Basic characterization and carbon capture study of an indigenous activated carbon

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Abstract. The current research article deals with the fundamental characterization and carbon capture study of an indigenous activated carbon (AC) named MODISORB PL 4, derived from bituminous coal. Physical characterization to study the porous properties is carried out using N₂ adsorption/desorption at 77 K on a 3 Flex Micromeritics Setup. The activated carbon sample has a BET surface area of 1213.0 ± 16 m²/g, a pore volume of 0.285 cm³/g, and a pore size of 33.44 Å. The structural analysis carried out by powder XRD confirms the presence of graphite lattice in the adsorbent AC. The surface morphology is studied by FE-SEM analysis, which revealed that adsorbent activated carbon is microporous. The CO₂ adsorption study is carried out for a relative pressure range of 0 to 1 and temperature varying from 298-333 K. The experimental data confirm the exothermic and physisorption behavior of the process. Isotherm models; Toth and Sips are fitted with the experimental CO₂ adsorption data, in which both resulted in a good fit for the temperature and pressure range taken. The corresponding isotherm constants are illustrated in the article. Further, a comparison study is carried out with the existing literature to compare the CO₂ uptake at ambient conditions, revealing that the assorted AC sample has immense potential for gas sorption, energy storage and carbon capture.

Keywords: Carbon capture, CO₂ adsorption, adsorption isotherm, activated carbon

1. Introduction

Adsorption systems are among the most promising clean technologies in the modern world, dealing with many environmental issues. The rate of CO₂ emission into our atmosphere is increasing and is expected to reach 37-40 Gt by 2030 [1]. Carbonaceous materials like activated carbons (ACs) are the most favorable candidates for carbon capture and carbon dioxide-based sorption systems, as they are cheap, thermally stable, hydrophobic in nature, and have an affinity towards CO₂ [2]. Moreover, ACs are up-and-coming candidates in other fields like petrochemical, environmental, food & beverages, automobile and chemical sectors [3]. Serafin et al. [4] prepared and characterized different activated carbons derived from various biomass materials, having higher CO₂ adsorption capacity. The ACs were prepared by KOH activation and carbonization. It was noted that micropores in the 0.30-0.86 nm range were responsible for efficient CO₂ adsorption at 1 bar and 273 K. Maximum CO₂ uptake and selectivity (6.03 mmol/g at 1 bar and 273 K) was obtained for pomegranate peel based activated carbon. Gomez-Delgado et al. [5] prepared various ACs via KOH activation from Pinus canariensis cones. Effects of various parameters such as impregnating KOH/carbonized cone ratio (IR) and temperatures (873-1073 K) were examined. The study showed that the activated carbon prepared with
IR=3 at 973 K resulted in a BET surface area of 1900 m²/g and a maximum CO₂ uptake at 273 K of 6.4 mmol/g. Rashidi and Yusup [6] prepared palm shell kernel-based ACs via single-stage physical activated technique. The goal of the study was to examine the CO₂ uptake and product yield at room temperature and pressure under the impact of different input parameters, such as gas flow rate, temperature, and dwell time. At 850 °C, a gas flow rate of 450 cm³/min, 25.15 percent of product yield, holding time of 60 min, the maximum CO₂ uptake of 2.13 mmol/g was obtained. The produced ACs are economical as per the industrial applications, as they showed similar CO₂ uptakes compared to the ACs prepared by double-stage activation techniques. Pal et al. [7] reported a benchmark study on CO₂ uptakes onto various Biomass-derived ACs (BACs) (mangrove and waste palm trunk). The BACs were prepared from waste palm trunk and mangrove, and were activated at 900 °C and carbonized at 500 and 600 °C. The maximum CO₂ absorption of 2.175 g/g (absolute adsorption) by waste palm trunk AC carbonized at 500 °C, and at an adsorption temperature and pressure of 25 °C and 5.04 MPa, respectively, was shown in the study.

Furthermore, many studies are available in the literature that deals with the adsorption isotherm study of few ACs samples indigenous and other foreign grades [8-10]. Nevertheless, studies related to fundamental morphological characteristics of indigenous ACs and their CO₂ capture ability under ambient conditions are still very limited in the literature. In the present analysis, an indigenous AC named ‘MODISORB PL 4’ is taken for the study. Basic morphological characterization viz… BET analysis, XRD, EDAX, FE-SEM and CO₂ adsorption capacity are tested for the temperature varying from 298 K to 333 K and for pressure ranging from 0 to 1 bar.

