CO$_2$ capture on an optimally prepared highly microporous KOH-activated carbon from rice husk

Captura de CO$_2$ en un carbón activado con KOH altamente microporoso preparado de manera óptima a partir de cáscara de arroz

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Abstract

In this study, rice husk was used as a low-cost agro-waste to produce optimally a high microporous KOH-chemically activated carbon for efficient CO$_2$ capture. In order to find the optimum conditions to prepare this carbon-based adsorbent, the rice husk was subject to different carbonization temperatures, followed by various KOH impregnation ratios, activation temperatures, and activation times, in absence of an inert atmosphere. All developed carbons were characterized by using different analytical methods. Results showed that the rice husk carbonization at 600 °C by 1 hour followed by KOH-chemical activation using a mass impregnation ratio of 1:3 at 600 °C during 1 h, produced an activated carbon of microporous structure, with a high surface area of 1384.4 m^2/g and a high total pore volume of 1.0854 cm^3/g, these obtained morphological and textural properties were correlated with their exhibited CO$_2$ adsorption capacity of 110.78 mg/g under atmospheric conditions, measured by the thermogravimetric method. The results indicate that KOH chemical activation under no inert gas conditions as an optimized synthesis route does seem to be a suitable modification technique that offered to prepare with economic feasibility a valuable activated carbon to be potentially used in CO$_2$ capture technologies.

Keywords: rice-husk, KOH-chemically activated carbon, CO$_2$ capture, adsorption, microporous.

Resumen

En este estudio, la cáscara de arroz se utilizó como un desecho agrícola de bajo costo para preparar de manera óptima un carbón activado químicamente utilizando KOH altamente microporoso para la captura eficiente de CO$_2$. Con el fin de encontrar las condiciones óptimas de preparación de este adsorbente a base de carbono, la cáscara de arroz se sometió a diferentes temperaturas de carbonización, seguidas de diversas relaciones de impregnación con KOH, temperaturas de activación y tiempos de activación, en ausencia de una atmósfera inerte. Todos los carbones desarrollados se caracterizaron utilizando diferentes métodos analíticos. Los resultados mostraron que la carbonización de la cáscara de arroz a 600 °C por 1 hora seguida de la activación química con KOH usando una relación de impregnación en masa de 1:3 a 600 °C durante 1 h, produjo un carbón activado de estructura microporosa, con alta área superficial de 1384.4 m^2/g y alto volumen de poro total de 1.0854 cm^3/g, estas propiedades morfológicas y texturales obtenidas se correlacionaron con su capacidad de adsorción de CO$_2$ exhibida de 110.78 mg/g en condiciones atmosféricas, medida por el método termogravimétrico. Los resultados indican que la activación química de KOH en condiciones sin gas inerte como ruta de síntesis optimizada parece ser una técnica de modificación adecuada que ofrecía preparar con viabilidad económica un valioso carbón activado para ser potencialmente utilizado en tecnologías de captura de CO$_2$.

Palabras clave: cáscara de arroz, carbón activado químicamente con KOH, captura de CO$_2$, adsorción, microporoso.

1   Introduction

At present, it is widely recognized that climate change is occurring due to drastic increase in atmospheric concentrations of carbon dioxide gas (CO_2), which is known as the main gas of greenhouse (Yan *et al*., 2017). The CO_2 is mostly emitted at great scale by the most concentrated fixed sources of CO_2; electric power generating plants, and other great industrial processes after burning fossil fuels such as natural gas, petroleum, and coal (Lillia *et al*., 2018). In order to abate the atmospheric CO_2 gas emission, and reduce the negative environmental impacts caused by high atmospheric CO_2 concentrations, in the last decades, several promising approach CO_2 capture technologies have been developed, such as; chemical adsorption in basic solutions (Singto *et al*., 2017), membrane purification (Guo *et al*., 2018), cryogenic methods (Yousef *et al*., 2018), and adsorption in solid adsorbents (Zeng *et al*., 2022) between others. However, currently, amongst these technologies, the CO_2 adsorption process over solid adsorbents has been extensively studied as one of the main carbon capture and storage technologies (CCS) at great scale, due to low operating cost, low energy requirements, low secondary waste generation and applicability over a wide range of temperatures and pressures, this technology is based in the use of different highly efficient, selective and economical adsorbent materials of nature varied such as: hydrotalcites (Garcés-Polo, 2018), zeolites (Ullah *et al*., 2018), metal oxides (Gutiérrez-Bonilla *et al*., 2017), metal organic frameworks (Azmi and Aziz, 2019), agricultural residuals (Salazar-Pinto *et al*., 2021) and activated carbons (Boujibar *et al*., 2018). Among these solid materials mentioned above, the adsorbents with microporous structures are suitable for CO_2 adsorption purposes, because due to this remarkable feature, have achieved excellent CO_2 capture performance and selectivity.

