

PHYSICAL ADSORPTION PROPERTIES OF NATURAL FIBERS AND NATURAL FIBER BASED ACTIVATED CARBONS FOR CO₂ EMISSIONS

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Abstract

In this research, sisal, hemp and flax fibers have been treated via carbonization and physical activation to produce activated carbon. The efficiency of carbonization and physical activation using carbon dioxide (CO₂) gas were investigated. The manufacture, characterization and CO₂ adsorption behavior of natural fiber based activated carbon samples are reported. Breakthrough plots and adsorption capacities at different temperatures for CO₂ capture are presented. The results indicate that activated samples have higher surface areas compared to the carbonized and untreated natural fibers. Moreover, adsorption capacity was greatly influenced by the sample temperatures.

1 Introduction

Current indicators of climate change have brought increased awareness and interest in controlling the release of greenhouse causing gases. The rising of the average Earth temperature that started late in the 19th century it is projected to continue for an undetermined period of time. Since the early 20th century, Earth's average surface temperature has increased by about 0.8 °C [1]. Several studies have reported that “global warming” is caused at least in part by increasing concentrations of anthropogenic greenhouse gases and volatile organic compounds (VOC) produced by activities such as the burning of fossil fuels. Because these gases can absorb, release and reabsorb heat from the sun [2, 3, 4, 5] it is likely that their contribution to the climate change through the greenhouse effect is significant. CO₂ accounts for 80% of current greenhouse emissions that contribute the global climate change [6]. Therefore, the regulation of CO₂ emission is critical to diminish the impact of the greenhouse effect. CO₂ is emitted into the atmosphere mainly from the combustion of fossil fuels used in power generation, transportation, and industrial sources [7]. There is an urgent need for efficient and innovative methods to control its release in particular from coal-fired power plants. The present work explores the use of non expensive resources such as natural fibers for emission reduction and capture through innovative approaches.

2 Materials and testing methods Natural fibers from plants, trees and shrubs adsorb the same amount of carbon dioxide they produce; they generate organic waste and leave residues during processing. They are 100% biodegradable and are an important renewable resource [8]. Natural fibers can play a key role in the emerging “green” economy based on energy efficiency, industrial processes that reduce carbon emissions and recyclable materials that minimize waste. Biological fibers are natural and effective means of CO₂ capture, yet one that is less explored in terms of scalable implementation for industrial and power plant emissions. Normal use of plants to industrially produce natural fibers (yarn, rope, textile materials, etc.) results in a high amount of waste and recycling of this waste to produce useful end products would be beneficial for the industry. [9] This study is an investigation of the use of natural fiber waste such as banana, hemp, flax and sisal to prepare activated carbons.

Granular activated carbons (GAC) have been the industry standard for many years as adsorbents to remove gas phase contaminants in air circulation systems and air-purifying respirators [10]. GAC offer cost-effective high efficiency option pure product recovery for reuse. Granulated activated carbon can be formulated into a modules that can be removed after saturation, regenerated and used again [11]. In this study, natural fiber based activated carbons are prepared with carbonizing and physically activating the carbonized fibers.

The surface area of an adsorbent is an important factor in the adsorption process. Generally, the larger the surface area, the higher is the adsorption capacity [12]. In this study, the surface area was determined from the isotherm plots nitrogen adsorption by the samples at 77 K in the range of relative pressure (P/P₀) from 0.02 to 1 using a Micromeritics ASAP 2020 automatic physisorption analyzer. All samples underwent degassing and analysis processes in the instrument. The degassing process pretreats the adsorbent sample by applying some combination of heat, vacuum and/or flowing gas to remove adsorbed contaminants acquired from atmospheric exposure, and was performed at 300°C for 1 hour prior to the analysis. The analysis process involves the incremental dosing of nitrogen to the adsorbent samples. The quantity of nitrogen required to form a monolayer over the external surface of the adsorbent and its pores was determined at particular pressures. With the area covered by each adsorbed nitrogen gas molecule known, the surface area was calculated [13].