2. Experimental section
The adsorbent AC is provided by M M Corporation, Ahmedabad, India. Different physical properties of the adsorbent activated carbon such as BET surface area, pore size and volume, pore size distribution (PSD), structural information and surface morphology are studied by BET analysis, XRD, FE-SEM and EDAX, respectively. The CO₂ adsorption isotherm is carried out using a 3 Flex Micromeritics setup at 298, 313, and 333 K for P/P₀=0 to 1. The detailed analysis of all the aforementioned tests is discussed in the upcoming sections.

2.1. Physical Characterization
The BET surface area, PSD, pore-volume and diameter are analyzed using 3 Flex Micromeritics Version 3.02 using the N₂ adsorption/desorption technique. The analysis is done at -196 °C and a relative pressure range of 0 to 1. The AC sample is degasified overnight at 300 °C before the test. The tested activated carbon has a BET surface area of 1213.016 m²/g, a pore volume of 0.285 cm³/g, and an average pore diameter of 33.44 Å. Nitrogen adsorption/desorption isotherms onto the Modisorb PL 4 pellet along with the BET report is shown in Figure 1. The isotherm curves of N₂ adsorption and desorption almost follow the same path indicating that the processes are reversible in nature. The packing density of the AC sample is 0.43-0.52 g/cm³ which is provided by the manufacturer. Figure 2 shows pore size distribution (PSD) analysis of the activated carbon pellet. The PSD analysis is carried out using NLDFT given by the software package of 3 Flex Micromeritics. It clear from the figure that the AC pellet is microporous as the pore volume is well below 20 Å. Moreover, the pore size distribution is more concentrated in the pore width range of 4-16 Å.
Figure 1. Adsorption/desorption isotherms of nitrogen on AC Modisorb PL 4 at -196 °C

Figure 2. Pore size distribution of Modisorb PL 4
X-ray powder diffraction (XRD) on the Rigaku Smart lab instrument is used to analyze the structural properties of the activated carbon sample using CuKa radiation with $\lambda = 1.54$ Å. For the analysis, 40 kV and 40 mA of tube voltage and current are maintained. The diffraction patterns with a step size of 0.02° and a scanning speed of 2 °/min are taken for 2θ ranging between 10 to 80°. Figure 3 shows the XRD patterns of the activated carbon sample. Five sharp diffraction peaks are observed at $2\theta = 26.603^\circ$, $31.558^\circ$, $36.113^\circ$, $42.465^\circ$, and $44.670^\circ$. Further interpretations of XRD analysis are carried out using X’Pert High Score Plus software. The peaks at $2\theta = 26.603^\circ$, $42.465^\circ$, and $44.670^\circ$ denoted the presence of graphite with (002), (100), and (101) planes, respectively. The peaks at $2\theta = 31.558^\circ$ and $36.113^\circ$ may be due to some impurities (which may be present because of the pelletization of the AC).

![XRD analysis of MODISORB PL 4](image)

The surface morphology and microstructure of the adsorbent activated carbon are studied by FE-SEM using a Supra 55 Zeiss at a magnification of 5 KX at a 5 kV accelerating voltage. The FE-SEM photograph of the activated carbon is shown in Figure 4. It is depicted from the figure that the AC sample consists of smaller flakes and a rock-type hybrid structure and is a microporous adsorbent, which confirms the suitability for CO$_2$ adsorption. Area-wise Energy Dispersive X-Ray Analysis (EDAX) is carried out on powdered activated carbon to explore the elemental composition. The results of the EDAX analysis are shown in Figure 5 and Table 1. The analysis confirmed the highest carbon percentage in the activated carbon sample. The study also revealed the presence of residual mineral ions in the AC sample, which can be related to the peaks observed at $2\theta = 26.603^\circ$, $42.465^\circ$, and $44.670^\circ$ during the XRD analysis.

| Element | Weight % | Element | Weight % |
|---------|----------|---------|----------|
| C K | 80.83 | Fe K | 0.74 |
| O K | 9.90 | Mo L | 0.90 |
| Mg K | 0.44 | Sb L | 1.94 |
| Al K | 1.19 | Si K | 1.86 |
| Ca K | 2.19 | | |
Figure 4. FE-SEM image of Modisorb PL 4 at 5 KX magnification

Figure 5. EDAX analysis of AC Modisorb PL 4
2.2. CO₂ adsorption
The carbon capture study is conducted using a 3 Flex Micromeritics Setup at varying temperatures ranging from 298 to 333 K for a relative pressure range (P/P₀) of 0 to 1. The results are illustrated in Figure 6. The figure clearly indicates that with a rise in temperature, the adsorption of CO₂ decreases due to the decrease in binding strength between the adsorbate and the adsorbent. In addition, the decrease in the ability of CO₂ adsorption at higher temperatures suggests that the sorption process that occurs is exothermic and a physisorption process.