Therefore, the development and use of novel microporous structured materials as solid adsorbents are highly desirable and potentially important for CO_2 capture technologies. It is clearly seen that the carbon-based materials due to its notable advantages usually related to their attractive morphology and textural properties, additionally its low-cost, are significantly necessary in this concern. This materials-type, have been widely employed in various technological applications as pollutant removal from both aqueous and gaseous media (De Andrade *et al*., 2015). Specifically for CO_2 adsorption purposes, the activated carbons have shown high adsorption capacity at ambient temperature and pressure, are very stable to reuse over various CO_2 adsorption cycles and can be regenerated at low temperatures for short times, as a consequence, all these features make them technologically economical compared to other possible CO_2 adsorbents studied. In particular, the CO_2 adsorption properties of activated carbons largely depends on the surface area and micropore characteristics, because the gases adsorption is mainly governed by pore diffusion, that allow the easy transport of gaseous molecules into the microporous structure at a large surface area and large pore volume, which offer more active sites to trap CO_2 molecules and more pollutant storage (Yunes, *et al*., 2013). On the other hand, it well known that the development of carbon-base materials highly microporous with large surface areas and large pore volumes can be achieved through chemical or physical activation processes. With these activating processes, are development carbons with predominance of mesoporous and microporous structures, increasing the accessibility of large molecules to the external pore openings or small molecules in microporous network, as a consequence, both types of pores on adsorbent materials are important for use in wastewater or gas treatment (Granados-Correa *et al*., 2016; Xi *et al*., 2022). Therefore, in terms of CO_2 capture, an understanding of the preparation variables influence of activated carbon adsorbents with developed high microporous structure, high surface area and high total pore volume that improve the interaction between gas molecules and carbon surfaces, is the goal of many investigations. Particularly, the physical and chemical activation processes are utilized in general for the manufacture of improved activated carbons from different carbon precursors. Chemical activation is advantageous compared to physical activation because is carried out in only one stage, it allows prepare activated carbons at shorter time treatment of precursors, and uses relatively moderate temperatures (400-800 °C) in the presence of dehydrating agents under inert gas conditions (Smisek and Cerny, 1970), the chemical activation provides better-developed pore structure in activated carbons than physical activation, resulting in the generation of large surface area and uniform pore distribution, properties that allow to capture a great diversity of molecules of different sizes as CO_2 (Budinova *et al*., 2006), or to remove other important waste gases such as H_2S from waste

treatment plants (Li and Li, 2020). In general, the chemical activation method involves impregnating precursors with different chemical agents of relatively low commercial cost such as; phosphoric acid, zinc chloride, potassium hydroxide, and sulfuric acid (Mochizuki *et al.*, 2016). These chemical agents act as dehydrating materials, oxidants and reduce the formation of volatile materials and thereby favoring higher product yield (Hayashi *et al.*, 2000). Has been reported that among these chemical activators, KOH is the most commonly used and efficient activating agent for the preparation of highly microporous carbons with high surface area and high total pore volume, recognized these remarkable properties as key features that makes them privileged adsorbents to achieve a efficient and selective CO_2 adsorption capacity (Lee *et al.*, 2016).

In this regard, many activated carbons can be prepared from abundantly available and low-cost carbon-containing precursors, mainly of agricultural waste products rich in lignocellulose, cellulose, hemicellulose, lignin, proteins, water and sugars, of which it can cite a wide variety of cereal husks, legumes and fruits, as well as different seeds, bagasses and fruit bones, among others, all considered as excellent sources due to their high-carbon and low-ash contents (Danish and Ahmed, 2018; Ogungbenro *et al.*, 2018). For instance, it is well known that rice (*Oryza sativa L.*), is one of the most important cereal crops in the world, as a consequence is the principal dietary component of the population in most countries in Asia, Africa, and to a lesser extent in the European Union and Latin America (Romero and Gatica, 2019). Therefore, rice is economically and socially important around the world, and their crops is very adaptable, promoting the existence of different varieties (Salgado-Delgado *et al.*, 2022). Due to its high consumption and consequently its extensive cultivation, large amounts of agricultural waste like rice husk are produced. In fact, in México the rice husk is one of the agricultural waste product that is generated in large quantities, since rice is one of the 4 main grains that are mostly consumed in México and more then 254 000 tons are produced annually (Sagarpa, 2017), and of the total of this production, 20% in weight is rice husk which represents a serious environmental problem and do not have a proper mechanism for disposal (Serrano *et al.*, 2012). In addition, it has been reported that the rice husk due to its high content of cellulose, hemicellulose, lignin and ashes, it is a material of low nutritional value, and due to its low digestibility, it is rarely

used as animal food (Trujillo-Ramírez *et al.*, 2022). Therefore, the use of rice husk as raw material to prepare an attractive carbon-based adsorbent with CO_2 adsorption properties could solve this problem, because it would reduce the waste volume and the resulting low-cost product will be very useful as a decontaminating adsorbent.

The aim of the present study is to develop a high-quality KOH-chemically activated carbon adsorbent from low-cost and highly available rice-husk waste for CO_2 capture at room conditions. For this reason, the present investigation has the following purposes: 1) Prepare a carbonaceous materials from rice husk as precursor, 2) KOH-chemical activation of carbonaceous residues prepared, under various activation conditions: different mass ratio of carbonaceous residue/KOH, activation temperatures and times, 3) Chemical, microstructural, surface, textural and morphological characterization of carbon-based materials, 4) Investigate the CO_2 adsorption behavior on the best prepared material, and additionally, 5) Study the effects of the physicochemical properties on the CO_2 adsorption performance.

2 Experimental

2.1 Materials and reagents

Natural rice-husk (RH) was used as a precursor material which was collected in the locality of Cuernavaca Morelos, México. Potassium hydroxide (KOH, 86% purity) and hydrochloric acid (HCl, 37% purity) were purchased from Merck and Baker ACS, respectively, and all chemicals were of analytical grade and used without further purification, also distilled water was used to solutions preparation and for materials washing. All used gases in this study were supplied by Infra México with the follows specifications: carbon dioxide ultra-dry (CO_2, 99.99% purity), helium (He, 99.98% purity) and nitrogen (N_2, 99.90% purity).