Breakthrough time is one important parameter to characterize the predictive performance of adsorbents. The modified Wheeler equation is widely used for the prediction of breakthrough times [14]. Using this equation (Equation 1), the kinetic adsorption capacity and gas adsorption rate of a packed charcoal adsorbent can be obtained by the linear relationship between gas breakthrough time and the adsorbent weight. The 50% breakthrough times (minutes) obtained were plotted against the adsorbent mass (g) to obtain a regression line for the calculation of the adsorption capacity (W_e) for each adsorbent at a certain concentration [13].

$$t_b = \frac{W_e}{C_0 Q} \left[W - \frac{\rho_B Q}{k_V} \ln \left(\frac{C_0}{C_x} \right) \right] \quad (1)$$

t_b —breakthrough time(min), C_x -exit concentration(g/cm³), C_0 -inlet concentration(g/cm³),
 Q -volumetric flow rate (cm³), W -weight of adsorbent (g),
 ρ_B -bulk density of packed bed (g/cm³), k_V -kinetic adsorption rate constant (min⁻¹),
 W_e -kinetic adsorption capacity (g/g)

3 Experimental

The initial surface areas of the natural fibers were measured and the samples were carbonized at 600°C in a tube furnace to investigate the influence of carbonization on material porosity (Figure 1). The tube furnace is 6 cm diameter x 110 cm length and able to be heated to a temperature up to 540°C.

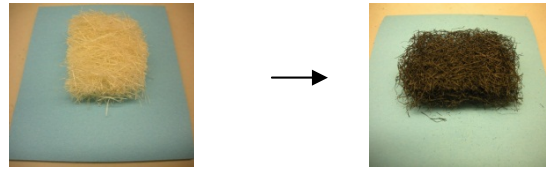


Figure 1. Sisal Fiber (4 cm x 6 cm) Carbonized Sisal Fiber (4cm x 6 cm)

The natural fibers were cut to 1.5-2 cm in length and treated with Resole type phenolic resin GP 486G34 (Georgia Pacific Resins, Inc.). Loose crystal packaging in the carbonized precursor is preferable from the standpoint of pore opening during the activation step; therefore phenolic resin is regarded as a preferred precursor [15]. The fibers were mixed with phenolic resin to prepare natural fiber reinforced composite materials. The composite is cured and carbonized to convert the phenolic resin to secondary carbon. The final synthesis involves physical activation with CO₂ gas to develop a connected network of micropores within the carbon fibers as illustrated in Figure 2. The natural fiber composites shown in Figure 3 and Table 1 are carbonized at 5°C/min with nitrogen gas until 800°C and physically activated at 800°C for 3 hours with CO₂ gas.

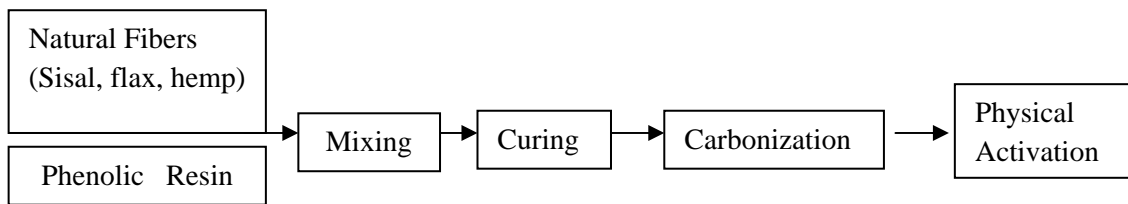


Figure 2. Natural fiber based activated carbon synthesis route

















Fiber Name	Plant	Fiber (4cmx6cm)	Cured with Resin (d=5cm)	Carbonized and Activated Samples
Sisal				
Banana				
Flax				
Hemp				

Figure 3. Natural fibers: plants, untreated specimens, cured samples and activated samples

The efficiency of CO₂ capture from a simulated flue gas by using natural fiber-based activated carbon substrate is evaluated under different system conditions. The samples were placed in a stainless-steel chamber and simulated gas flow through the chamber (Figure 4). The chamber has an internal diameter of 4 cm and is immersed in a temperature controlled water bath. The breakthrough concentration of CO₂ was measured with a CO₂ analyzer (Quantek 906) and the adsorption capacity was determined.