**Figure 6.** Experimental equilibrium data of CO₂ adsorption onto AC at 298-333 K

2.2.1. Comparison of CO₂ uptakes
Recent studies show that BACs have a significant potential for carbon capture under ambient conditions. Table 2 shows comparative values of CO₂ uptakes of various BACs taken from the open literature and current work results. The selected activated stands well with the other BACs under similar conditions. In fact, the CO₂ uptake of the selected AC is better than BACs derived from palm fruit bunch, which is quite appreciable. Therefore it is noteworthy to mention that the selected AC is a suitable candidate for gas adsorption/separation, energy storage, adsorption based heat pumps and carbon capture.

**Table 2.** Comparison of CO₂ uptakes onto ACs under ambient conditions

| Activated Carbon Precursor | CO₂ uptake (mmol/g) | Reference |
|----------------------------|---------------------|-----------|
|                            | T=273 K             | T=298 K   |
| Fern leaves                | 4.52                | 4.12      | [4]        |
| Pomegranate peels          | 6.03                | 4.11      | [4]        |
| Carrot peels               | 5.64                | 4.18      | [4]        |
| Coffee ground              | 6.89                | 4.00      | [11]       |
2.3. Isotherm modeling

All the experimental data at various temperatures are fitted with the Sips and Toth model, given by Eq. (1) & (2), respectively. The corresponding isotherm constants are given in Table 3. It is depicted from Figure 7 shows that both the isotherm model provides an excellent fit for all the temperature and pressure ranges taken in the study. Both the isotherm models are suitable for heterogeneous adsorbents like activated carbon and depict monolayer adsorption. Moreover, the increasing trends of the heterogeneity factor ‘t’ with an increase in temperature refers to higher adsorption energies. Also, decreasing the values of the limiting uptake ‘q_m’ shows the exothermic behavior of CO₂ adsorption with increasing temperature.

\[
q = \frac{q_m(KP)^t}{1+(KP)^t} \tag{1}
\]

\[
q = \frac{q_m(KP)}{(1+(KP)^t)^t} \tag{2}
\]

**Table 3. Isotherm constants for CO₂-MODISORB PL 4 pair**

| Isotherm model | Temperature (K) | Sips | Toth |
|----------------|-----------------|------|------|
|                | 298             | 313  | 333  |
|                | 313             | 333  | 313  |
|                | 333             | 298  | 313  |
|                | 333             | 298  | 313  |

|                | q_m (mmol/g)    |      |      |
|----------------|-----------------|------|------|
|                | 11.27064        | 3.32619 | 0.9497 | 96.64889 | 6.01578 | 1.10384  |
|                | 0.00015         | 0.00066 | 0.00133 | 0.00014 | 0.00077 | 0.00146  |
|                | 0.76358         | 0.86636 | 0.94236 | 0.25417 | 0.51708 | 0.77890  |
3. Conclusion

In the present work, basic characterization and CO$_2$ adsorption study are carried out on bituminous coal-based activated carbon called MODISORB PL 4. The BET analysis is carried out on the sample AC sample using the N$_2$ adsorption/desorption technique, which revealed a surface area of 1213.016 m$^2$/g with a pore volume of 0.285 cm$^3$/g. The CO$_2$ adsorption study is carried out for a relative range of pressure (P/P$_0$=0 to 1) and different temperatures (298 K, 313 K, 333 K) using a 3 Flex Micromeritics Setup. Experimental results proved that the adsorption behavior was physisorption as increment and decrement in CO$_2$ adsorption capacity are noticed with an increase in pressure and temperature, respectively. A comparison is made for CO$_2$ uptake at ambient conditions with various grades of biomass-derived ACs, which shows that the selected AC has potential for gas sorption and carbon capture. Toth and Sips isotherm models are fitted with the obtained experimental data of CO$_2$ uptake, and both of them resulted in a good fit for the whole pressure and temperature range. The isotherm data of the selected AC is significant and can be used to compare other indigenous commercially available activated carbons. Moreover, studies like TGA and FTIR will further enable us to describe the surface morphology and adsorbent properties of the assorted activated carbon, which is included in our future work.