2.2 Rice husk preparation and carbonization process

The rice husk collected was thoroughly washed with enough distilled water to remove soluble impurities and dried in an oven at 110 °C for 2 h. After, the cleaned and dried material was finely ground

in an agate mortar, then, the powdered rice-husk was carbonized directly in a muffle furnace, for this purpose, by separated around 5 g of ground and dry material was placed in a 50 mL porcelain crucible into the center of the muffle furnace and burned at different temperatures (400, 500, 600 y 700 °C) for 1 h. After carbonization, the obtained carbonized materials were cooled down at room temperature, crushed in an agate mortar, and sieved in a 60 mesh in order to obtain a uniform size of 0.25 mm and to remove large particles and other impurities. The carbonized materials were weighted very accurately, stored and labeled as: CRH-400, CRH-500, CRH-600 and CRH-700 respectively. In order to verify the carbonization optimization process, each carbonized material prepared was comparatively characterized, by means of N_2 physisorption measurements to know its Brunauer-Emmett-Teller (BET) surface area (A_{BET}), total pore volume (V_{Tp}), mean pore diameter (d_p), the pore size distribution by the Barrett-Joyner-Halenda (BJH) method and N_2 adsorption-desorption isotherms. By scanning electron microscopy (SEM) for known the sample morphologies, the sample microanalysis was done by energy dispersive X-ray spectroscopy (EDXS), and X-Ray Diffraction (XRD) for to determine the structural properties. Moreover, the carbon yield of samples, R(%) were calculated according to following equation (1):

$$R(\%) = \frac{\text{Dry final weight (g)}}{\text{Dry initial weight (g)}} \times 100 \qquad (1)$$

2.3 KOH-chemical activation process

The carbonized material prepared that show the better textural properties as well as better carbonization yield, was subjected to a KOH-chemical activation by wet impregnating. For this purpose, the selected sample it was impregnated with potassium hydroxide (KOH) activing agent at five different CRH/KOH mass ratios from 3:1 to 1:3 at constant activation temperature of 600 ºC during 1h. Each prepared mixture was stirred constantly for 2h at room temperature with the help of a magnetic mixer-stirrer, and after dried in an oven at 110 °C for 18 hours with the purpose of removing excessive moisture supplied by the solution. After of impregnation process, the samples were introduced into muffle furnace and activated at temperature of 600 °C for 1 h. The resulting materials were washed with HCl 10% (v/v) solution and abundant amount of distilled water until pH of 6.0-7.0 was reached, in order to achieve a complete removal of unreacted

dehydrating KOH agent and soluble impurities present. The resulting materials were dried in an oven at 110 °C for 18 h and labeled denoting their respective CRH/KOH impregnation mass ratio as: RHKOH-31, RHKOH-21, RHKOH-11, RHKOH-12 and RHKOH-13 respectively. Finally, the prepared samples were characterized using morphological, textural, and structural techniques and stored for further experimentations.

2.4 KOH-chemical activation temperature

In order to find the optimum KOH-chemical activation temperature for activated carbon preparation. The sample KOH impregned at optimal conditions, that exhibits better textural properties, was chosen and subjected at the same KOH impregnation process described above, but now using activation temperatures of 500 ºC and 700 ºC during 1h respectively. Moreover, the samples obtained at this experimental stage where textural and morphological characterized with different analytical techniques in order to identify the optimal activation temperature conditions.

2.5 Carbonized and KOH-chemically activated samples characterization

Each carbonized sample prepared at different temperatures (400, 500, 600 y 700 °C) for 1 h, and each KOH-activated carbon samples prepared under different CRH/KOH impregnation mass ratios, different activation temperatures and activation times were comparatively characterized through by using several analytical methods; the Brunauer-Emmett-Teller (BET) surface area (S_{BET}), total pore volume (V_{Tp}), mean pore diameter (d_p), pore size distribution by Barrett-Joyner-Halenda (BJH) method and N_2 adsorption-desorption isotherm were determined by N_2 physisorption measurements at liquid nitrogen temperature (77K) by using a Micromeritics Belsorp Max Inc. Japan equipment. Prior to this measurement, all samples were degassed in a nitrogen stream at 300 °C for 2 h, in order to remove contaminants adsorbed or any moisture. The porous morphology of the carbon-based materials was investigated by using scanning electron microscopy with a JEOL-JMS-5900LV microscope fitted with energy dispersive X-ray (EDXS) detector using a microprobe EDS Oxford for elemental analysis, for this purpose, the samples were mounted onto aluminum brackets using aluminum tapes, and were previously sputter coater

with gold by using a Denton Vacuum DESK II for 120 s. The carbon sample structures were performed by X-ray diffraction (XRD) by using a Bruker X-ray diffractometer model D8 Discover, equipped with Cu-Kα radiation (λ= 1.54060 Å). The diffraction data were analyzed in the 10° to 75° range in 2θ with at 0.04 s of step size, and were identified according to their referring diffraction lines of corresponding standard samples by using the Joint Committee of the Powder Diffraction Standard (JCPDS) cards.

2.6 CO$_2$ adsorption experiments

In order to investigate the CO$_2$ adsorption capacity onto prepared carbon materials, CO$_2$ adsorption experiments were carried out by placing activated carbon samples previously degasified inside a steel high vacuum reactor type Parr of 50 mL of capacity at 1atm and 25 ºC, under an ultra-dry CO$_2$ gas flow (99.99% purity). The CO$_2$ adsorption capacity in milligrams of CO$_2$ adsorbed per gram of adsorbent (mg/g), on the basis of weight loss of CO$_2$ that was physically or chemically adsorbed in the prepared carbons were determined by thermogravimetric and differential scanning calorimetry (TGA-DSC) analysis by using a thermal gravimetric analyzer TA Instruments SDT Q600 coupled with mass spectrometer TA Instruments-Waters; around 5 mg of samples previously exposed to purified CO$_2$ flow into the steel high vacuum reactor were used and heating at a rate of 25 °C/min up 800 ºC in helium atmosphere, at a constant gas flow rate of 100 mL/min.

