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Enhanced Adsorption of Carbon Dioxide by Phosphoric Acid-Modified Soybean Curd Residue Biochar

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Biochar is being increasingly applied for carbon dioxide (CO_2) capture to preserve environmental quality. The use of soybean waste, soybean curd residue (SCR) as CO_2 adsorbents can help to reduce the uncontrolled disposal of SCR. In this research, SCR-based biochar (Biochar@SCR) was prepared by pyrolysis process. For chemical activation, Biochar@SCR was immersed for 12 hours in 42.5 wt.% H_3PO_4 solution at 1:1 ratio (g precursor/g H_3PO_4) to obtain Biochar@SCR-M1. Biochar@SCR-M2 was produced when Biochar@SCR-M1 was pyrolyzed again at 500ºC for 2 hours. Elemental and functional groups analyses showed the presence of elemental phosphorus (P) and functional groups of P=O or P=OOH for Biochar@SCR-M1 and Biochar@SCR-M2, suggesting the chemical modification using H_3PO_4 was successful. Morphological analysis revealed the formation of pores after the pyrolysis process and chemical treatment with H_3PO_4. Analysis of CO_2 adsorption depicted that the adsorption capacities of SCR, Biochar@SCR, Biochar@SCR-M1, and Biochar@SCR-M2 were 3.00 mg/g, 25.21 mg/g, 30.50 mg/g, and 36.00 mg/g, respectively. This result proved the increased CO_2 sorption for H_3PO_4-treated Biochar@SCR, suggesting that phosphoric acid modification is an effective method for preparing biochar with high carbon dioxide adsorption.

Key words: Soybean curd residue; phosphoric acid; biochar; pyrolysis; carbon dioxide

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The world has seen significant economic development and progress over the last few years as a result of expansion and industrial development. Because of rapid industrialization, Malaysia, China, South Africa, India, Brazil, and Russia have seen a dramatic increase in the rate of Gross Domestic Product (GDP) [1]. According to Danish & Wang [2], extensive usage of natural resources due to increased economic expansion causes severe environmental difficulties. Kasayanond et al. [3] mentioned that the far-reaching growth of Malaysia would lead to the increase in the amount of ecological problems, especially carbon dioxide (CO_2) emission [3]. Aeknarajindawat et al. [1] stated that the pursuit of commercial events, such as the use of petroleum in power production, transportation, residential, and industrial activities, contributes to greenhouse gas emissions (GHG). Harun et al. [4] showed that environmental issues should be managed and energy efficiency encouraged in the manufacturing process, notably in Malaysia's building and construction, transportation, electricity, gas, water, and agriculture sectors. These findings indicate that environmental problems in Malaysia must be addressed by improving carbon emission efficiency and lowering the CO_2 concentration in the atmosphere.

Several technologies such as membrane separation, alkanol amine solvent, and ionic liquid absorption have been introduced to reduce the concentration of CO_2 in the environment. However, all these technologies are costly to implement, require high pressure, and are not environmentally friendly [5-6]. Reducing CO_2 by adsorption process using solid adsorbent attained attention recently due to various advantages such as broad range of working temperatures, high performance and easy to implement. For CO_2 capture and storage, various porous materials have been utilized in the past, including zeolite, amine-doped silica, and porous polymers [7]. However, the dynamic synthesis technique and incorrect usage of raw chemical resources may harm these materials. Therefore, porous carbon compounds are the most promising adsorbents for CO_2 adsorption due to their ease of preparation, cheap energy costs, and superior adsorption capabilities [8].

