Surface Modifications of CuO Doped Carbonaceous Nanosorbents and their CO_2 Sorption Properties

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Article info

Abstract

In this study, carbonized apricot stones and rice husk were utilized as feedstock for the synthesis of CuO-loaded carbonized sorbents for the removal of carbon dioxide (CO_2) from gas mixtures. The specific surface area of carbonized sorbents increased with increasing carbonization temperature, resulting in a porous structure with enhanced sorption capacity. The presence of pores and the development of porosity in the sorbents were confirmed by SEM images. CuO nanoparticles were well-dispersed on the surface of carbonized sorbents, and the particle sizes were between 60–100 nm. Chemical interactions between acidic carbon dioxide and basic copper oxide led to improved adsorption properties. The sorption characteristics of the carbonized sorbents were studied under dynamic conditions, and the results showed that CuO-loaded carbonized apricot stones and rice husk had the maximum sorption capacity for CO_2, with efficiencies of 98% and 91%, respectively. These findings indicate that carbonized apricot stones and rice husk can be utilized as low-cost and eco-friendly feedstock for the production of efficient CO_2 sorbents.

1. Introduction

The increasing concentration of carbon dioxide (CO_2) in the atmosphere is believed to be one of the major causes of global warming and climate change. To address this issue, the development of effective CO_2 capture technologies has become a major focus of research in recent years [1, 2]. Among the different types of sorbents used for CO_2 capture, carbonaceous materials derived from agricultural waste have gained significant attention due to their potential as a sustainable and low-cost alternative [3–5]. Specifically, sorbents based on apricot stones (AS) and rice husk (RH) have emerged as promising candidates for CO_2 capture due to their high absorption capacity, ease of regeneration, and ability to capture at normal temperatures and pressures [6, 7].

However, during the carbonization process, oxygen-containing groups are formed on the surface of carbonaceous sorbents, which results in an acidic property and a decrease in CO_2 adsorption capacity [8]. To overcome this limitation, surface modifications have been proposed as an effective approach to enhance the CO_2 adsorption properties of carbonaceous sorbents [9]. One such modification is the removal of acid functional groups and the introduction of base components to the surface. Previous research has shown that the replacement of acidic groups with nitrogen-base groups on carbonaceous sorbents leads to improved CO_2 adsorption [10].

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In addition to nitrogen-base groups, the incorporation of metal oxides has been proposed as another means to improve the CO_2 adsorption properties of carbonaceous sorbents. Among the different metal oxides, copper oxide (CuO) nanoparticles have been found to be particularly effective in enhancing the CO_2 removal efficiency of carbonaceous sorbents [11–13]. CuO nanoparticles have a higher adsorption capacity for CO_2 compared to other metal oxides such as calcium oxide and magnesium oxide, and they require less energy for regeneration [14–16]. Copper oxide nanoparticles are a favorable choice for CO_2 adsorption at room temperature because they require lower temperatures compared to other metal oxides such as calcium oxide and magnesium oxide [17]. The study examined the physical and chemical behavior of CuO particles during CO_2 adsorption and revealed that $CuCO_3$ is primarily formed on the surface of CuO at low temperatures (<573 K). Although the chemical reaction between CuO and CO_2 is slower than physical attraction, CuO exhibits superior CO_2 adsorption properties compared to Cu_2O with a physisorption of 9.0 cm^3 g^{-1} and chemisorption of 9.5 mmol g^{-1}, without compromising its productivity and properties [18–20].

In this study, we prepared CuO-doped carbonaceous sorbents derived from RH and AS using the impregnation method and characterized them using optical microscopy, SEM, FT-IR, and BET surface area analysis. The CO_2 adsorption properties of the sorbents were evaluated using gas sorption analysis. By exploring the effects of CuO on the adsorption properties of carbonaceous sorbents, this study contributes to the development of more effective and sustainable CO_2 capture technologies.

2. Experimental part

2.1 Materials

RH and AS were obtained from local sources. Sodium hydroxide (NaOH) and Copper (II) chloride dihydrate ($CuCl_2$ $2H_2O$) were purchased from Sigma-Aldrich and used as received. Deionized water was used for all synthesis and characterization procedures. The RH and AS samples were carbonized according to the literature [21]. RH and AS were clearly washed with water, then oven-dried at about 110 °C for 24 h. Prepared samples were placed in a crucible and burned in a muffle furnace under an argon gas (Ar) flow of 50 cm^3 min^{-1} at 700 °C for 1 h and finally, carbonized rice husk (CRH) and carbonized apricot stones (CAS) samples has been prepared.

