biochar

The biochars were prepared by the pyrolysis method using chemical activation of the soursop (Anonna muricata) seeds and defatted soursop seeds as precursor materials to obtain biochar (BC), resulting from the treatment and processing of the soursop fruit and being an agroindustrial waste. The soursop seeds were acquired from a fruit pulp factory in the region through manual recollection. These were cleaned with ionic water, posteriorly it was dried at 100 °C and then passed through a granulometric sieve until obtaining a particle size between 4 and 2 mm using mesh number 2 (size 2 mm). A portion of soursop seed was taken to carry out the defatting process, the precursor was weighed and packed in cellulose paper and placed in a refluxed system in hexane for 6 h, following the process described by Prandy, et al. [15]. The extracts were separated by rota-evaporation to recover the solvent; the sample was weighed and dried to 100 °C to eliminate the hexane excess. The reagents used were $MgCl_2$, CaCl₂, from Bioquigen, and hexane (>98%) from Sigma-Aldrich hydrochloric acid (Sigma-Aldrich, 37%). The carbons were prepared according to described by Acevedo, et al. [16], using a tubular resistor Lindberg Blue M of 1200 °C TF55035A-1 at 700 °C for a period of 2 h (heating ramp of 5 °C for minute) and maintaining a flow of 50 mLmin⁻¹ of CO₂ and N₂ mixture (high purity gases,



Fig. 1 Scheme of the carbonization system

analytic grade), as can be seen in Fig. 1 [17]. $MgCl_2$ and $CaCl_2$ were used as activating agents at a constant concentration of 5% w/v. The samples of activated carbons were mixed in HCl 0.01 M to eliminate the activate excess and washed with refluxing in distilled water to a constant pH closer to pH 7.

The adsorbent materials were obtained by pyrolysis of soursop seeds in a tubular oven with a constant flux of CO_2 and N_2 mixture out to the bubbler for the retention of bio-oils. The samples were classified by precursor type and activate agent; six samples were obtained that describe the following with their abbreviations:

Soursop seeds	SS
Defatted soursop seeds	DSS
Biochar	BC
Defatted Biochar	DBC
$Biochar + MgCl_2$	MgBC
$Biochar + CaCl_2$	CaBC
Degreased Biochar + $MgCl_2$	MgDBC
Degreased Biochar + $CaCl_2$	CaDBC

2.3 DRX (X-ray diffraction)

The XRDs were obtained by a diffractometer model Mini-Flex with CuK α radiation ($\lambda = 1540$ Å). The data were obtained in a range of 5 to 90° in 20 with an increment of 0.05° as described et al L.M. Esteves [18]. To determine the crystal sizes, the FWH was calculated by the main DRX peaks in the Origin software and using the Debye–Scherrer equation.

2.4 FTIR spectra

Infrared spectra were collected by the FTIR-ATR method using an equipment Thermo Scientific model NICOLET iS50 FT-IR spectrometer with a ZnSe window to determine surface groups on the materials. 64 scans were used by each sample [19].

2.5 DRIFTS analysis

The same equipment FTIR collected the CO_2 absorption spectra using a diffuse reflectance accessory with ZnSe. The sample was cooled to 20 °C in an atmosphere of He gas, taking reference spectra of the clean. Then, supply the sample with a flow of CO_2 (30 mLmin⁻¹) for 30 min. Finally, the sample was cleaned again with the flow for 10 min, and the last spectrum was collected; this was the absorbed CO_2 spectrum. To collect the spectra, with a resolution of 4 cm⁻¹ and 250 scans were used [20].

2.6 BET surface area

The values of surface area, diameter, and the pores volume were characterized with a Micromeritics ASAP 2020 analyzer by physisorption of N₂ at -196 °C. The samples were previously dried for 12 h in a muffle at 150 °C and degassed employing the vacuum system of the ASAP 2020 equipment for 6 h. The Brunauer–Emmett–Teller (BET) analysis of adsorption–desorption isotherms was employed to calculate the surface area and the pore volume was

calculated from the N_2 desorption curve by the Barrett-Joyner-Halenda (BJH) method [21].

2.7 CO₂ adsorption

The carbon dioxide adsorption at 20 °C, the amount of CO_2 physisorpbed, and the analysis showed the amount of CO_2 physisorpbed in the biochars. The measurements were carried out in the ASAP 2020 Micromeritics analyzer. The samples were degassed under vacuum for 6 h at 150 °C. The weight of the samples was around 100 mg [22]. The measurement of CO_2 adsorption was described by theoretical adsorption isotherm models. Through the study of different models such as Langmuir and Freundlich or models such as Redlich-Peterson, Sipps, and Toth, which can describe the interaction biochar- adsorbate in addition to offering characteristics about the nature of the adsorbent and its adsorption mechanism.

2.8 NH₃ desorption measurements at the programmed temperature (TPD-NH₃)

The NH₃ desorption measurements at the programmed temperature (TPD-NH₃) were carry out in an Auto-ChemII 2920 unit (micromeritics®). Prior to analysis, samples were dried at 150 °C with He (25 mLmin⁻¹) for 1 h. The samples were then purged with Heat 400 °C for 30 min and finally cooled to 70 °C to adsorb NH₃ in a 10% NH₃/He mixture (50 mLmin⁻¹) for 30 min. Samples were cleaned with a He flow 25 mLmin⁻¹ for 1 h to remove excess NH₃. Then, a constant flow of He from 70 to 900 °C was passed to a heating ramp of 10 °C.min⁻¹ to obtain the TPD profile [23].