Biochar is one of the suitable and potential porous carbon adsorbents. Raw materials such as agricultural waste, food waste, crop residues, animal

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manure. and industrial solid wastes can be used to produce biochar. The use of waste in the production of biochar adsorbents for CO_2 capture could aid waste management. In this research, soybean curd residue (SCR) wastes from the manufacturing of soybean-based products had been used as the raw material for the production of biochar for CO_2 adsorption. In Japan, China, Singapore, and the rest of the world, about 0.8, 2.8, 0.01, and 14 million metric tons of SCR, respectively, are discarded each year to produce soymilk and tofu. According to Rahman et al. [9], one metric ton of soybean produces around seven metric tons of soymilk and two metric tons of SCR, and tofu preparation necessitates a large volume of water, resulting in a higher amount of SCR and liquid waste. Those who do not know how to utilize SCR properly burn it as fuel, dump it in landfills, or toss it in rivers, indirectly increasing environmental pollution due to its rapid putrefaction. About 16 billion yen per year is set aside for SCR disposal. To reduce the environmental issues of this waste, SCR could be used as a raw material to produce biochar for the adsorption of CO_2. SCR offers an appealing, sustainable source for functional carbon materials due to the well-known levels of vegetable proteins, which seems to serve as a good nitrogen source. The study by Li et al. [10] proved that SCR has the potential to be developed as porous carbon, as a multipurpose renewable absorbent for efficient CO_2, toluene, and water vapor capture. Recently, Lin et al. [11] utilized soybean biomass as both carbon and nitrogen sources to create nitrogen-doped porous carbon by template-assisted carbonization, followed by KOH activation. Due to the templating effect, the resultant had a significantly larger specific surface area, allowing the tested supercapacitor to have a higher energy density. These studies laid the foundation for an essential soybean residue utilization mechanism.

Various chemical treatments, such as H_2SO_4, KOH, and $ZnCl_2$, have been proposed and tested to increase biochar sorption capability. According to Chu et al. [12], phosphoric acid (H_3PO_4) treatment has several advantages over these methods, such as low corrosivity to the equipment, relatively low pyrolysis temperature, cheap, and minor pollution to the environments. The surface area of the resulting biochar has also been found to be improved by acid treatment, with increasing impregnation ratio, type of acid, and activation temperature [13]. Peng et al. [14] discovered that after activation with 1 M of hydrochloric acid, the surface area of biochar made from reed increased from 58.75 to 88.35 m^2/g. Starch rice food waste formed from phosphoric acid–modified biochar by the study from Cao et al. [15], on the other hand, demonstrated the greatest BET surface area of 1547 m^2/g when activation temperature (600°C) and impregnation ratio were raised. Wu et al. [16] investigated Cr(VI) sorption on modified biochar made from pomelo peel and found that H_3PO_4 treatment at 450°C could produce a porous structure adsorbent. Taha et al. [17] used biochar treated with H_3PO_4 at 80ºC to remove a mixture of 15 different pesticides from water and found this adsorbent can be successfully utilized to decontaminate pesticides from an aqueous environment. Zhao et al. [18] mentioned that micropores were predominantly produced on modified biochar as a result of the interaction between H_3PO_4 and the carbon structure of biochar. The micropores of the pretreated particles were substantially larger than those of the untreated particles due to acid catalysis and crosslinking, resulting in a dramatic increase in specific surface areas of the pretreated particles. Micropores (< 2 nm) play a crucial role in the sorption of both inorganic and organic contaminants. These studies proved the effectiveness of H_3PO_4 treatment in the preparation of biochar with a high adsorption capacity. In this research, SCR was pyrolyzed to produce Biochar@SCR, and the obtained biochar was treated with H_3PO_4. The obtained adsorbents were then characterized based on functional group, elemental, and morphological analyses. The carbon adsorption capacity for all the prepared adsorbents was investigated using TGA analysis.

MATERIALS AND METHODS

1. Chemicals and Materials

Soybean curd residue (SCR) was collected from a local supplier in Perlis. Analytical grade phosphoric acid (H_3PO_4) was purchased from Sigma-Aldrich (Missouri Mo, USA).

