Amine Functionalized Carbon-based Soybean Curd Residues (SCR) as Potential Adsorbent for Carbon Dioxide Adsorption

D S Zakaria¹ · S K Mahmad Rozi¹,* · H N Abdul Halim¹ and S Mohamad²

¹Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis, 01000 Kangar, Perlis.
²Faculty of Science, Department of Chemistry, University of Malaya, 50603, Kuala Lumpur.

E-mail: khalijahrozi@unimap.edu.my

Abstract. Currently, carbon dioxide (CO₂) capture can preserve environmental quality by using carbon-based adsorbent. In this research, Polyethylenehexamine (PEHA) functionalized carbon-based soybean curd residues (carbonized SCR-PEHA) was prepared for CO₂ adsorption. Analysis of functional groups of the prepared adsorbent using Fourier Transform Infrared Spectroscopy (FTIR), confirmed the functionalization of PEHA on the carbonized SCR. CO₂ uptake of the carbonized SCR-PEHA was compared with the bare SCR using Thermogravimetric Analyzer (TGA) analysis. TGA results revealed that the adsorption capacity of CO₂ for carbonized SCR-PEHA and bare SCR are 8.816 mg/g and 3.027 mg/g respectively. It was observed that functionalization of the PEHA on the surface of carbonized SCR had improved the adsorption capacity of CO₂ by 2.92 times as compared to bare SCR. The phenomenon can be explained from the interaction of the CO₂ with the available amine sites provided for the carbonized SCR-PEHA which significantly improved the CO₂ adsorption. Hence, the carbonized SCR-PEHA demonstrate potential adsorbent for CO₂.

1. Introduction

Greenhouse gases are heat trapping and making the earth become warmer. The main source of greenhouse gas emissions is from human activities for instance the combustion of fossil fuels for electricity, food, and transport. Many environmental issues have been posed by the continuous use of fossil fuels, such as the ever-increasing amount of greenhouse gas (CO₂) in the atmosphere, the concentration of which has risen exponentially from 325 ppm (1967) to 409 ppm (2017) [1]. It is clear that the introduction of CO₂ capture and storage (CCS) technologies play an important role in achieving the required reduction of CO₂ emissions in order to prevent permanent and everlasting ozone destruction [2].

Several technologies have been introduced to minimize the concentration of CO₂ in the environment, such as membrane separation, alkanol amine solvent, and ionic liquid absorption. However, all these technologies are costly to implement and not environmentally friendly. Moreover, the technologies required high pressure and lower the yield of the methane concentration in the output [3]. The adsorption of CO₂ by the solid adsorbent is favored among the different techniques introduced due to various advantages such as high performance, broad range of working temperatures, cost efficiency and protection agreement [4]. Nowadays, a wide range of porous materials, including zeolite [5], amine-
doped silica [6] and porous polymers [7] have been used for CO$_2$ capture and storage. These materials, however, also suffer from the dynamic method of synthesis and improper use of raw chemical materials. The promising adsorbents for CO$_2$ adsorption are mostly prepared from porous carbon materials due to simple to prepare, low energy costs and improved adsorption properties [8]. A wide variety of carbon precursors, including microporous organic polymers [9], and biomass materials are prepared with different kinds of porous carbon materials [10].

Carbon based adsorbent from the biomass are environmentally safe for CO$_2$ capture since it can be created from freely available biomass and waste including crop residue [11,12], wood waste [12], animal manure, food waste [13] industrial solid residues [14], and wastewater sludge [4,15,16]. Furthermore, the use of waste for carbon based adsorbent production in capturing CO$_2$ could help in improving waste management [17]. Activated carbon is commonly carbon-based adsorbents used to eliminate common air toxins as an adsorbent. The use of activated carbon as effective adsorbent is limited considering its excellent adsorbent capability and high costs and regeneration problem [18].

Biomass from the agriculture waste such as sugarcane bagasse, cotton stalk, vegetable waste, peanut shells and sawdust have been used as promising CO$_2$ adsorbents [17]. The agricultural waste can lower the cost of preparation of the adsorbent and can reduce environmental pollution. In this study, soybean curd residues as low price, abundant and renewable resources had been chosen as our potential CO$_2$ adsorbent. Soybean curd residue (SCR) is a by-product of soybean products processing which is generated in abundance throughout the world [19]. China generates about 2.8 million tonnes SCR annually [20]. Huge amount of SCR is a current major challenge to the soybean products processing plants due to the fact that the uncontrolled disposal of SCR is liable to cause adverse environmental impacts and threaten the public health. Use of the waste SCR as carbon-based adsorbent can solve this environmental issue and reduce the cost for the preparation of the CO$_2$ adsorbents. In this study, the bare SCR undergo pyrolysis process under N$_2$ flow to vaporized the bare SCR. The SCR was functionalized with PEHA to increase the active sites for the CO$_2$ interaction and indirectly increased the CO$_2$ adsorption on the carbonized SCR-PEHA adsorbent.