2.8.1 X-ray photoelectron spectroscopy (XPS)

XPS spectral analyses were conducted using a Thermo Scientific ESCALAB 250 XI spectrometer. The measurements were performed with a pass energy of 25 eV, an energy step of 0.05 eV, and a time of 50 ms. The pressure within the analysis chamber was maintained around 10^{-8} mbar.

2.9 Isosteric heats of adsorption

The isosteric heat of adsorption is a thermodynamic property that provides useful information about the adsorbentadsorbate interaction and the energetic heterogeneity of the adsorption surface. Based on the modified Clausius-Clapeyron equation:

$$q_s t = -RT\left(\frac{\partial In(P)}{\partial n}\right)$$

where *R* is the gas constant (8.314 JmolK⁻¹), n is the amount of CO_2 adsorbed (molkg⁻¹), P is the pressure of adsorption (kPa) and T is the temperature in Kelvin (293 K in this case). The isothermal heat corresponds to the energy released in the adsorption process and depends on the temperature and surface coverage. In this study, the isotherms of each sample were used to determine the dependence of the isosteric heat on the adsorbate concentration. The analyses were performed in gas analyzer with prior degassing at 300 °C for 3 h [24].

3 Results and discussion

3.1 Characterization of soursop seeds

The oil content in the soursop seed was approximately 14.5%, moisture was 7%, protein was 14.2%, and ash was 2.1%. In the seed samples, the TGA mass changes are associated with the loss of moisture or volatile matter in the samples (70-220 °C). Subsequently, the loss of hemicellulose, cellulose, and lignin can be observed up to 900 °C [25], which is depicted in Fig. 2. In the defatted seed samples, temperature changes are more noticeable, particularly in the regions of 70-200 °C and 340-600 °C. The removal of fatty acids embedded in the hemicellulose or cellulose fibers causes thermal degradation to occur more easily. This analysis shows that about 7% can be associated with moisture and volatiles, 55-65% with hemicellulose and cellulose, and approximately 25-30% with lignin. These quantitative results are consistent with those obtained through ADF and NDF. The values of NDF and ADF were 73.4 and 88.4, respectively. This suggests that the resulting carbons could have a higher proportion of disordered porous structures, as has been described by Meng et al. (2021) (Fig. 3).



Fig. 2 TGA and DTG curve of soursop seeds (SS)

Fig. 3 TGA and DTG (percent mass loss) analysis of defatted soursop seeds (DSS)

3.2 FTIR spectra

The FTIR spectra of the soursop seeds (Fig. 4a) and defatted soursop seeds (Fig. 4b) showed signals characteristic of biomass organic. These signals correspond to fatty acids, proteins, and the fiber composed of lignin, cellulose, and hemicellulose. Signs of hydrogen bonds stand out between 3200 and 3400 cm⁻¹ and C–H vibration bonds corresponding to 2853 and 2923 cm⁻¹ (only in the precursors); C–O group signals at 1743 cm⁻¹ and other signals below 1600 cm⁻¹ are also highlighted, which are features of deformation of C–O

and C-C bonds vibration characteristic of compounds that contains aromatic rings [26]. After the pyrolytic process. some changes are observed depending on the activating agent and the defatted process. The main bands appeared at 1580 cm⁻¹ (C=O), 1400 cm⁻¹ (C=C), and 1105 cm⁻¹ (C–O–C) [27]. In this case, it is assumed that the pyrolysis process promotes the generation of C=C aromatic skeletal vibrations, as well as changes in C-O-C symmetric and asymmetric vibratory ester groups in cellulose and hemicellulose in the precursor materials, respectively. Comparing the spectra in the presence of an activating agent, the peaks that appear at 850 cm^{-1} are the same in both samples. According to previous research [28], the signals 1040 cm^{-1} , and 1400 cm⁻¹ appear in the MgDBC and CaDBC samples; these peaks could be affixed to lengthen of groups (-C=O)and (-C-H), which suggests that the MgCl₂ or CaCl₂ in degreased samples may give a hydrophilic biochar.

3.3 X-Ray diffractions

The XRD patterns of the biochars obtained are displayed in Fig. 5. The broad peak at 25° is due to the amorphous structure. In the samples, CaBC and CaDBC appear to have a peak at 30° related to CaO with a crystal size of 20 nm and 26 nm, respectively. For MgBC and MgDBC, the peak of MgO appears at 42.6° , and similarly, the crystal size crystal of MgO increases in the defatted sample, reaching 3 nm for MgBC and 16 nm for MgDBC. This increase in the crystal size of CaO or MgO in the degreased samples could be explained by the poor interaction of the salts on the

Fig. 4 FTIR spectra: **a** FTIR biochars analysis activated with metal salts; **b** FTIR analysis of defatted biochars, where SS is the sample of soursop seeds, DSS is the sample of defatted soursop seeds, BC and DBC are biochars of soursop seeds and defatted soursop seeds,

respectively; MgBC and CaBC are biochars activated with metallic salts; and finally, MgDBC and CaDBC are the biochars activate of defatted soursop seeds

Fig. 5 XRD spectra of biochars

lignocellulosic surface. Besides, the amorphous structure is favored using MgCl₂ [29].