2. Instruments

The functional group of the prepared adsorbents were characterized by FTIR spectroscopy (Perkin Elmer Spectrum-65, USA) in the adsorption mode with 4 scans and a resolution of ±4 cm^{-1}, wavenumber range of 4000 - 450 cm^{-1}, with a diamond as a detector. Morphology and elemental composition of the adsorbents were analyzed by using a field emission scanning electron microscope (Hitachi TM3000, Tokyo, Japan) equipped with energy dispersive X-ray spectroscopy.

3. Preparation of Adsorbent

3.1. Preparation of SCR

The collected SCR was washed multiple times and dried for 48 hours in an oven at 50ºC. Once dried, the bare SCR was ground using a 60 mm sieve.

3.2. Preparation of Biochar@SCR

Biochar@SCR was prepared by pyrolysis process under 30 mL/min nitrogen flow. The furnace was heated until the desired temperature of 500ºC was reached. Pyrolysis activity was conducted for 2 hours and the carbonized SCR was cooled to room temperature.

3.3. Preparation of Modified Biochar@SCR

The chemical treatment on Biochar@SCR using phosphoric acid (H_3PO_4) was adapted from the reported study by Chu et al. [12]. Biochar@SCR was immersed for 12 hours in 42.5 wt.% H_3PO_4 solution at 1:1 ratio (g precursor/g H_3PO_4) and dried overnight. The product was named Biochar@SCR-M1. After the modification, Biochar@SCR-M1 was pyrolyzed again at 500°C for 2 hours, and the product was named Biochar@SCR-M2. Biochar@SCR-M2 was synthesized to observe the effect of the pyrolysis on the H_3PO_4-treated biochar. The pyrolysis process was carried out under continuous nitrogen flow until the temperature decreased to room temperature.

3.4. CO_2 Adsorption Measurement

The adsorption capacity of SCR, Biochar@SCR, Biochar@SCR-M1, and Biochar@SCR-M2 for CO_2 was tested using a thermogravimetric analyzer (TGA, SDTQ-600). The CO_2 adsorption tests were adapted from published work by Foo et al. [19]. The analysis was carried out under isothermal condition. About 8-12 mg of each prepared adsorbent was loaded in an alumina pan and heated at a rate of 20°C/min to 110°C/min in N_2 atmosphere (75 mL/min) to remove contaminants in the sample for each experiment. The samples were kept at the gasification temperature under N_2 for 15 min. Then, N_2 was switched to CO_2 (75 mL/min) to initiate the isothermal gasification for 70.00 min. The continuous weight loss of the biomass and heat flow were recorded at isothermal of 30°C.

RESULTS AND DISCUSSION

Functional Group Analysis

The functional groups of SCR, Biochar@SCR, Biochar@SCR-M1, and Biochar@SCR-M2 were characterized using FTIR spectroscopy, and their spectra are shown in Figures 1(A)-(D). As seen in Figure 1(A), SCR showed peaks at absorptions of 3324 cm^{-1}, 1750 cm^{-1}, and 1048 cm^{-1} due to O-H stretching, C=O stretching, and C-O stretching, respectively [17]. In addition, peaks observed at 2922 cm^{-1}, 2853 cm^{-1} and 1620 cm^{-1} represent the asymmetric, symmetric CH_2, and C=C stretchings, respectively [20]. The spectrum of Biochar@SCR (Figure 1(B)) showed no peaks for O-H, C=O and C-O stretchings, suggesting these functional groups were decomposed during the pyrolysis process. Similar results were reported in the published work by Wang et al. [21]. The peak at 1635 cm^{-1} was attributed to the C=C stretching of alkene. After treatment with H_3PO_4, Biochar@SCR-M1 (Figure (C)) showed new peaks at 1350 cm^{-1}, 1070 cm^{-1}, and 805 cm^{-1}, which correspond to P=O bond, P-O-P chain, and P-O-C stretching, respectively [22]. Another sharp peak at 1650 cm^{-1} showed the C=C stretching in this material. Similar peaks were observed in the spectrum of Biochar@ SCR-M2 (Figure 1(D)).