3 Results and discussion

3.1 Carbonized rice-husk preparation

From carbonization process of natural rice-husk, it was found that the optimum carbonization temperature was at 600 °C during 1 h, which provided a carbonization yield of 21.67%. Table 1 shows summarized the most important textural properties of the carbonaceous materials prepared under different carbonization temperatures ranging from 400 ºC to 700 ºC during 1 h, as well as the percent carbonization yields. It can be seen from these results, that the carbonaceous residue obtained at 400 °C sample (CRH-400), clearly exhibited the better textural properties in terms of surface area (A_{BET}), total pore volume (V_{Tp}) and mean pore diameter (d_p) comparable than the other carbonized samples prepared, and it seems to be the more suitable carbonaceous sample, however, in this sample a complete carbonization was not reached at this tested carbonization temperature. At 500 °C the sample (CRH-500) only a volatilization of tar products derived from the lignocellulosic components of raw material is presented. The carbonaceous material prepared at carbonization temperature of 700 ºC sample (CRH-700), was quite clear not selected as suitable product because showed an ash content, according to Mansha *et al.* (2012), the ash is usually produced when the rice-husk is treated at temperatures above of 550 ºC, and their amount, increase as the calcination temperature increases, as a consequence the ash composed mainly of amorphous silica its converts itself into crystal silica that is not suitable for CO$_2$ adsorption, then, amorphous silica is the major component of rice-husk ash and their color varies from grey to white, on this bases, the amount of black carbon in the sample decreases. In fact, was also found that this prepared sample (CRH-700) showed the lowest values of BET surface area (176.22 m^2/g) and total pore volume (0.215 m^3/g) as summarized in Table 1. On the other hand, it is important to note that from carbonization temperatures ranging from 400 ºC to 700 ºC, a decrease in the carbonization yield ranged from 29.28% to 21.63% was observed, which is attributed to the loss of volatile matter and to disintegration of lignocellulosic organic material

Table 1. Main textural properties and carbonization yields (%) of carbonaceous materials obtained under different carbonization temperatures.

Samples	Carbonization temperature (°C)	A_{BET} (m^2/g)	V_{Tp} (cm^3/g)	d_p (nm)	*r_p (nm)	Carbonization yield (%)
CRH-400	400	333.88	0.234	2.42	1.21	29.28
CRH-500	500	278.14	0.224	2.42	1.21	23.30
CRH-600	600	234.67	0.226	3.28	1.64	21.67
CRH-700	700	176.22	0.215	3.38	1.65	21.63

*Pore size distribution based on the Barrett-Joyner-Halenda (BJH) method.

present in the natural rice-husk, resulting in the evolution of gaseous products leading to decreased carbon yield. Therefore, carbonization temperature was found to have significant effect on carbonization yield. Also it was observed that from carbonization temperatures ranging from 600 ℃ to 700 ℃, the carbonization yields remains constants, this behavior may be due to that when the activation temperature excedes 600 ℃, most of the volatiles present in the sample have been completely released. Therefore, at more calcination temperature, no any significant difference between carbon yields were found. From mean pore diameter analysis of carbonous materials, the results show that when the carbonization temperature increase from 400 ℃ to 700 ℃, an increased mean pore diameter of 2.42 nm to 3.38 nm was reached, according to Sentorun-Shalaby *et al.* (2006), this behavior can be attributed to extensive degassing at more carbonization temperature, which results in widening of the pores and causing a partial collapse of the porous structure, and, hence, decrease the BET surface area for material, as was observed. In this context, it can to deduce that when the carbonization temperature increase, permits to have more mesopores than micropores, which favor the large molecules adsorption contrary to micropores that favor the small molecules adsorption like CO_2 molecules, however, would be expected that a well-microporous structure will be obtained by dehydrating agent action through a KOH-chemical activation process of carbonized material. On the other hand, a fine analysis of results obtained by BJH method about pore size distribution, showed that the pore radii (r_p) values of carbonized samples were from 1.21 nm to 1.65 nm or as pore diameters were from 2.42 nm to 3.2 nm, when was increased the carbonization temperature from 400 ℃ to 700 ℃, consequently these values were mainly of mesoporous character, which is a material that contains pores with diameters between 2 and 50 nm, according to the International Union of Pure and Applied Chemistry (IUPAC) nomenclature. Therefore, based on the obtained results, the sample (CRH-600) prepared by direct carbonization of lightweight rice-husk of fibrous nature at 600 ℃ during 1 h, was chosen as the more suitable carbonaceous material, for a performing further KOH-chemical activation process, in terms by obtaining a complete carbonization yield of 21.67%, which guaranteed the production of a stable carbonized material, rich in carbon and that developed an initial porosity, and functionality.
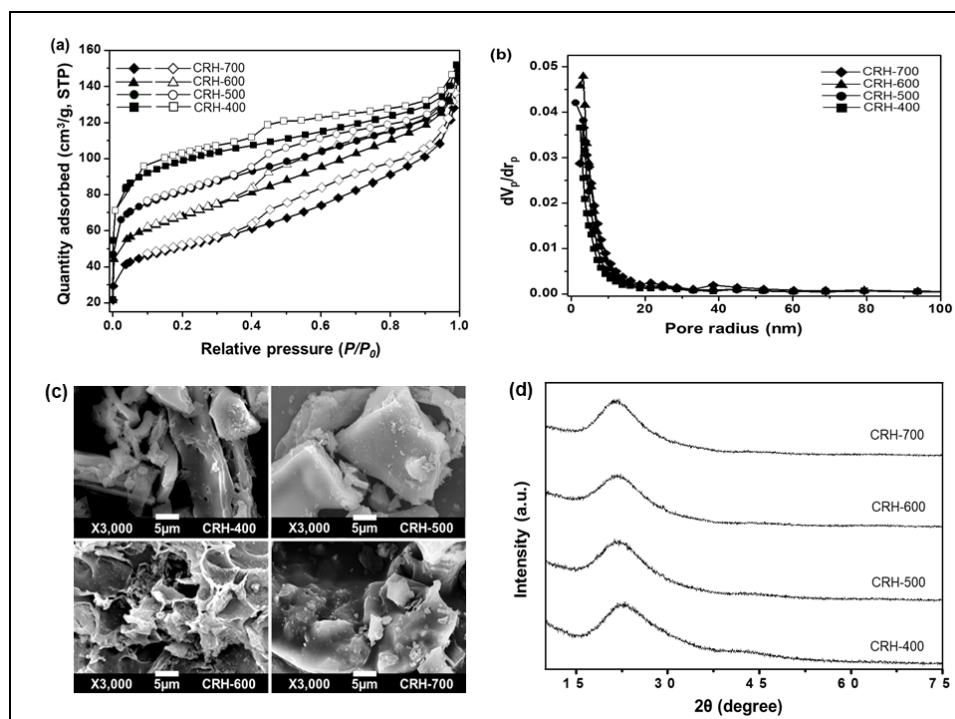