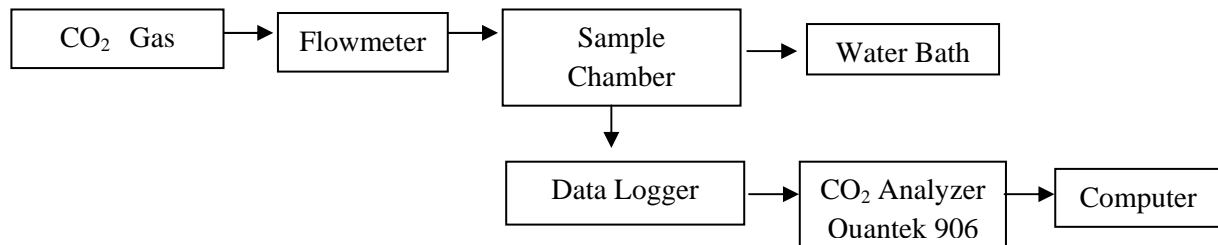


Figure 4. Experimental Setup Schematic for Breakthrough Determination

4 Results

The BET surface area was measured for the natural untreated fibers, the carbonized samples and activated samples as tabulated in Table 1.

Sample Name	BET Surface Area (m ² /g)
Sisal	0.017
Carbonized Sisal without Resin	0.834
Carbonized and Activated Sisal	355.104
Flax	0.012
Carbonized Flax without Resin	0.855
Carbonized & Activated Flax	653.890
Hemp	0.157
Carbonized Hemp without Resin	5.566
Carbonized and Activated Hemp	168.370

Table 1. BET surface areas of the experimental samples

The burn off fraction was calculated as 72-80% for all the carbonized samples and was between 49 and 55% for the activated samples.