3.4 BET analysis

The BET surface was studied by N_2 analysis at -196 °C. A decrease into the surface area (S_{BET}) was showed in the samples treated with CaCl₂. Besides, the defatting process and the incorporation of CaCl₂ do not improve the surface area. However, the addition of MgCl₂ showed unexpected results. An increase in the S_{BET} was observed for MgBC, but the defatting decreases substantially the SBET for MgDBC due to decreases in the volume of the pore, maintaining a similar pore size. The BET area shows a mesoporosity in the material which is useful for the process of agile CO₂ kinetics within the active sites of the micropores for its adsorption process. It is also shown that the activation temperature is an important factor in the formation and distribution of the porosity obtained in these materials. The results obtained are similar to other studies in which chemical activation was carried out with metallic salts [4, 17] and obtaining

Table 1 Results of N₂ surface area analysis

Biochar	SBET Area* (m ² g ⁻¹)	Poro size (nm)	Vpore (cm ³ g ⁻¹)	Adsorption isosteric heat (Qst) (kJmol ⁻¹)
BC	110	4.7	0.12	9.4
DBC	59	6.9	0.10	8.0
MgBC	221	6.1	0.30	8.3
CaBC	85	8.1	0.17	6.9
MgDBC	26	8.1	0.05	11.0
CaDBC	86	4.6	0.10	8.6

*Corroborated value within the optimal range P/P⁰

Fig. 6 Incremental pore-size distribution curves of biochars

materials with possible viability in the adsorption process (Table 1).

Figure 6 shows the pore size distribution graphs of the biochars obtained, showing the increase in the pore diameter of all solids with respect to the increase in the total pore volume; this increase is notably observed in the production of narrow and wide mesopores < 50 nm, this is important given that having wider mesopores the speed of access of CO_2 to the interior of the active sites of the micropores is more favorable.

3.5 CO₂ adsorption

In the Fig. 7 it observed the isotherms of CO_2 adsorption, where the quantity of stored CO_2 in the biochars was similar, considering that the surface area of the samples was different. It is emphasized that the N₂ analysis could give erroneous results due to the fact that cryogenic N₂ cannot be accessed in some micropores [30]. The isotherms are characteristic of type I behavior, which is observed in microporous materials. Although CO_2 adsorption isn't a usual method for surface area, according to the isotherms obtained (Langmuir shape) of this biochar, most of the pores are in the narrow frame. The quantity of adsorbed CO_2 increases with

Fig. 7 CO_2 adsorption isotherm of biochars

 Table 2
 Frendlich and Langmuir models constants and variance data

Adsorption models	Constants		Variance of residu- als (reduced chesecuare)
BC			
Langmuir	$nm(mmolg^{-1})$ KL(bar ⁻¹)	44.7331 81.7128	0.525545
Freundlich	Kf(mmolg ⁻¹) l/n	69.4846 0.51598	24.5029
DBC			
Langmuir	$nm(mmolg^{-1})$ KL(bar ⁻¹)	49.6402 67.9341	0.46491
Freundlich	Kf(mmolg ⁻¹) l/n	72.9061 0.05349956	22.5425
CaBC			
Langmuir	$nm(mmolg^{-1})$ KL(bar ⁻¹)	62.2777 50.90756	1.06168
Freundlich	Kf(mmolg ⁻¹) l/n	98.6397 0.0596728	25.3654
CaDBC			
Langmuir	$nm(mmolg^{-1})$ KL(bar ⁻¹)	52.5426 78.4297	0.923365
Freundlich	Kf(mmolg ⁻¹) l/n	82.8279 0.0564639	31.9698
MgBC			
Langmuir	$nm(mmolg^{-1})$ KL(bar ⁻¹)	52.1674 94.4995	0.605914
Freundlich	Kf(mmolg ⁻¹) l/n	78.4443 0.0479149	45.341
MgDBC			
Langmuir	$nm(mmolg^{-1})$ KL(bar ⁻¹)	43.1575 79.1675	0.379337
Freundlich	Kf(mmolg ⁻¹) l/n	66.1917 0.0519659	22.2324

Table 3 Non-linear analysis of Redlich, Toth and Sips models and variance values

Adsorption models	Constants	Variance of residuals (reduced chesecuare)	
BC			
Redlich-Peterson	K _{RP} A _{RP} (bar ⁻¹) g	8323.71 63.6065 0.646191	0.0238325
Toth	$KT(mmolg^{-1})$ $\alpha_{RP}(bar^{-1})$ l/t	6368.2 2.28672 0.49438	24.3923
Sips	b(bar ⁻¹) nm 1/ns	44.7357 5.0553 0.0619503	0.53145
DBC			
Redlich-Peterson	K _{RP} ARP(bar ⁻¹) g	6945.41 46.9569 0.634203	0.00137466
Toth	$KT(mmolg^{-1})$ $\alpha_{RP}(bar^{-1})$ l/t	737.763 0.0147207 0.0672859	0.473363
Sips	b(bar ⁻¹) nm 1/ns	49.6415 - 20.9106 - 0.307825	0.473363
CaBC			
Redlich-Peterson	K _{RP} A _{RP} (bar ⁻¹) g	12,113.2 49.6595 0.529836	0.173026
Toth	$KT(mmolg^{-1})$ $\alpha RP(bar^{-1})$ l/t	61.4104 0.0167484 1.01414	1.0731
Sips	b(bar ⁻¹) nm 1/ns	62.2809 61.4062 1.02852	1.0731
CaDBC			
Redlich-Peterson	$\begin{array}{c} K_{RP} \\ A_{RP}(bar^{-1}) \\ g \end{array}$	1555.41 0.00327877 3.07783	32.2377
Toth	$KT(mmolg^{-1})$ $\alpha_{RP}(bar^{-1})$ l/t	7.2346 0.0127506 7.26276	0.93119
Sips	b(bar-1) nm 1/ns	- 8948.33 41.49 - 239.717	32.5309
MgBC	1,110	20,111	
Redlich-Peterson	$\begin{array}{c} K_{RP} \\ A_{RP}(bar^{-1}) \\ g \end{array}$	8587.19 69.5857 0.724438	0.0036996
Toth	$ \begin{array}{l} KT(mmolg^{-1}) \\ \alpha_{RP}(bar^{-1}) \\ l/t \end{array} $	132.616 0.0105824 0.393376	0.621061
Sips	b(bar ⁻¹) nm 1/ns	52.1683 0.0182518 0.000193147	0.621061
MgDBC			
Redlich-Peterson	KRP A _{RP} (bar ⁻¹) g	6508.18 55.8978 0.675408	0.000911218