Figure 1. Main characterization of natural rice carbonized materials obtained under carbonización temperatures from 400 ℃ to 700 ℃, (a) N$_2$ adsorption-desorption isotherms, (b) pore radius distributions, (c) SEM and EDS studies and (d) XRD Diffraction patterns.

As a result, Fig. 1 shows the different main characterizations of all obtained carbonaceous materials from rice-husk under different carbonization temperatures. In this regard, the N_2 adsorption-desorption isotherms obtained from carbonaceous materials at relative pressure of $p/p_o = 0.99$, were of similar behavior and exhibited for all carbonous materials type IV isotherms (Fig. 1(a)), according to the IUPAC classification, which correspond to mesoporous solids. The hysteresis curve of isotherms depicts the pores type and give an idea about the surface characteristics (Ayinla *et al.*, 2019), as a result, the isotherms obtained reveals H3-type hysteresis that are characteristic of pores with a slit shape of uniform sizes. Fig. 1(b) shows the pore size distribution curves obtained by the Barrett-Joyner-Halenda (BJH) method. The trend observed, regardless of the increase in the carbonization temperature ranging from 400 ºC to 700 ºC among all the prepared carbons, only a peak of homogeneous mesopore size distributions of approximately 90% with pore radius (r_p) in the average from 1.21 to 1.65 nm values were observed in all distribution curves. Therefore, this notable homogeneous porous structures developed under direct carbonization treatment, gives a idea about of the suitability to use this natural and fibrous rice-husk as excellent precursor to produce an advantageous low-cost carbon-base adsorbent for CO_2 capture, even without a KOH-chemical activation process.

SEM micrograph of carbonized materials at 3000X are shown in Fig. 1(c), in general were observed materials with many homogeneous large holes of diameters about 5 μm, which is clearly visible that were porous materials. Fig. 1(d) shows the X-ray diffractograms of carbonaceous materials prepared under different carbonization temperatures. It was observed in all diffractograms, an unordered crystalline structure, indicative of amorphous nature materials with a degree of non-arrangement in the molecular chain, which is an advantageous property for well-defined adsorbents, this entails the best material for the production of activated carbons (Cheol-Min and Katsumi, 2002). In general, it is interesting to note that the XRD patterns of all carbons are similar in terms of peaks and intensities that appears in 20º of 2θ degree. Therefore, it is highlight notorious that an amorphous carbonaceous material, was prepared with a reasonable surface area, total pore volume, and yielding 21.43% carbon product when was calcined at 600 °C for 1 h. In fact, this microporous-mesoporous carbonous material obtained could be already used as CO_2 adsorbent but with a limited surface area of 234.67 m^2/g. However, when this carbon material it be KOH-chemically activated, would be expected to undergo noticeable surface and textural changes, which would imply an efficient capture of CO_2. Therefore, was showed that only the carbonization process, including carbonization temperature and carbonization time, not have a significant effect on the microporosity, surface area, and total pore volume pore of the resulting product, but can have a significant influence on the produced carbon yield, the precursor type used, in this case, the rice husk.