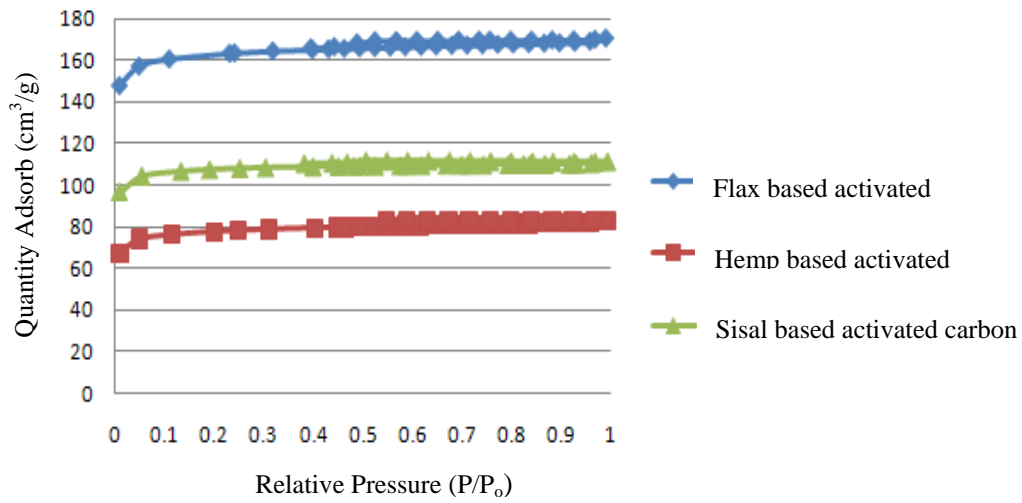
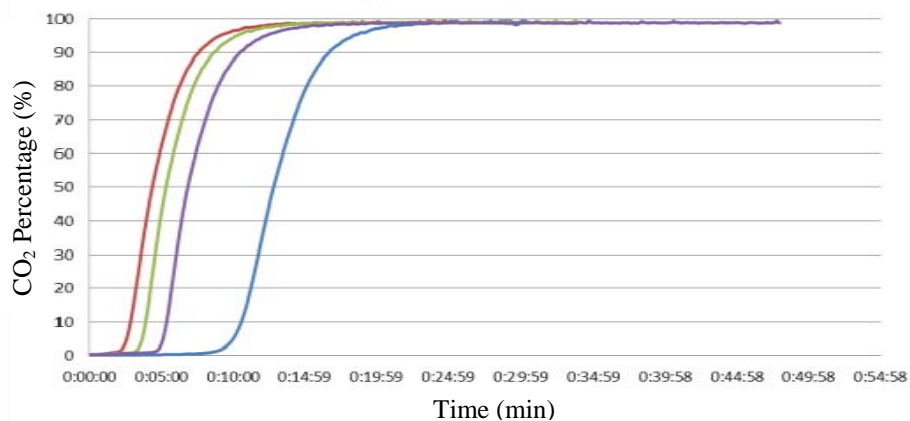
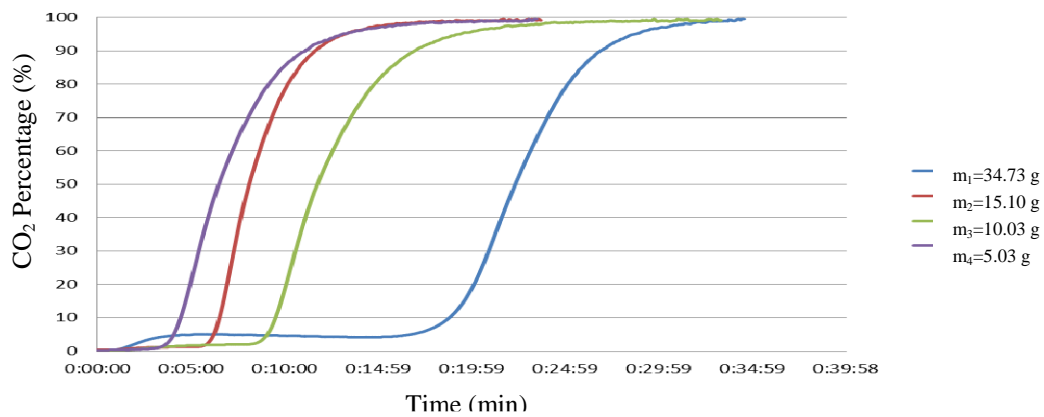


Figure 5. Nitrogen adsorbtion isotherms

According to the isotherm plots in Figure 5, the shape of isotherms are of Type I. representing the Langmuir-type monolayer adsorption characteristic of microporous adsorbents [16].