2.2 Synthesis of copper oxide nanoparticles on carbonized sorbents

After the carbonization process, CuO nanoparticles were synthesized on carbonized sorbents (CS) using a previously reported method [22]. Firstly, 0.1 M $CuCl_2$ $2H_2O$ solution and 1 g CS were mixed for 17 and 24 h at room temperature. Then, the samples were dried at 90 °C. Next, 50 mL of 0.1 M NaOH solution was prepared, and CS were mixed for 2 h before being filtered. It has been previously established that the CO_2 adsorption capacity of activated carbons derived from coal can be enhanced by the addition of sodium hydroxide [23]. Finally, the samples were calcined at 350 °C for 4 h (Fig. 1).

2.3 Carbon dioxide adsorption studies

The obtained samples were studied for CO_2 adsorption under standard conditions (24 °C, 1 atm). A cylindrical glass column with a diameter of 3 cm and a length of 10 cm was used to provide a gas flow. After placing 5–7 g of the sample in the column, the entire system was degassed for 2 h. An inert atmosphere was then created by introducing Ar gas. Finally, a gas mixture consisting of 5% CO_2 and 95% N_2 flowed through the CS in the column at a rate of 10 ml min^{-1} (see Fig. 2).

2.4 Characterizations

The total CO_2 concentration in the gas mixture was determined using a Chromos GC-1000. The adsorption behaviors of the samples were studied by evaluating the percentage removal efficiency of CO_2, using the equation: $R_e = [(C_0 - C)/C_0] \cdot 100$, where C_0 is the initial concentration of CO_2 in the gas mixture, and C is the CO_2 concentration in the gas mixture after adsorption by the sorbents.

The morphology and particle size of the CuO-doped carbonaceous sorbents were characterized by optical microscopy (Leica DM 6000 M) and SEM (Quanta 3D 200i) at an accelerated voltage of 20 kV and a pressure of 0.003 Pa.

FT-IR spectra of the samples (tablets pressed with KBr) were recorded using an IR spectrometer (Nicolet-5700) in the wave number range from 4000 to 400 cm^{-1} with Fourier transformation.
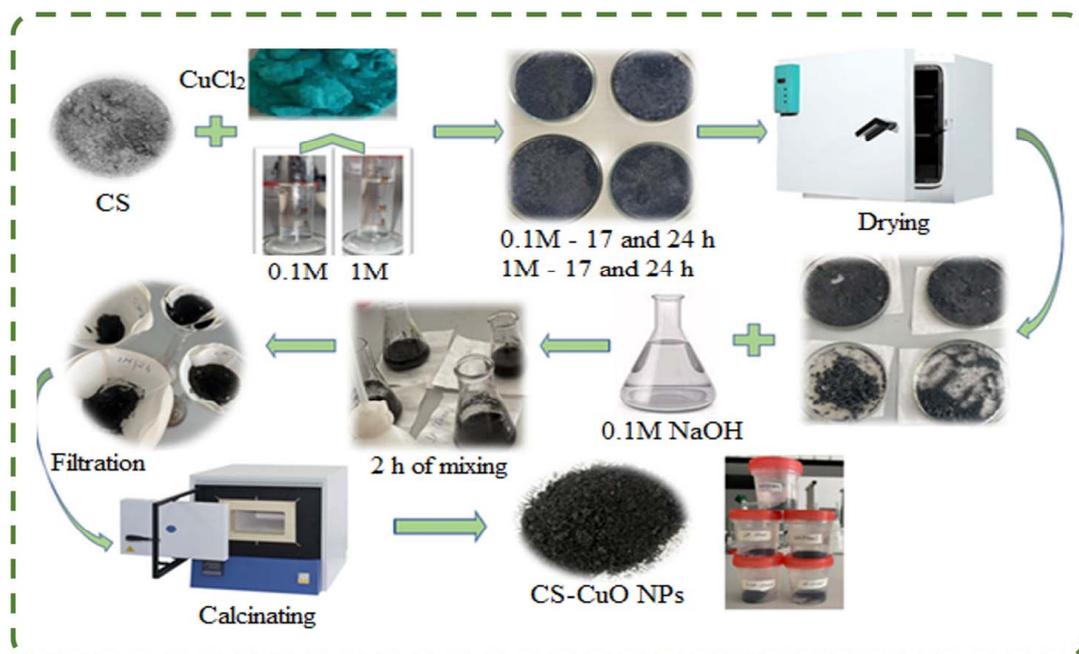
Fig. 1. Synthesis of copper oxide nanoparticles on surface of carbonized sorbents.

The specific surface area of the samples was determined using the BET method with a SORB-TOMETR-M apparatus.