3.2 KOH-chemical activation

The main textural characteristics of KOH-chemical activation of the optimized carbonized sample (CRH-600) previously prepared under different CRH/KOH impregnation mass ratios at 600 °C during 1 h, are summarized in Table 2. The analysis of these results shown that the sample (CRHKOH1-3), prepared with a mass impregnation ratio of 1:3 during 1h, exhibited a remarkable increase in textural properties; higher BET surface area of 1384.4 m^2/g and large total pore volume of 1.0854 cm^3/g compared to others KOH-impregnations studied. In general, was observed that the KOH activation caused the development of microporous and this mass effect becomes more and more noticeable as KOH agent is increased resulting in an enhanced surface area and total pore volume. As an explanation to this behavior, it can be deduced that the excess of KOH agent promotes gasification of char increasing their surface area formation and porosity. According to Wang and Kaskel, (2012), three activation mechanism occurs with the KOH-treatment: 1) redox reaction between potassium compounds generated during activation and carbon generates a network porosity, 2) the formation of H_2O and CO_2 during the chemical activation acts to gasify the carbon adding on the porosity development, and 3) the metallic K intercalates into the carbon matrix thereby expanding the lattice. Then, a more thorough study about the effective porous properties of this activated carbon, was achieved using a mass impregnation ratio of 1:3 during 1h of activation time, showed that this material has the best micropore properties: micropore radius (r_{mp}), micropore area (A_{mp}) and micropore volume (V_{mp}) based on the pore size distribution by the Barrett-Joyner-Halenda (BJH) method.
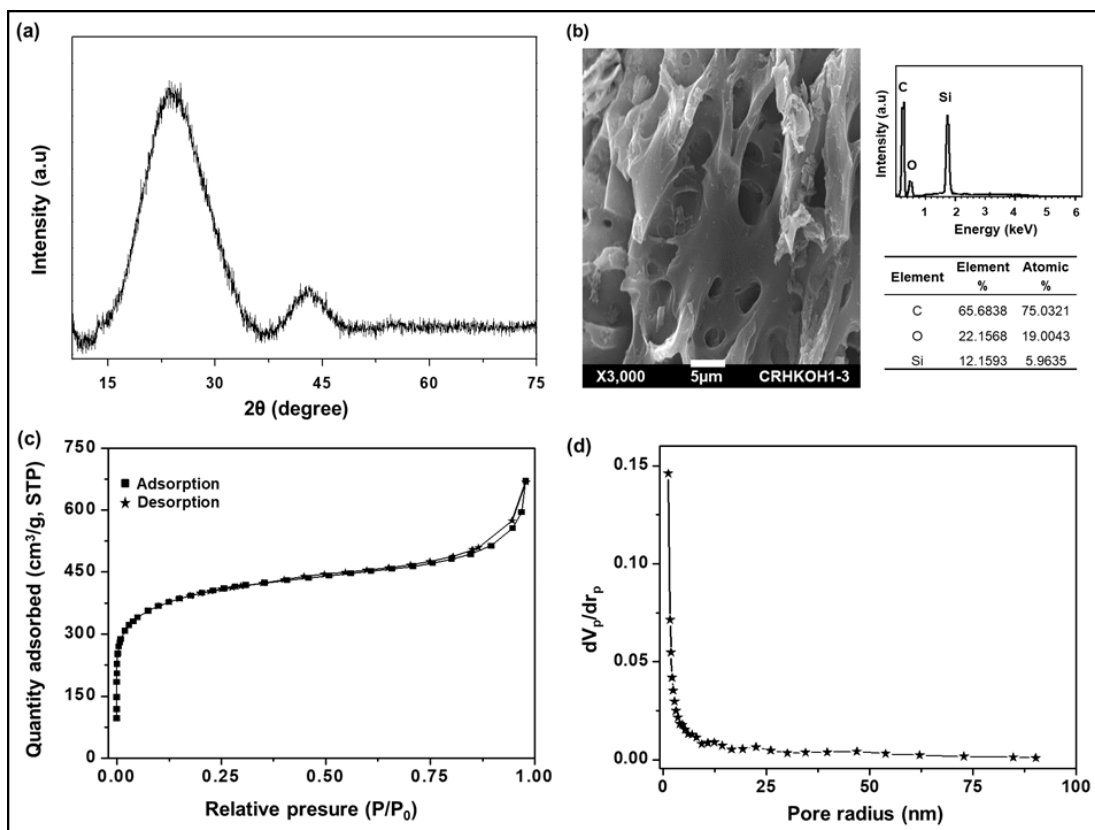
Figure 2. Features of prepared sample CRHKOH1-3 as a CO$_2$ adsorbent: (a) XRD Diffraction patern, (b) SEM and EDS study, (c) N$_2$ adsorption-desorption isotherm and (d) pore radius distribution.

Table 2. Main textural properties of activated carbons KOH-chemically activated at different CRH/KOH impregnation mass ratios.

Samples	Mass impregnation ratio	Activation time (h)	A_{BET} (m^2/g)	V_{Tp} (cm^3/g)	d_p (nm)	*rmp (nm)	*A_{mp} (m^2/g)	*V_{mp} (cm^3/g)
CRHKOH3-1	3:1	1	183.69	0.0980	2.1352	1.21	20.02	0.0228
CRHKOH2-1	2:1	1	474.16	0.3381	2.8521	1.21	121.15	0.1716
CRHKOH1-1	1:1	1	626.92	0.7727	4.9068	1.21	225.58	0.5753
CRHKOH1-2	1:2	1	629.70	0.7600	4.8506	1.21	188.12	0.5492
CRHKOH1-3	1:3	1	1384.40	1.0854	3.13610	1.20	283.10	0.5775

*Based on the pore size distribution by the Barrett-Joyner-Halenda (BJH) method.

According to summarized results showed in Table 2 was observed that through KOH impregnation process, were found substantial differences in the textural characteristic evolutions of KOH-activated carbons, and that the CRHKOH1-3 sample, exhibit to be an optimized KOH-activated carbon for CO$_2$ capture. According to these results, it is important to note that the increase of KOH during the chemical activation showed that a marked narrower microporous structure was developed which is very

significant and ideal for CO$_2$ capture purposes, characteristic demonstrated by their N$_2$ adsorption-desorption isotherm behavior at 77K (Fig. 2(c)) and pore radius distribution analysis which showed the predominance of microporous (> 90%) in this prepared activated carbon sample (Fig. 2(d)). Results of micropore surface area (A_{mp}) as well micropore volume (V_{mp}) of all developed KOH activated carbons are displayed in Table 2. For comparation, both of them textural values tend to increase with the