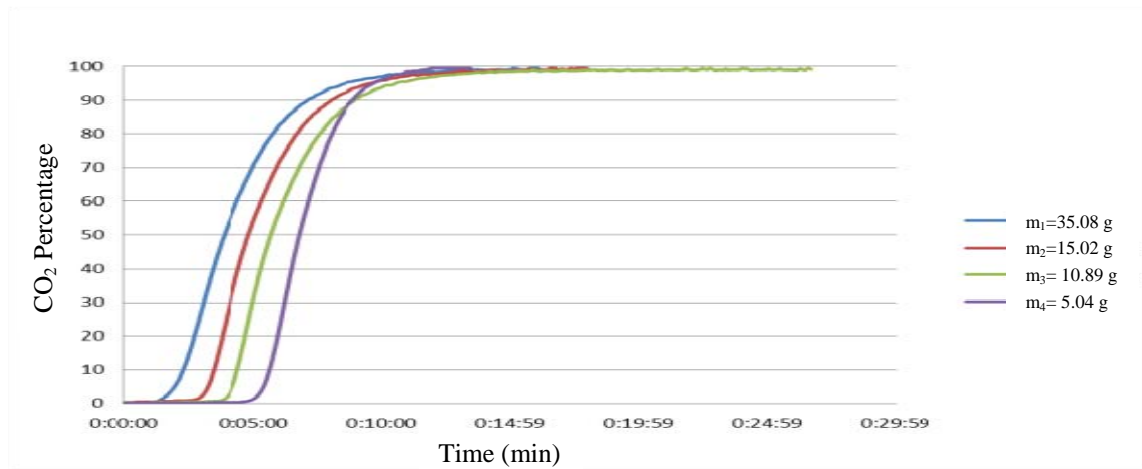
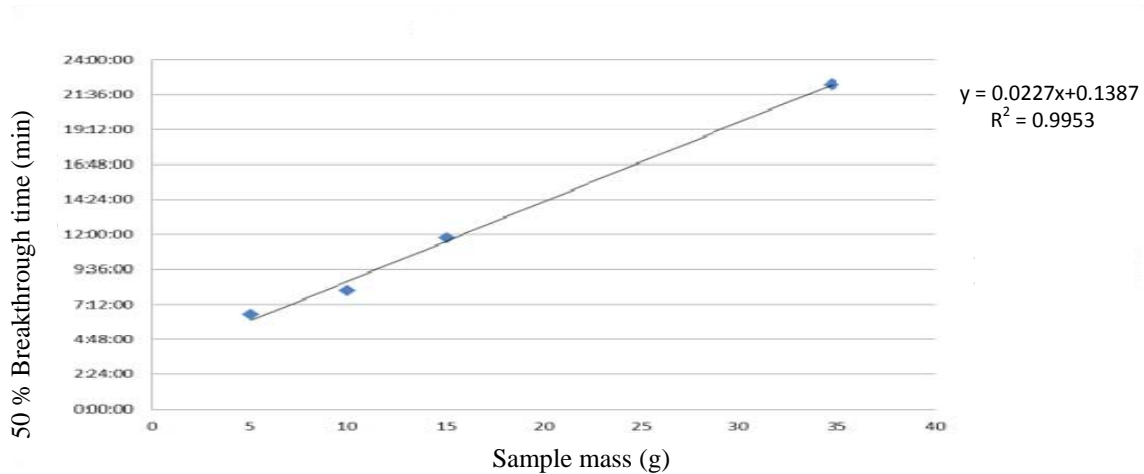


Figure 6. Breakthrough Curves of granular activated coconut carbon at room temperature, 60°C and 80°C respectively.

A control experiment was performed to determine the CO₂ adsorption capacity by coconut based granular activated carbon. Adsorption capacity (W_e) was calculated using the modified Wheeler equation (Equation 1). The time in minutes when $C_x/C_0 = 0.5$ is referred to as the 50% breakthrough time (breakthrough stands for saturation time in this experiment), which was determined from Figure 6 for each breakthrough curve at different adsorbent mass. The 50% breakthrough times (minutes) obtained were plotted against the adsorbent mass (g) to obtain a regression line, as shown in Figure 7.