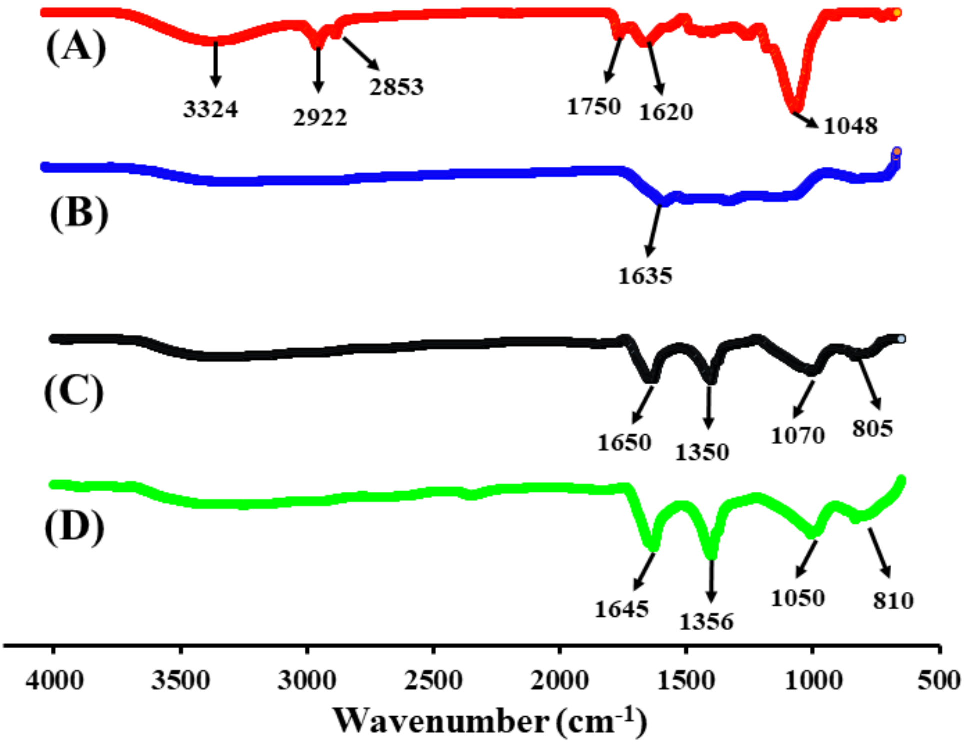

Figure 1. FTIR spectra of (A) SCR; (B) Biochar@SCR; (C) Biochar@SCR-M1; and (D) Biochar@SCR-M2