increasing concentration of activating agent KOH used in the chemical impregnation process, the micropore widths were with a varied size, uniformly structured and only suffered a slight decreased at more KOH content showing pore diameters values from 2.42 to 2.40 nm. It is expected that at higher (V_{mp}) value as correspond to CRHKOH1-3 sample, it will be better the CO_2 adsorption capacity due that this material will has the ability to store large amounts of CO_2 in their micropores, and facitate to easier diffusion into the microporosity region compared to the others samples. Also a very good correlation should be expected between high microporous surface area (Amp) values and the CO_2 capture capacity, as will have a high surface interaction between the gas molecules and a major amount of active sites, that it will be adsorbed better the gas CO_2. On the other hand, the physisorption of CO_2 molecules and their selectivity would be expected to increase with the presence of more micropores because micropores will induce a much fasted diffusion of CO_2. On the other hand, the chemical composition of the optimal activated carbon obtained (CRHKOH1-3 sample) also showed that this adsorbent is mainly composed of carbon element (Fig. 2b). It is worth noting that the microporosity of solid adsorbents play a selective and crucial role in CO_2 molecules adsorption, due to that a solid adsorbent having well-developed micropores and channels, it facilitates the accessibility of gaseous molecules to the adsorbent interior (Sajjadi *et al.*, 2019). According to the best of our knowledge, CO_2 physisorption in micropores by diffusion, is due to the proximity of the walls inside the micropores exalts the adsorption potential, causing that CO_2 molecules can be strongly retained in this micropores, under practical conditions at 25 °C and 1 atm. Then, taking in consideration this important feature, in the CRHKOH1-3 sample, notably the narrow micropore volume of 0.5775 cm^3/g with a micropore size diameter of 2.4 nm, can be easily occupied by the small CO_2 molecules with kinetic diameter of 0.33 nm (Wei *et al.*, 2012). In general, more abundant microporous structure to ensure that CO_2 molecules easily come into contact with the active sites that provide their extended specific surface area, improving the interaction between CO_2 gas molecules with the CRHKOH1-3 micropores. In conclusion, it is evident from the above that the adsorbent microporosity plays an essential role in CO_2 capture behavior and that the development of new micropores in the activated carbon structure contributes favorably

for gas adsorption. As a consequence, a better understanding of microporosity influence properties of the as-prepared KOH-activated carbon on the CO_2 adsorption behavior was attained.

The conventional chemical activation method used to prepare porous activated carbons from carbon precursors, are commonly carried out by impregnation with an activating agent at high temperatures, under inert gas conditions (Rangabhashiyam, 2013). From an economically rational point of view to prepare activated carbons under these conditions, some disadvantages are identified; involve the use of expensive equipment such as vertical tube furnaces with controlled temperature or horizontal quartz reactors, and use for long times constant flows of inert gases such as nitrogen. It is important to note that when it is desired to produce these materials on a large scale, it turns out to be a technological costly process. As an important highlight of this study, a highly microporous KOH-chemically activated carbon of low-cost with unique CO_2 adsorptive, was achieved in the absence of an inert atmosphere and without the use of any described expensive equipment, then, it should be noted that under these mild chemical activation conditions, the preparation of a potential activated carbon was facilitated and economized.

3.3 KOH-chemical activation temperature

It is well known that the chemical activation is used as a process for preparing activated carbons with excellent product properties, and that this process is also highly dependent on the activation temperature parameter (Plaza *et al.*, 2009). Therefore, the production of activated carbons at optimal temperatures to achieved high microporosity is very important. As a result of this study, a rice husk-based highly microporous activated carbon was low cost-effectively prepared at 600 ºC as optimal chemical activation temperature during 1 h, under not inert gas conditions, thus showing a promising strategy for economic large-scale production because it decreases the treatment cost and has good potential for technological applications. In general, the obtained results show the optimally and novel preparation of a KOH activated carbon from rice-husk with improved textural and morphological features, which showed mainly to be a solid adsorbent amorphous in structure, highly porous in morphology, highly-

Table 3. CO_2 adsorption capacities (mg/g) of some previously reported activated carbons from different raw materials, including rice husk.

Adsorbents	CO_2 adsorption capacity (mg/g)	Surface area (m^2/g)	Micropore size (nm)	Reference
Cupric nitrate/African palm shell activated carbon	217.00	1361	< 2	Acevedo *et al.*, 2020
Date seeds activated carbon	141.14	502.7	2	Ogungberno *et al.*, 2017
Fly ash activated carbon	26.39	161	< 2	Alhamed *et al.*, 2015
Garlic peel activated carbon	124.90	1262	0.8	Huang *et al.*, 2019
Pollen-derived porous activated carbon	3.38	1460	1	Choi *et al.*, 2019
Rice husk activated carbon	110.78	1384.4	< 2.4	Present work
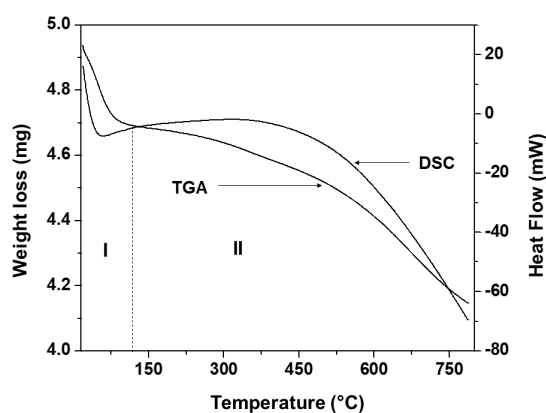
Figure 3. Thermal gravimetric analysis and differential scanning calorimetry (TGA-DSC) curves obtained for CO_2 adsorption on CRHKOH1-3 sample.

microporous material and with a homogeneous micropore size distribution (< 2 nm) according to IUPAC classification, key characteristics of an adsorbent potential for efficient and selective CO_2 capture.