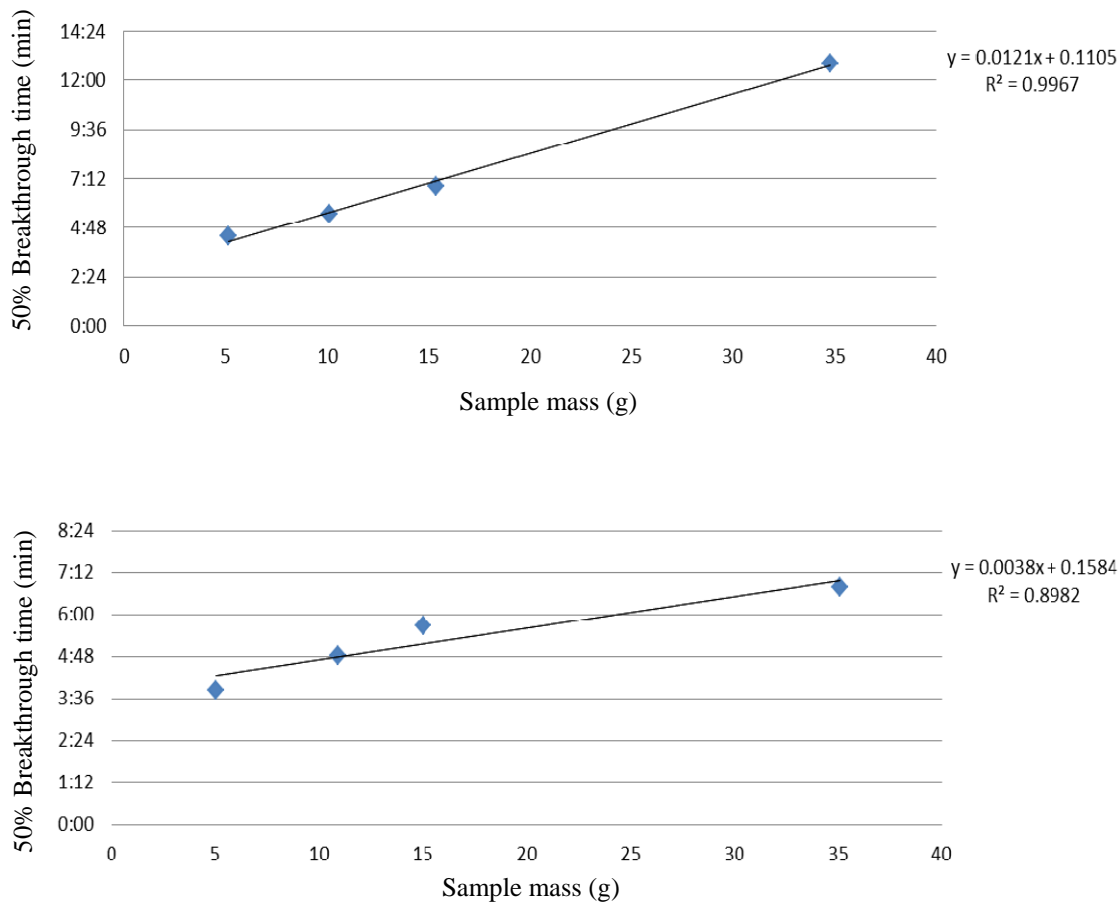


Figure 7. Plot of 50% breakthrough time vs. adsorbent mass at room temperature, 60°C and 80°C, respectively

The adsorption capacity of granular activated carbon for pure CO₂ in a the dynamic flow through experiment show a very pore retention capacity: **W_{e1}=6.54 mg/g, W_{e2}=5.476 mg/g and W_{e3}=1.094mg/g** at room temperature, 60°C and 80°C respectively.

5 Discussion

The results of this study show that natural, untreated fibers have inadequate microporous structure; therefore their BET surface areas are quite low. After the carbonization, BET surface area increases but it is a moderate increase. Carbonization only of the natural fibers is not an effective way to prepare highly microporous structures. When the fibers were mixed with phenolic resin, carbonized and activated their BET surface area increased significantly. The nitrogen adsorption isotherms also show that their structure changed, containing mainly micropores which are responsible for small molecule adsorption. The flax based composite had the highest surface area (more than 650 m²/g) and the highest percent of micropores being a potential candidate for a future adsorbent material. Burn off percentage was too high for all samples indicating that future studies are needed to create materials that will be less brittle and have good adsorbent characteristics for CO₂. On the other hand, the breakthrough experiment conducted using granular activated carbon indicated that the adsorption capacity for this

material is also very reduced for CO₂ adsorption. Future studies will prepare composites based on flex and examine their adsorption capacity for CO₂ but also various VOC.

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