The data were analyzed using Microsoft Excel and OriginPro software. All measurements were performed in triplicate and the average values were reported.

3. Results and discussion

The specific surface area of the CAS and CRH increased with the increasing carbonization temperature, reaching a maximum and then slightly decreasing. As shown in Fig. 2, the specific surface area of CAS increased from 12 to 150 m^2 g^{-1}. The carbonization process led to an increase in the surface area and porosity and a decrease in density.

As the temperature increased, a burning process occurred, which removed the main components from both samples and turned most of them into ashes. The increase in the carbonization temperature led to the release of organic components, which resulted in the formation of a porous structure of a solid sample and an increase in the specific surface area.
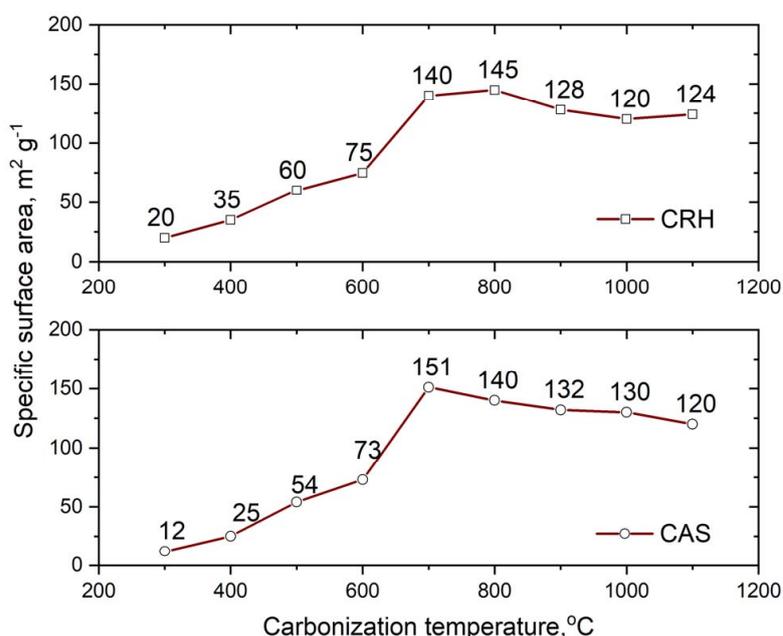
Fig. 2. Effect of carbonization temperature on the specific surface area of CRH and CAS samples.
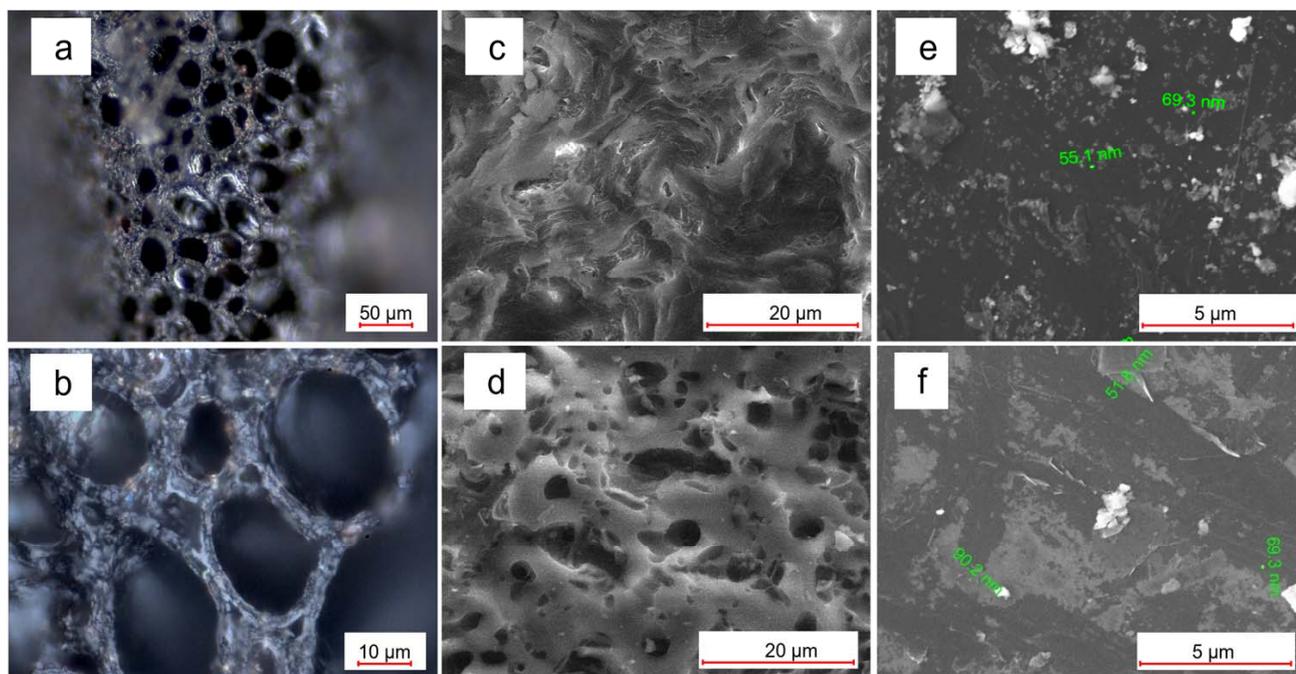
Fig. 3. Optical microscope (CAS (a), CRH (b)) and SEM images (raw AS (c), CAS (d), CAS-CuO (e), CRH-CuO (f)).