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References

[1] Gautam, Sahoo S. Effects of geometric and heat transfer parameters on adsorption–desorption characteristics of CO₂-activated carbon pair. *Clean Technologies and Environmental Policy*. 2020 Jun 6:1-21. https://doi.org/10.1007/s10098-020-01866-3.

[2] Gautam, Kumar G, Sahoo S. Performance improvement and comparisons of CO₂ based adsorption cooling system using modified cycles employing various adsorbents: a comprehensive study of subcritical and transcritical cycles. *International Journal of Refrigeration*. 2020 Apr 1;112:136-54.

[3] Bagheri S, Muhd Julkapli N, Bee Abd Hamid S. Functionalized Activated Carbon Derived from Biomass for Photocatalysis Applications Perspective. *International Journal of Photoenergy*. 2015 Feb 23; 1-30. http://dx.doi.org/10.1155/2014/218743

[4] Serafin J, Narkiewicz U, Morawski AW, Wróbel RJ, Michalkiewicz B. Highly microporous activated carbons from biomass for CO₂ capture and effective micropores at different conditions. *Journal of CO₂ Utilization*. 2017 Mar 1;18:73-9.

[5] Gomez-Delgado E, Nunell G, Cukierman AL, Bonelli P. Tailoring activated carbons from Pinus canariensis cones for post-combustion CO₂ capture. *Environmental Science and Pollution Research*. 2020 Feb 8; 27:13915–29.

[6] Rashidi NA, Yusup S. Production of palm kernel shell-based activated carbon by direct physical activation for carbon dioxide adsorption. *Environmental Science and Pollution Research*. 2019 Nov; 26:33732-46.

[7] Pal A, Uddin K, Saha BB, Thu K, Kil HS, Yoon SH, Miyawaki J. A benchmark for CO₂ uptake onto newly synthesized biomass-derived activated carbons. *Applied Energy*. 2020 Apr 15;264:114720.

[8] Singh VK, Kumar EA, Saha BB. Adsorption isotherms, kinetics and thermodynamic simulation of CO₂-CSAC pair for cooling application. *Energy*. 2018 Oct 1;160:1158-73.

[9] Singh VK, Kumar EA. Thermodynamic analysis of single-stage and single-effect two-stage adsorption cooling cycles using indigenous coconut shell based activated carbon-CO₂ pair. *International Journal of Refrigeration*. 2017 Dec 1;84:238-52.

[10] Singh VK, Kumar EA. Experimental investigation and thermodynamic analysis of CO₂ adsorption on activated carbons for cooling system. *Journal of CO₂ Utilization*. 2017 Jan 1;17:290-304.

[11] Travis W, Gadipelli S, Guo Z. Superior CO₂ adsorption from waste coffee ground derived carbons. *RSC advances*. 2015;5(37):29558-62.

[12] Coromina HM, Walsh DA, Mokaya R. Biomass-derived activated carbon with simultaneously enhanced CO₂ uptake for both pre and post combustion capture applications. *Journal of Materials Chemistry A*. 2016;4(1):280-9.

[13] Wang J, Heerwig A, Lohe MR, Oschatz M, Borchardt L, Kaskel S. Fungi-based porous carbons for CO₂ adsorption and separation. *Journal of Materials Chemistry*. 2012;22(28):13911-3.

[14] Ello AS, de Souza LK, Trokourey A, Jaroniec M. Coconut shell-based microporous carbons for CO₂ capture. *Microporous and Mesoporous Materials*. 2013 Nov 1;180:280-3.

[15] Plaza MG, González AS, Pevida C, Pis JJ, Rubiera F. Valorisation of spent coffee grounds as CO₂ adsorbents for postcombustion capture applications. *Applied Energy*. 2012 Nov 1;99:272-9.

[16] Vargas DP, Giraldo L, Silvestre-Albero J, Moreno-Pirajaín JC. CO₂ adsorption on binderless activated carbon monoliths. *Adsorption*. 2011 Jun;17(3):497-504.

[17] Sevilla M, Fuertes AB. Sustainable porous carbons with a superior performance for CO₂ capture. *Energy & Environmental Science*. 2011;4(5):1765-71.

[18] Parshetti GK, Chowdhury S, Balasubramanian R. Biomass derived low-cost microporous adsorbents for efficient CO₂ capture. *Fuel*. 2015 May 15;148:246-54.