3.4 CO_2 adsorption measurements

CO_2 adsorption measurements were performed in order to evaluate the CO_2 capture capacity in the optimized KOH-activated rice hulk-derived carbon, which was referred to the final product prepared from carbonized rice-husk directly calcined at 600 ºC during 1 h and KOH-chemical activated using a mass impregnation ratio of 1:3 during 600 ºC by 1 h (sample CRHKOH1-3). Fig. 3 shows the thermogravimetric analysis-differential scanning calorimetry (TGA-DSC) thermograms of the CO_2 adsorption on CRHKOH1-3 at 25 ºC, 1 atm, and 30 min of equilibrium time. The results shown that two stage occur during the CO_2 desorption process as was increased the temperature; at stage I, the observed DSC thermogram showed an endothermic peak at 57.56 ºC, attributed to the loss of physically-adsorbed water and that corresponded to 4.92% of the weight loss. In stage II, an exothermic broad peak was observed, that starts at 118.64 ºC and is associated with the carbonaceous material (CO_2) desorption. Later, a thermal stability was observed. Thus, a CO_2 adsorption capacity of 110.78 mg/g was obtained for the optimized CRHKOH1-3 sample, and was highly dependent on their morphological and textural features. However, a chemical activation or a direct carbon surface modification with specific salts solutions (Acevedo *et al.*, 2020; Gao *et al.*, 2022) should to induce changes in the amount and type of functional groups on the material surface, influencing the CO_2 capture and enhancing its basicity thereby improving the interactions between weak acidic gas molecules like CO_2 and carbon surfaces, involving in the CO_2 adsorption systems a mechanism that included the interaction of CO_2 molecules with the functional groups on the carbon surface (Wang *et al.*, 2013). In our case, it well knows, that the KOH chemical activation process is most often employed

Table 4. CO_2 adsorption capacities in (mg/g) at 25 ℃ and 1 atmosphere of the optimally prepared carbonaceous residue with the lowest capacity versus the KOH activated carbons with the highest capacity.

Samples	CO_2 adsorption capacity (mg/g)
*CRH-600	50.85
**CRHKOH3-1	97.68
**CRHKOH2-1	101.64
**CRHKOH1-1	103.84
**CRHKOH1-2	105.60
**CRHKOH1-3	110.78

*Carbonaceous residue without KOH activation.

**KOH activated carbons at diferent mass impregnation ratio of CRH-600/KOH at 600 ℃ by 1 h.

to generate porosity via either solid-solid reactions (Chiang and Juang, 2017) and that KOH clearly exerts strong oxidation in the carbonaceous structure, generating a network of micropores, featured key to gas capture, and where the KOH is completely consumed during the drastic oxidant reaction at high temperature, or the unreacted KOH is removed when the KOH-activated sample is washed by stirring with 10% HCl solution by 2 hours according to the experimental method (Petrovic *et al*., 2021). Based on these observations, activated carbons chemical surface changes due to possible incorporation of KOH functional groups, did not occur with this treatment.

In regards, CO_2 adsorption capacities of low-cost carbon adsorbent optimally prepared here (CRHKOH1-3 sample) was found to be comparable and in some cases better than that of other activated carbons prepared from other raw agro-waste materials for this gas, reported in the specialized literature, as shown in Table 3, and these obtained values are product of multiple factors that correspond mainly to the different physicochemical characteristics of CO_2 adsorbents. Therefore, this study shows that KOH chemical activation in absence of an inert atmosphere as optimized synthesis route, does seem to be a suitable modification technique for obtaining an effective CO_2 adsorbent with improved morphology and textural properties to be potential used in CO_2 capture technologies.

On the other hand, for comparative purposes the CO_2 adsorption capacities in (mg/g) of the optimally prepared carbonaceous residue with the lowest capacity versus the KOH activated carbons with the highest capacity, were included the Table 4. These obtained values show noticeable difference, usually carbonaceous materials produces a low surface area or even non-porous carbons that are useless for CO_2 capture. Therefore, the hight affinity to CO_2 capture of other products are due to the chemical activation process with KOH and from the textural and morphological characteristics advantageous of materials.

Conclusions

A high microporous KOH-chemically activated carbon was optimally prepared by using rice husk as a high available and low-cost precursor. It was found that the optimal conditions for activated carbon preparation were by carbonization of precursor material at 600 ℃ by 1 h followed by chemical activation using a CRH/KOH mass impregnation ratio of 1:3 at 600 ℃ during 1 h, in the absence of atmosphere inert, resulting in KOH-activated rice husk-derived carbon with a high surface area of 1384.4 m^2 /g, high total pore volume of 1.0854 cm^3/g and highly microporous and that these significantly improved physicochemical properties were correlated with their CO_2 adsorption performance. The results showed a CO_2 adsorption capacity of 50.85 mg/g at 25 ℃ and 1 atmosphere in the only carbonized material. In contrast, this adsorption capacity performance was improved evidently after KOH-impregnation until 110.78 mg/g under environmental conditions, attributed to its particular high microporosity, large surface area, and high pore volume. Therefore, this study shows that the optimized synthesis route studied, offered to prepare with economic feasibility, a valuable activated carbon using rice husk as the abundantly available and low-cost source and show that KOH chemical activation in absence of an inert atmosphere as does seem to be a suitable modification technique for obtaining an effective CO_2 adsorbent to be potential used in CO_2 capture technologies.

Nomenclature

RH	natural rice-husk
CRH	charred natural rice husk
CRH-400	natural rice-husk burned at 400 °C
CRH-500	natural rice-husk burned at 500 °C
CRH-600	natural rice-husk burned at 600 °C
CRH-700	natural rice-husk burned at 700 °C
RHKOH-31	impregnation mass ratio of CRH/KOH, 3:1
RHKOH-21	impregnation mass ratio of CRH/KOH, 2:1
RHKOH-11	impregnation mass ratio of CRH/KOH, 1:1
RHKOH-12	impregnation mass ratio of CRH/KOH, 1:2
RHKOH-13	impregnation mass ratio of CRH/KOH, 1:3
CRHKOH-13	impregnation mass ratio of CRH/KOH, 1:3
A_{BET}	surface area
V_{Tp}	total pore volume
d_p	mean pore diameter
r_p	pore radius
r_{mp}	micropore radius
A_{mp}	micropore area
V_{mp}	micropore volume

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