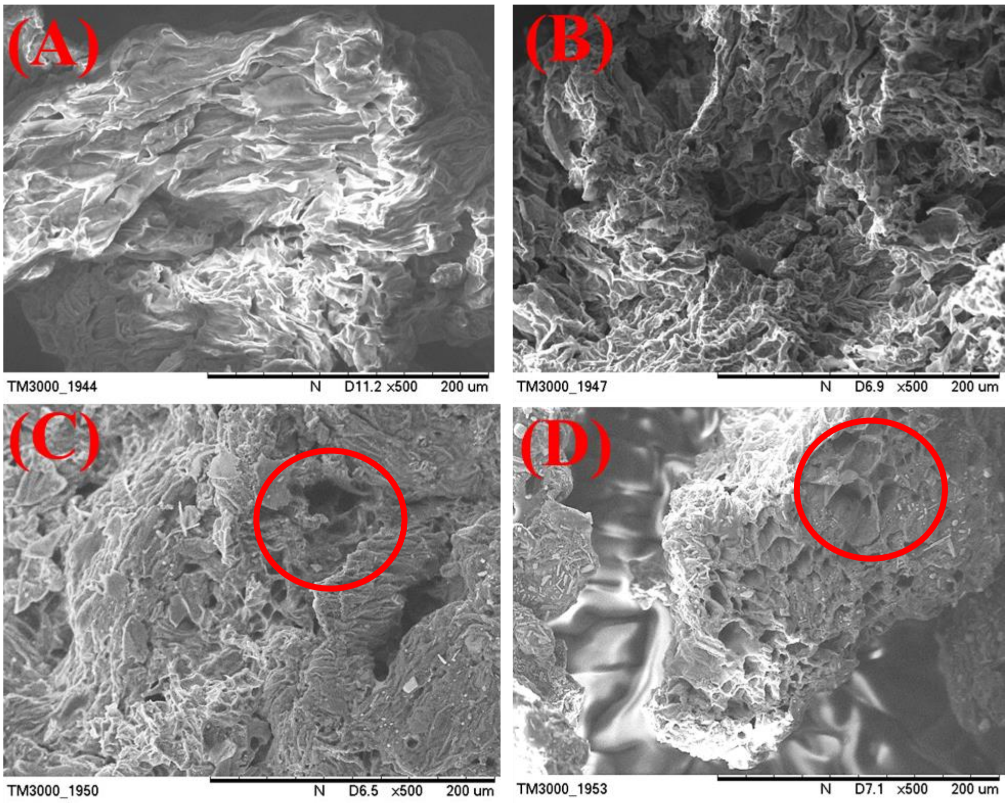

Figure 2. SEM images of (A) SCR; (B) Biochar@SCR; (C) Biochar@SCR-M1; and (C) Biochar@SCR-M2

Morphological Analysis

SEM analysis of SCR, Biochar@SCR, Biochar@SCR-M1, and Biochar@SCR-M2 (Figures 2 (A)-(D)) allowed the investigation of the surface morphology of the prepared adsorbents. As shown in Figure 2(A), SCR possessed a dense, rough and stem-shaped structure that may originate from the cellulosic and hemicellulosic structures of the SCR polymeric cell wall. A porous structure was observed for Biochar@SCR (Figure 2(B)). This phenomenon is due to the decomposition of cellulose and hemicellulose of SCR at elevated temperatures during the pyrolysis process [23]. A similar result had been observed by Salehi et al. [24]. Larger porous structures could be seen for Biochar@SCR-M1 and Biochar@SCR-M2 (specified by red circles in Figures 2 (C) and (D)) after H_3PO_4 treatment because glycosidic links in polysaccharides (hemicellulose and cellulose) and aryl ether bonds in lignin may break after acidic hydrolysis. Further chemical changes, such as dehydration, degradation, and condensation, also occur during this stage, resulting in a loss in molecular weight and morphological phase redistribution [12].

Elemental Analysis

Elemental analysis was used to examine the elements present in the preparation of SCR, Biochar@SCR, Biochar@SCR-M1, and Biochar@SCR-M2; the data are tabulated and shown in Table 1. As seen in the results, SCR contained major elements such as C, O, and N. After the pyrolysis process, a high percentage of C was observed in Biochar@SCR, and the amount of O dropped due to the decomposition of hydrophilic functional groups during this stage. The presence of P in Biochar@SCR-M1 and Biochar@SCR-M2 showed H_3PO_4 had been successfully introduced on the surface of Biochar@SCR during the acid treatment stage.

Table 1. EDX results of SCR, Biochar@SCR, Biochar@SCR-M1 and Biochar@SCR-M2

Material	Percentage of elements (%)			
	C	O	N	P
SCR	46.8	43.4	9.8	-
Biochar@SCR	63.6	23.2	12.4	-
Biochar@SCR-M1	63.5	22.2	12.0	2.3
Biochar@SCR-M2	68.4	15.8	9.1	2.9