 Table 3 (continued)

Adsorption models	orption models Constants		Variance of residuals (reduced chesecuare)	
Toth	$\begin{array}{c} KT(mmolg^{-1})\\ \alpha_{RP}(bar^{-1})\\ l/t \end{array}$	604.874 0.0126315 0.0669239	0.38882	
Sips	b(bar ⁻¹) nm 1/ns	43.1594 0.0342075 0.000432134	0.38882	

the pressure, which it can be observed that the biochar has the highest adsorption of CO₂ without activating agents. In fact, these isotherms don't show inflections that mean that the mesopores are clogged by the oils not volatilized in the heating ramp. The fitting data are described in the Tables 2 and 3, using Langmuir, Freundlich, Redlich-Peterson, Toth, and Sips models. These models give an account of how the adsorbate interacts with the biochar and explain how the mechanism of CO₂ adsorption works. The Langmuir model has the major fit with the experimental data obtained for defatted biochar (DBC) and defatted biochar with CaCl₂, suggesting that this process generates a homogeneous surface on the biochars. On the other hand, other biochars fit the Redlich-Peterson model by supposing that the materials have roughness, and the surface properties are heterogeneous. Consequently, the type of activating agent modifies the surface of the biochar [31].

The evaluation of two-and three-parameter adsorption models and their equilibrium isotherm data allow us to accurately define the surface properties, adsorption mechanisms, and affinity of adsorbents [32]. Therefore, from the CO_2 tests carried out on the biochars and their respective data, the Langmuir, Freundlich, Redlich-Peterson, Sips, and Thot models were tested and analyzed the adsorption behavior, considering the variance of these data in the experimental equilibrium isotherms. In this way, the conditions for the design of adsorption systems would be optimized.

4 Langmuir model

This model proposed by Ivan Langmuir [33] It is a first choice due to the form of CO_2 adsorption and is based on the assumption of a microporous structure that provides an adsorption process at specific homogeneous points on the biochar surface in addition to a monolayer of the adsorbate. It focuses on the premise that biochar has a finite adsorbent capacity (at equilibrium), where the saturation point is achieved without allowing further adsorption. This Langmuir model is plotted to adapt the amount adsorbed in the following equation as described by G. Crini et al. (2007).

$$n_e = \frac{n_m b P_e}{1 + b P_e} \tag{1}$$

In this expression, ne is the capacity of adsorbed $(mmolg^{-1})$, Pe is the gas pressure (bar), nm is the highest theoretical adsorption (mmolg-1) and b is the Langmuir isotherm constant.

5 Freundlich model

The Freundlich isotherm is other option very frequent and useful theoretical model in CO_2 adsorption to interpret equilibrium adsorption. it is adjusted for adsorption on surfaces where the adsorbent with a heteroatom-rich surface interacts with the adsorbate molecules (heterogeneous surface). determines the exponential decrease of adsorption energy to the same extent that the sorption centers end. [34, 35].

The Freundlich equation is as follows:

$$n_e = K f P_e^{(1/n)} \tag{2}$$

6 Redlich-Peterson

The Redlich-Peterson isotherm model is combined with the characteristics of both the Freundlich and the Langmuir without following the monolayer adsorption model [36], which introduced three parameters in the equation. It has a linear pressure dependence in the numerator, the exponential function and the denominator, which represent an equilibrium adsorption over a wide range of pressures. This model can be used to different systems due to its versatility [37]. However, it must be taken into account that when the adsorption approaches low pressure, the ideal Langmuir condition is reached, and if it approaches high pressure, the ideal condition is Freundlich. The nonlinear model for Redlich-Peterson presents itself as follows:

$$n_e = \left(\frac{KrP_e}{1 + ArP_e^g}\right) \tag{3}$$

7 Toth model

The Thot model, although it is an empirical equation, is a model that can improve the adjustments but does not take into account the Langmuir isotherm, it efficiently describes heterogeneous adsorption systems that develop in low and high pressure environments [38]. The following equation shows the Toth model in its non-linear form:

$$n_e = \left(\frac{K_t P_e}{\left(aT + P_e\right)^{\frac{1}{t}}}\right) \tag{4}$$

8 Sips model

The Sips isotherm, like Redlich, is an adjusted form of the Langmuir and Freundlich expressions. In contrast, this model predicts different adsorption systems, limiting of adsorbate adsorption that occurs in the Freundlich and Redlich models. The nonlinear mathematical model of the Sips isotherm is shown below [34]:

$$n_e = \left(\frac{n_m b p_e^{\frac{1}{n}}}{1 + b P_e^{\frac{1}{n}}}\right) \tag{5}$$

The analysis of variance of residuals (reduced chesecuare) was applied in order to calculate the unknown isotherm parameters, and this models with the lowest variance value presented in the experimental data which were examined. The value of variance of residuals is obtained by Gnuplot (5.4 version) by applying the equations of the different models' software, and the model with the best results was chosen.