The results of microscopic studies revealed that the carbonization of the feedstock significantly changed the composition and structure of the obtained samples, which affected their sorption capacity. Figure 3 showed the presence of pores with a diameter of 5–20 µm on the surface of CAS (Fig. 3a) and CRH (Fig. 3b).

SEM images of CAS before and after carbonization, as shown in Fig. 3 (c) and (d), respectively, revealed the development of porosity in the sorbent primarily due to structural transformations of the organic base. At high carbonization temperatures, the burnout of organic components occurred, which prevented access to the closed internal porous structure, leading to a sharp increase in the volume of pores. A similar phenomenon was observed in the sample of CRH.

SEM images of CuO NP-loaded carbonized sorbents from RH and CAS are demonstrated in Fig. 3 (e) and (f). The SEM images showed that nanoparticles of CuO were well-dispersed on the surface of carbonized sorbents, and the particle sizes were between 60–100 nm. The improvement in adsorption properties was mainly due to the presence of chemical interactions between the acidic carbon dioxide molecule and the basic copper oxide, and to a lesser extent, the increase in the specific surface area of carbonized sorbents during the carbonization.

Figure 4 showed the IR spectra of carbonized samples and after doping by CuO. The region with
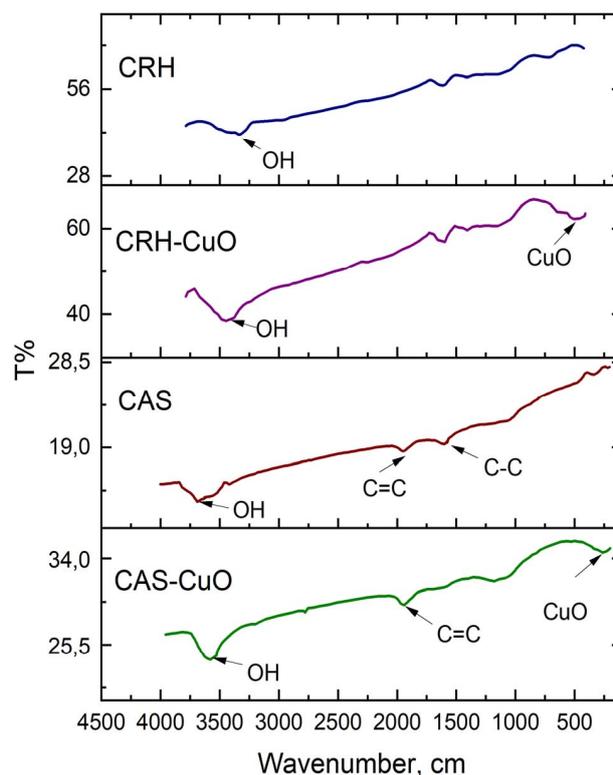
Fig. 4. FT-IR spectra of pure and CuO doped carbonized sorbents.

absorption at 3500 cm^{-1} was associated with the presence of hydroxyl groups and chemisorbed water on the surface. The absorptions at 1620 cm^{-1} were attributed to vibrations of the C=C bond. Peaks with intensity at 1400 cm^{-1} corresponded to vibrations of the C-O bond in the carboxyl group.
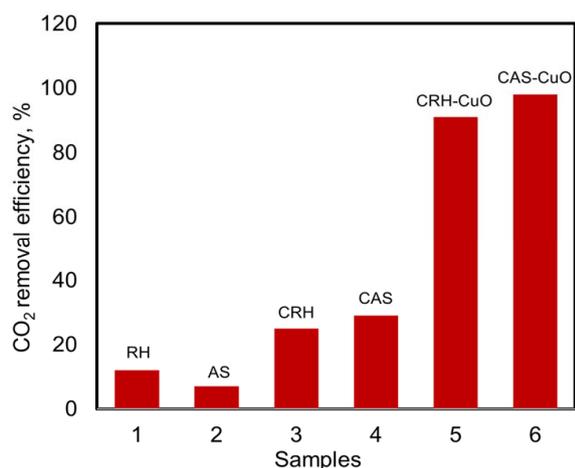
Fig. 5. Comparison of removal efficiency (E) of sorbents for CO_2.