CO_2 Adsorption Analysis

Thermogravimetric analysis (TGA) was used to evaluate the CO_2 adsorption capacities of the SCR, Biochar@SCR, Biochar@SCR-M1, and Biochar@SCR -M2. As shown in Figure 3, the adsorption capacities of SCR, Biochar@SCR, Biochar@SCR-M1, and Biochar@SCR-M2 were 3.00 mg/g, 25.21 mg/g, 30.50 mg/g and 36.00 mg/g, respectively. The high adsorption capacity of CO_2 of the adsorbents was enhanced, mainly for Biochar@SCR-M1 and Biochar @SCR-M2 due to the presence of porous structures of these adsorbents. These porous structures would offer sites for the sorption of CO_2, thus enhancing the adsorption capacities of Biochar@SCR-M1 and Biochar@SCR-M2. As seen in the results, Biochar@SCR-M2 gave the highest CO_2 adsorption capacity because the second pyrolysis after acid treatment reduced the amounts of elements such as oxygen and nitrogen, producing Biochar@SCR-M2 with high hydrophobicity and low polarity. Thus, it would reduce the competition of CO_2 with polar molecules like H_2O during the adsorption of CO_2 [25]. This phenomenon can be well explained by using the notion of "like-dissolves-like", which is polar biochar reacting with polar H_2O and non-polar biochar reacting with non-polar CO_2. Since the two dipoles in the linear CO_2 molecule cancel each other out, the CO_2 molecule becomes non-polar, having a higher interaction with non-polar biochar than H_2O and other polar molecules; this is advantageous for selective CO_2 adsorption over competing gases on biochar [26].

Comparison with other Reported Adsorbents in the Literature

The CO_2 adsorption performance of Biochar@SCR-M1 and Biochar@SCR-M2 in this study was compared to several published modified biochar, as presented in Table 2. Notably, Biochar@SCR-M1 and Biochar@SCR-M2 demonstrated comparable CO_2 adsorption capacities with other reported adsorbents, suggesting that the treatment with phosphoric acid is an alternative way to turn soybean waste, soybean curd residue (SCR) as a potential adsorbent in the field of CO_2 capture.