Furthermore, the values of the rate constants obtained with these models are not related to the structural and chemical parameters of the activated carbon. This shows that the CO_2 adsorption mechanism is not determined by mass transfer or chemisorption or chemical adsorption due to the formation of chemical bonds between the adsorbent and the adsorbate in the surface monolayer. Additionally, in the samples it is observed that the presence of mesoporosity favors the diffusion of the gas towards the micropores, which are the effective sites of CO_2 adsorption [39].

Considering the models used for CO_2 adsorption, the model that presents the best fit in most of the samples is the Redlich-Peterson model, which facilitates a hybrid analysis that combines characteristics of the Langmuir and Freundlich models, making it a more versatile model for describing adsorption on heterogeneous surfaces at different adsorbate concentrations. Statistical simulation suggests that this model more accurately captures adsorption in the prepared activated carbons, showing that these solids present different types of combined surfaces, while the CaDBC sample fit better to the Tohl model as indicated in Table 2, since this model does not take into account the non-line indicating that there is a heterogeneity on the surface of this material.

Fig. 8 CO₂ DRIFTS analysis of activated carbons

8.1 CO₂ DRIFTS

Drifts under constant CO₂ flow were performed to know the species adsorbed on the surface of solids and are shown in Fig. 8. The chemical groups of the surface O_2 atoms is decisive for the different modes of CO₂ adsorption. Chemisorption of CO₂ reveals both basic and active sites, for example, acid-base pairs if carbonate-like species are built, acidic sites where the CO₂ molecule retains its linear geometry after adsorption [40]. The presence of isolated or low-coordination superficial O2 anions represents the formation of monodentate carbonates, generally those present in edges. Lewis acid-base pairs manifest as bidentate carbonate (M-O₂ pair site, M is the metal cation Ca or Mg) and bicarbonate production involves surface hydroxyl groups. DRIFTS analysis show that they correspond to CO₂ gas between 2400 and 2200 cm⁻¹ associated with acidic sites where the carbonic dioxide molecule preserves the linear geometry [40]. The signals found around 1600 cm^{-1} correspond to monodentate carbonates.

8.2 NH₃ desorption measurements at the programmed temperature (TPD-NH₃)

In general, the strong acid is classified according to the desorption peaks and the temperature at which they appear, as follows: weak (< 150 °C), medium (150 and 400 °C), and strong (>400 °C). They can also be correlated with Lewis's acid sites (below 400 °C) and Brønsted acid sites (above 400 °C) [20]. The strong of the acid sites was determined by NH₃ TPD (Fig. 9). Three of the obtained biochars were compared: biochar activated with CaCl₂ (CaBC), biochar activated with MgCl₂ (MgBC), and non-activated biochar (BC). The TPD plots show that the

Fig. 9 NH₃ TPD profiles for BC, MgBC and CaBC

 $MgCl_2$ activation process increases the acid sites in the biochar, on the other hand, the $CaCl_2$ activation process shows that the strong acid sites decrease, i.e., the Brönsted acid sites decrease considerably. Although MgBC has a higher surface area, it does not adsorb more CO_2 than CaBC due to the interaction on the biochar.

8.3 X-ray photoelectron spectroscopy (XPS)

Figure 10 shows the XPS results for the biochars obtained in the study to C 1 s and N 1 s. In the biochars (BC), three distinct peaks are identified, which are generally attributed to contributions from C=C in graphitic carbon (284.6 eV), C-C (285.5 eV), and COOR groups (288.0-289 eV). The relative intensity of the peaks corresponding to C-C hybridisation increases with the incorporation of Mg (MgDBC 3.35%), suggesting a higher presence of defects in the structure during the activation process. In the MgBC samples, this peak increases due to a higher concentration of defective oxygen associated with MgO (which has a smaller particle size) [41, 42]. Additionally, upon activating the biochars with Ca and Mg and assessing the impact of fats, very similar signals for carbon and nitrogen were observed, which is related to the amount of proteins of lignocellulosic precursor. Nitrogen can be present in various forms in biochar, depending on the biomass source and pyrolysis conditions. For biochars from soursop seeds, N1s signals were found at ~ 398.0-398.6 eV. This peak is attributed to nitrogen atoms that are part of pyridinetype aromatic rings. Additionally, a peak was detected at ~ 399.8-400.4 eV, which is associated with nitrogen atoms that are part of pyrrole-type aromatic rings, including nitrogen in pyrrolidine-type structures.

8.3.1 FTIR spectra after CO₂ adsorption on biochars

Figure 11 shows the Infrared spectra after CO_2 adsorption on biochars. The characteristic bands of carbonyl (C=O), hydroxyl (OH), aromatic (C=C) and aliphatic (C-H) groups [26–28] kept similar after CO_2 adsorption. The above behavior indicates that the CO_2 adsorption does not noticeably modify the surface of the biochars. The above bands were also observed in the FTIR and DRIFTS of in situ CO_2 adsorption of the samples observed in Figs. 4 and 8 respectively.

8.4 Isosteric heats of adsorption

To calculate the isosteric heat of adsorption of CO₂, the modified Clausius Clapeyron equation was used at a constant temperature using the pressure data and the moles of adsorbed CO₂ obtained in the CO₂ adsorption isotherm. Table 1 shows the average value of isosteric heat of adsorption of CO₂ to biochars. The isosteric heat of adsorption was ranged from 8.0 to 11.0 kJmol⁻¹ and it was still located in the range of physical adsorption ($< 50 \text{ kJmol}^{-1}$). This behavior indicates that no strong chemical bond was formed between CO₂ and the biochars surface. The sample MgDBC showed the higher q_{st} value that the other samples, following BC sample, which reveal a strong affinity of the MgDBC and BC to CO_2 molecule. Likewise, the degreased biochars that were prepared with Ca and Mg activators presented a higher average Qst value, compared to their corresponding undegreased samples. This possibly indicates that the degreasing process favors the presence of higher energy sites, which causes a greater affinity of CO₂ and the surface of these samples.