The IR spectrum of CuO showed the appearance of peaks with intensity at 516 cm^{-1} associated with the presence of Cu-O inorganic groups on the surface. The appearance of absorption bands at these wavenumbers indicated the surface modifications of both carbonized sorbents with CuO and the removal of the C-O carboxyl group.

The sorption characteristics of carbonized sorbents were studied under dynamic conditions by filtering the gas mixture through a fixed sorbent bed (Fig. 5). The efficiency of CuO loaded carbonized sorbents for CO_2 removal from the gas mixture was investigated. The percentage of CO_2 removal for adsorbents in a continuous tubular contractor is presented in Fig. 5. The data obtained showed that CAS-CuO (E = 98%) and CRH-CuO (E = 91%) had the maximum sorption capacity for CO_2. The sorption capacity of raw RH and AS was very low, with the CO_2 removal efficiency varying in the range of 7–12%.

At the same time, the CO_2 removal efficiency of unmodified sorbents does not exceed 30%. CAS-CuO is as efficient for CO_2 removal as other absorbers. This is due to the structure of the granular sorbent, which is a system of micropores and capillaries that hold carbon dioxide inside the granule.

The chromatographs of carbon dioxide in the gas mixture (a) and after the sorption on CAS-CuO (b) in a continuous tubular contractor are shown in Fig. 6. Apparently, CAS-CuO adsorbent showed a very high sorption capacity for carbon dioxide. The sorption ability of CAS-CuO is mainly ascribed to its high surface area and the presence of copper oxide nanoparticles.

4. Conclusion

In conclusion, this study investigated the potential of CAS and CRH as adsorbents for CO_2 capture from gas mixtures. The results showed that the specific surface area of the carbonized samples increased with increasing carbonization temperature, which led to the development of a porous structure and an increase in sorption capacity. The incorporation of CuO nanoparticles onto the carbonized sorbents further improved their adsorption properties due to chemical interactions between the CO_2 molecule and CuO. Under dynamic conditions, the CuO-loaded CAS and CRH exhibited high CO_2 removal efficiency, with the CAS-CuO achieving a maximum efficiency of 98%. This study highlights the potential of using agricultural waste as low-cost and efficient adsorbents for CO_2 capture and provides insight into the role of carbonization and nanoparticle doping in enhancing their sorption properties.
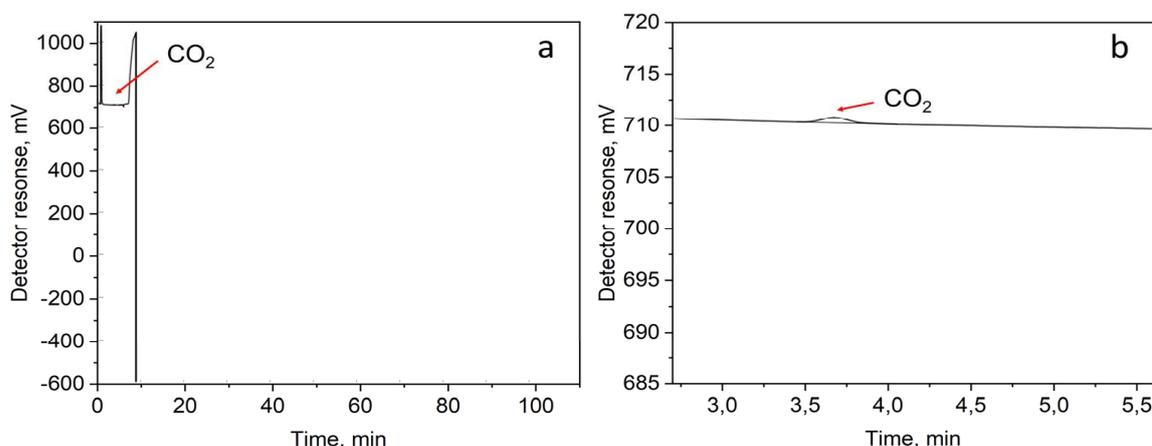
Fig. 6. Chromatograph of carbon dioxide in gas mixture (a) and after the sorption on CAS/CuO (b) in continuous tubular contractor.

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