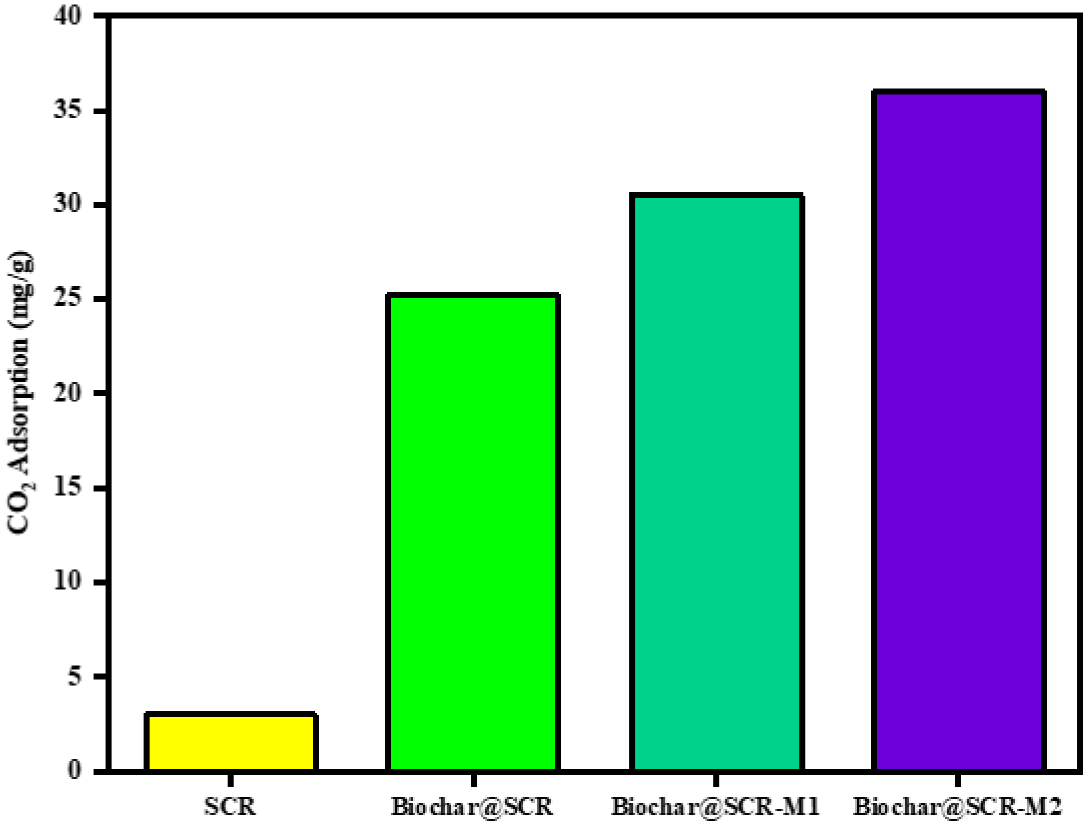

Figure 3. CO_2 adsorption capacities of SCR, Biochar@SCR, Biochar@SCR-M1, and Biochar@SCR-M2

Table 2. Comparison of Biochar@SCR, Biochar@SCR-M1, and Biochar@SCR-M2 with other reported adsorbents

Adsorbent	Modification method	Adsorption temperature (ºC)	Adsorption capacity (mg/g)	Reference
Cottonwood biochar/Mg oxyhydroxide	Pyrolysis at 600°C and modified with the salt $MgCl_2$ with 6 metal ratios.	25	27.79	[27]
Walnut shell biochar	Pyrolysis at 900°C	70	30.07	[28]
CA-char (modified cotton stalk biochar)	Fast pyrolysis at 600°C and modified with CO_2 and NH_3 mixture at 500°C	120	15.00	[29]
Amine-treated sawdust biochar	Pyrolysis at 450°C and treatment with monoethanolamine	30	19.10	[30]
NH_3-modified cotton stalk biochar	Pyrolysis at 600°C and modified with NH_3 at 700°C	120	28.00	[31]
Sawdust	Pyrolyzed at 850°C, treated with monoethanolamine and stirred for 20 min	30	44.80	[32]
Rubber seed shells	Pyrolyzed at 700°C, KOH impregnation and carbonization at 700°C for 120 min	25	43.51	[33]
Sawdust	Pyrolyzed at 700°C, N-doping (impregnation of biochar with urea phosphate, and calcination under N_2 at 700°C for 2 h)	25	58.97	[34]
Hickory chips	Pyrolyzed at 600°C, N-doped (ball milling with NH_4OH and dried in oven at 80℃ for 48 h)	25	37.4	[35]
Biochar@SCR-M1	**Pyrolysis at 500°C and treatment with 42.5 wt.% H_3PO_4**	**30**	**30.50**	**This study**
Biochar@SCR-M2	**Pyrolysis at 500°C and treatment with 42.5 wt.% H_3PO_4. Pyrolysis again at 500ºC for 2 hours**	**30**	**36.00**	**This study**

CONCLUSION

The agricultural waste, soybean curd residue was successfully converted into biochar using the pyrolysis process, and phosphoric acid treatment was used to modify the surface of Biochar@SCR for adsorption of CO_2. Their structures were confirmed using FTIR and SEM-EDX analyses. Characterization results proved that the Biochar@SCR-M1 and Biochar@SCR-M2 have a porous structure and mainly consist of P=O bond, P-O-P chain, P-O-C and C=C stretching. CO_2 analysis shows that the adsorption capacities of SCR, Biochar@SCR, Biochar@SCR-M1 and Biochar@SCR-M2 are 3.00 mg/g, 25.21 mg/g, 30.50 mg/g and 36.00 mg/g, respectively. The modified adsorbents, Biochar@SCR-M1 and Biochar@SCR-M2, have shown high adsorption capacities for CO_2 sorption due to their porous and hydrophobic structures. These characteristics may offer adsorption sites for CO_2 through pores on their surface and provide selective adsorption towards CO_2 as their hydrophobicity may repel polar molecules such as H_2O, thus reducing competition with polar molecules during CO_2 adsorption.

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