Figure 12 shows the isosteric heat of adsorption of CO_2 on biochars. In general, the biochars exhibited isosteric heats of 54 kJmol⁻¹ to 1.5 kJmol⁻¹, in the range of 0.1 to 1 molkg⁻¹ CO₂ adsorption capacity. In all cases, as CO₂ adsorption increased, isosteric heat decreased as occurs in most biochars. The above behavior is due to that the CO₂ is adsorbed first in the higher energy adsorption sites, therefore contributing to a higher initial isosteric heat of adsorption.

8.4.1 CO₂ adsorption mechanism

Considering the results obtained from the characterization analyses in this study, a soursop seed biochar with a heterogeneous surface (Fig. 13) could be proposed, which includes micropores and mesopores mostly, determined by N_2 physisorption, and different functional groups (hydroxyl, carboxyl, carbonyl, etc.) detected by FTIR. The CO₂ adsorption mechanism on biochar involves several steps, from the diffusion of CO₂ to its interaction with the biochar surface and the functional groups present. The steps of the process

Fig. 10 XPS analysis of activated carbons. *N2 signal was not detected to MgBC

are typical of an adsorption. For this, the CO_2 molecules move from the environment to the biochar surface by diffusion. Then these molecules adhere to the external surface of the biochar possibly through Van der Waals forces, which correspond to a physisorption. In certain cases, CO_2 can form chemical bonds with functional groups on the biochar surface, such as hydroxyl, carboxyl and carbonyl groups and other. Subsequently, CO_2 moves through the larger pores in the biochar structure and penetrates into the micropores, where it can be adsorbed more effectively due to the stronger interactions in these pores. Then, CO_2 molecules adhere to the inner walls of the pores, through physical interactions, as indicated by the low average isosteric heat values found in the soursop seed biochars and in the presence of reactive functional groups, chemical adsorption can occur within the pores or active sites, which can increase the adsorption capacity of the biochar. The nature of these active sites of the biochar corresponds mostly to surfaces with C=C or

Fig. 10 (continued)

C–C bonds, as indicated by the XPS spectra performed. Finally, a dynamic equilibrium between the adsorption and desorption of CO_2 can be reached. According to the DRIFTS analyses carried out, the CO_2 is adsorbed through carbonate, bicarbonate, and molecular species [43]. According to the models applied in this study, the Redlich-Peterson model has great prevalence over the others, which confirms that the biochars obtained have a varied (heterogeneous) surface, which means that the surface is not uniform and can have different characteristics at different points.

Fig. 12 Isosteric heat of adsorption of CO_2 on Biohars estimated by the Clausius–Clapeyron equation modified

9 Conclusions

The process of defatting the soursop seeds does not improve the surface of the biochars, but this, added to the activation process with CaCl₂, improved the adsorption of CO₂ since the surface of the biochar was heterogeneous. Furthermore, this activation process decreases the acidity of the biochar, allowing for better CO₂ adsorption. In the case of the activation process with MgCl₂, the surface area increased as did the acidity of the samples, which did not take advantage of CO₂ adsorption.

The biochars prepared in this research obtained surface areas between 26 and 221 m^2g^{-1} and pore volumes 0.05–0.30 cm³g⁻¹. The CO₂ adsorption capacities are within values of 30–42 cm³g⁻¹ which demonstrate that the micromesoporous porous network formed helps the GHG adsorption process given the broad mesoporosity that generates routes of greater accessibility of the adsorbate to the interior of the micropores.

The substituent groups of these biomolecules remain on the surface of the solid after carbonization, favoring the adsorption of CO_2 , especially in the case of solids with reduced surface areas, resulting in similar amounts of CO_2 adsorption as reported in previous research.

The fit of the CO_2 adsorption isotherms to the Langmuir and Redlich models suggests that the biochars have been

solid with a mostly mixed surface; biochars such as DBC and CaDBC were materials with a homogeneous surface due to their fit to the Langmuir model.

One way to improve surface area is to increase the heating rate because volatile loss is better than using a slow rate. it was evidenced in the pore size, since the pores were of similar size, but the surface area changed, having different values. This suggests that the porous structure was obstructed by the lack of volatile matter. Regarding the defatting process, an attempt would be made to use a supercritical fluid process to improve the radial pentagon of biochar synthesis.

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Data availability The authors of the present investigation corroborate that the data supporting the findings of this investigation are available

in the article, and additional information may be obtained by sending an email to the corresponding author, upon reasonable request.

Declarations

Conflict of interest The authors declare no competing interests.

Ethical approval The authors of this research certify that the presentation is a unique—original work and is not currently under review in any journal or other publication.

Consent to participate All the authors described in this work have seen, reviewed and agree with the entire content of the manuscript.

Consent for publication All authors agree to submit this manuscript for review and publication in this journal.

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References

 Afrouzi, H.N., Ahmed, J., Siddique, B.M., Khairuddin, N., Hassan, A.: Results in engineering review article a comprehensive review on carbon footprint of regular diet and ways to improving lowered emissions. Results Eng. 18, 101054 (2023). https://doi. org/10.1016/j.rineng.2023.101054

- Su, E.Y., Con, R., Paola, B., Salcedo, C., Rivera, C.V.: Puerta Roja de la Universidad de Sucre—Colombia evaluation of the ecological footprint and its relationship with the biological capacity at the puerta roja campus of the University of Sucre—Colombia. Rev. Investig. en Gestión Ind. Ambient. Segur. y Salud en el Trab. (2022). https://doi.org/10.34893/gisst.v8i1.422
- Abuelnoor, N., Alhajaj, A., Khaleel, M., Vega, L.F.: Chemosphere Activated carbons from biomass-based sources for CO₂ capture applications. Chemosphere 282, 131111 (2021). https://doi.org/ 10.1016/j.chemosphere.2021.131111
- Manyà, J.J., González, B., Azuara, M., Arner, G.: Ultra-microporous adsorbents prepared from vine shoots-derived biochar with high CO₂ uptake and CO₂/N₂ selectivity. Chem. Eng. J. 345, 631–639 (2018). https://doi.org/10.1016/j.cej.2018.01.092
- Torres, D., Sonia, J., Morales, P., Juan, V., Quintero, C.: "Evaluación de pretratamientos químicos sobre materiales lignocelulósicos chemical petreatments evaluation on lignocellulosic materials. Ingeniare. Rev. Chil. Ing. 25, 733–743 (2017). https:// doi.org/10.4067/S0718-33052017000400733
- Sharma, G., et al.: Activated carbon as superadsorbent and sustainable material for diverse applications. Adsorpt. Sci. Technol. (2022). https://doi.org/10.1155/2022/4184809
- Solı, J.A.: Soursop (Annona muricata L.) Seeds, therapeutic and possible food potential. Elsevier (2011)
- Komansilan, A., Abadi, A.L., Yanuwiadi, B., Kaligis, D.A.: Isolation and identification of biolarvicide from soursop (Annona muricata Linn.) seeds to mosquito (Aedes aegypti) larvae. Int. J. Eng. Technol. 12(3), 28–32 (2012)
- Acevedo, S., Giraldo, L., Moreno-Piraján, J.C.: Kinetic study of CO₂ adsorption of granular-type activated carbons prepared from palm shells. Environ. Sci. Pollut. Res. (2023). https://doi.org/10. 1007/s11356-023-26423-5
- Jasri, K., Saud, A., Jawad, A.H., Alothman, Z.A., Yousef, T.A., Al Duaij, O.K.: Diamond & related materials mesoporous activated carbon produced from mixed wastes of oil palm frond and palm kernel shell using microwave radiation-assisted K₂CO₃ activation for methylene blue dye removal : optimization by response surface methodology. Diam. Relat. Mater. (2023). https://doi.org/ 10.1016/j.diamond.2022.109581
- Acevedo, S.: Adsorption of CO₂ onto activated carbons preparedby chemical activation with metallic salts. Int. J. Chem. Reactor Eng. 15, 1–11 (2018). https://doi.org/10.1515/ijcre-2017-0198
- Giraldo, L., Vargas, D.P., Moreno-Piraján, J.C.: Study of CO₂ adsorption on chemically modified activated carbon with nitric acid and ammonium aqueous. Front. Chem. (2020). https://doi. org/10.3389/fchem.2020.543452
- Marrakchi, F., Hameed, B.H., Bouaziz, M.: Mesoporous and highsurface-area activated carbon from defatted olive cake by-products of olive mills for the adsorption kinetics and isotherm of methylene blue and acid blue 29. J. Environ. Chem. Eng. 8(5), 104199 (2020). https://doi.org/10.1016/j.jece.2020.104199
- Raffrenato, E., Van Amburgh, M.E.: Technical note : improved methodology for analyses of acid detergent fiber and acid detergent lignin. J. Dairy Sci. 94(7), 3613–3617 (2011). https://doi.org/ 10.3168/jds.2010-3701
- Prandi, B., Ruales, J., Van Camp, J., Sforza, S., Elst, K.: Valorization of soursop (Annona muricata) seeds as alternative oil and protein source using novel de-oiling and protein extraction techniques. LWT (2023). https://doi.org/10.1016/j.lwt.2023.114777
- Acevedo Corredor, S.: Preparación y caracterización de carbón activado granular obtenido a partir de cuesco de palma africana (Elaeis Guineensis) para la adsorción de CO₂ (2014)
- Acevedo Corredor, S.: Activación química de cuesco de palma africana (Elaeis Guineensis) con soluciones de sales metálicas en la preparación de carbones activados para la adsorción de CO₂ (2019)

- Esteves, L.M., Brijaldo, M.H., Passos, F.B.: Decomposition of acetic acid for hydrogen production over Pd/Al₂O₃ and Pd/TiO₂: influence of metal precursor. J. Mol. Catal. A Chem. **422**, 275–288 (2016). https://doi.org/10.1016/j.molcata.2016.02.001
- Castañeda, C., Tzompantzi, F., Gómez, R., Rojas, H.: Enhanced photocatalytic degradation of 4-chlorophenol and 2,4-dichlorophenol on in situ phosphated sol-gel TiO₂. J. Chem. Technol. Biotechnol. **91**(8), 2170–2178 (2016). https://doi.org/10.1002/jctb. 4943
- Brijaldo, M.H., Mancipe, S., Rojas, H.A., Viviana, P.L., Araiza, D.G., Díaz, G.: "Effect of boron on the surface properties of nickel supported on hydrotalcite-type mixed oxides in methanol decomposition. Mol. Catal. (2020). https://doi.org/10.1016/j.mcat.2020. 111262
- Brijaldo, M.H., Rojas, H.A., Martínez, J.J., Passos, F.B.: Effect of support on acetic acid decomposition over palladium catalysts. J. Catal. 331, 63–75 (2015). https://doi.org/10.1016/j.jcat. 2015.08.019
- 22. Giraldo, L., Moreno, J.C.: Adsorción de CO₂ en carbón activado con diferente grado de activación. Afinidad 67, 548 (2010). https://raco.cat/index.php/afinidad/article/view/269277
- Rojas, H.A., Martínez, J.J., Brijaldo, M.H., Passos, F.: Producción de alcohol cinamílico a partir de la hidrogenación selectiva de cinamaldehído usando catalizadores de oro soportados en óxidos metálicos. Rev. la Acad Colomb. Ciencias Exactas Físicas y Nat. 43, 539–549 (2019). https://doi.org/10.18257/racce fyn.852
- Balathanigaimani, M.S., Shim, W.G., Lee, J.W., Park, K.H.: Effects of structural and surface energetic heterogeneity properties of novel corn grain-based activated carbons on dye adsorption. Micropor. Mesopor. Mat. 118, 232–238 (2009). https://doi.org/ 10.1016/j.micromeso.2008.08.028
- Yang, H.: Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86, 1781–1788 (2007). https://doi.org/10.1016/j. fuel.2006.12.013
- Schroeder, P., do Nascimento, B.P., Romeiro, G.A., Figueiredo, M.K.K., da Cunha Veloso, M.C.: Chemical and physical analysis of the liquid fractions from soursop seed cake obtained using slow pyrolysis conditions. J. Anal. Appl. Pyrolysis **124**, 161–174 (2017). https://doi.org/10.1016/j.jaap.2017.02.010
- Hu, Q., Zhang, Z.: Application of Dubinin-Radushkevich isotherm model at the solid/solution interface: a theoretical analysis. J. Mol. Liq. 277, 646–648 (2019). https://doi.org/10.1016/j.molliq.2019. 01.005
- Yao, X., Li, L., Li, H., He, S.: A new method for preparing hydrophilic-activated carbon through ester hydrolysis in an alkaline environment. J. Mater. Sci. 49(14), 4807–4815 (2014). https:// doi.org/10.1007/s10853-014-8180-9
- Tu, W., Hallett, J.P.: ScienceDirect recent advances in the pretreatment of lignocellulosic biomass. Curr. Opin. Green Sustain. Chem. 20, 11–17 (2019). https://doi.org/10.1016/j.cogsc.2019.07. 004
- Kim, K.C., Yoon, T.U., Bae, Y.S.: Applicability of using CO₂ adsorption isotherms to determine BET surface areas of microporous materials. Micropor. Mesopor. Mater. 224, 294–301 (2016). https://doi.org/10.1016/j.micromeso.2016.01.003
- Abunowara, M., Bustam, M.A., Sufian, S., Eldemerdash, U.: Description of carbon dioxide adsorption and desorption onto malaysian coals under subcritical condition. Procedia Eng. 148, 600–608 (2016). https://doi.org/10.1016/j.proeng.2016.06.521
- Santhi, T., Manonmani, S., Smitha, T.: Removal of methyl red from aqueous solution by activated carbon prepared from the *Annona squmosa* seed by adsorption. Chem. Eng. Res. Bull. 14(1), 10–18 (2010). https://doi.org/10.3329/cerb.v14i1.3767

- Langmuir, I.: The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 345, 1918 (1914). https:// doi.org/10.1021/ja02242a004
- Crini, Ã., Badot, P.: Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies : a review of recent literature. Prog. Polym. 33, 399–447 (2008). https://doi.org/10.1016/j.progpolyms ci.2007.11.001
- Freundlich, H.M.F.: Over the adsorption in solution. J. Phys. Chem. 57, 1100–1107 (1906)
- Nasr, A.H.M.F., Latifa, A.J.F.: Aminated acrylic fabric waste derived sorbent for Cd (II) Ion removal from aqueous solutions : mechanism, equilibria and kinetics. J. Polym. Environ. (2020). https://doi.org/10.1007/s10924-020-01863-z
- Redlich, O., Peterson, D.L.: A useful adsorption isotherm. J. Phys. Chem. 63(6), 1024 (1959)
- Toth, J.: State equation of the solid-gas interface layers. Acta Chim. Hung. 69, 311–328 (1971)
- Yu, X.X., Liu, B., Shen, Y.H., Zhang, D.H.: Design and experiment of high-productivity two-stage vacuum pressure swing adsorption process for carbon capturing from dry flue gas. Chin. J. Chem. Eng. 43, 378–391 (2022). https://doi.org/10.1016/j.cjche. 2021.02.022
- Ausavasukhi, A., Kampoosaen, C., Kengnok, O.: Adsorption characteristics of Congo red on carbonized leonardite. J. Clean. Prod.

134, 506–514 (2016). https://doi.org/10.1016/j.jclepro.2015.10. 034

- Alavi, M.A., Morsali, A.: Ultrasonics sonochemistry syntheses and characterization of Mg(OH)₂ and MgO nanostructures by ultrasonic method. Ultrason. Sonochem. **17**(2), 441–446 (2010). https://doi.org/10.1016/j.ultsonch.2009.08.013
- 42. Lay, M., Rusli, A., Khalil, M., Ain, Z., Hamid, A., Khimi, R.: Converting dead leaf biomass into activated carbon as a potential replacement for carbon black filler in rubber composites. Compos. Part B 201, 108366 (2020). https://doi.org/10.1016/j.compositesb. 2020.108366
- Chen, S., Wenling, Wu., Niu, Z., Kong, D., Li, W., Tang, Z., Zhang, D.: High adsorption selectivity of activated carbon and carbon molecular sieve boosting CO₂/N₂ and CH₄/N₂ separation. Chin. J. Chem. Eng. 67, 282–297 (2024). https://doi.org/10. 1016/j.cjche.2023.10.015

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