2. Methodology

2.1 Materials

Soybean curd residues (SCR) were obtained from the local seller in Perlis. Analytical grade of Polyethylenehexamine (PEHA), ethanol, acetone and toluene were purchased from Sigma-Aldrich (Missouri Mo, USA).

2.2 Characterization of the adsorbents

The functional group of the prepared adsorbents were characterized by FTIR (Pekin Elmer Spectrum-65, USA) in the adsorption mode with 4 scans and a resolution of ±4 cm$^{-1}$, a wavenumber range of 4000 -400 cm$^{-1}$ with a diamond as a detector.

2.3. Preparation of carbonized SCR-PEHA

2.3.1. Preparation of bare SCR. The collected SCR were washed multiple times and dried for 48 hours in oven at 50 °C. Once dried, the bare SCR were ground using a 60 mm sieve [21].

2.3.2. Synthesis of carbonized SCR-PEHA. Figure 1 shows the synthesis of carbonized SCR-PEHA. For the preparation of carbonized SCR, the pyrolysis activity was adapted from the modified version of published method [22]. Bare SCR were pyrolyzed under 30 mL/min nitrogen flow to vaporized the bare SCR, leaving a char behind. The furnace was heated until the desired temperature of 500 °C was reached. Pyrolysis activity was conducted for 2 hours and the carbonized SCR were cooled to room temperature (25 °C). Carbonized SCR-PEHA were prepared by using modified procedure from reported study [21]. Briefly, carbonized SCR were impregnated with PEHA at mass ratio of 1:4 for 4 hours. The sample was mixed with 20 mL of toluene as the vehicle for the impregnation process. Carbonized SCR-PEHA was washed multiple times with ethanol and deionized water before oven-dried overnight.
2.4. CO₂ adsorption measurement

The adsorption measurement study was adapted from the previous method by [23]. The adsorption tests were carried out under isothermal conditions in a Thermogravimetric analyzer (TGA, SDTQ-600). In each gasification experiment, 8-10 mg of each sample was loaded in alumina pan and heated at a rate of 20 °C/min to 110 °C/min in N₂ atmosphere (75 mL/min) to remove contaminants in the sample. The sample was kept at the gasification temperature under N₂ for 15 min. Then, N₂ was switched to CO₂ (75 mL/min) to initiate the isothermal gasification for 70.00 min. The continuous weight losses of the biomass and heat flows were recorded at isothermal of 30 °C.

3. Results and Discussion

3.1. Functional group analysis

Figure 1. The preparation scheme of (A) Bare SCR (B) Carbonized SCR (C) Carbonized SCR-PEHA.
The functional groups of bare SCR and carbonized SCR-PEHA adsorbent were characterized using FTIR spectroscopy. The spectra of bare SCR and carbonized SCR-PEHA adsorbents are shown in Fig. 2. A wide band at 3314.5 cm\(^{-1}\) that results from hydroxyl group was observed on the spectrum of bare SCR in Figure 2 (A). In addition, the bands appeared at 2922.5 cm\(^{-1}\) and 2853.5 cm\(^{-1}\) were due to asymmetric and symmetric CH\(_2\) stretching, respectively. As seen in Figure 2 (A), the bands at 1744.5 cm\(^{-1}\), 1637.5 cm\(^{-1}\) and 1048 cm\(^{-1}\) show the strong C=O, C=C, and C-O stretching, respectively. These results proved that bare SCR is rich in hydrophilic functional groups (hydroxyl and carbonyl). As depicted from spectrum of carbonized SCR-PEHA in Figure 2 (B), there are no peaks for C=O and O-H stretching, suggesting that the decomposition of these functional groups during pyrolysis process. Furthermore, the new peaks appeared at 3381.5 cm\(^{-1}\) and 1561 cm\(^{-1}\) for carbonized SCR-PEHA are assigned to NH stretching and NH\(_2\) group, respectively [25]. These new bands indicated that polyethylenehexamine (PEHA) have been successfully functionalized onto the surface of carbonized SCR.

![Figure 2. FTIR spectrum of (A) bare SCR and (B) carbonized SCR-PEHA.](image)

3.2. CO\(_2\) capturing on the dried SCR and carbonized SCR-PEHA
The CO\(_2\) adsorption capacities of the both bare SCR and carbonized SCR-PEHA at ambient pressure (1 bar) were evaluated by TGA under both 100 vol.% of CO\(_2\). The CO\(_2\) uptake was calculated by measuring the sample weight change before and after the experiment over time. Figure 3 compares the CO\(_2\) uptake capacity as a function of adsorption temperature in the range from 0 to 70 °C. As shown in Figure 3, carbonized SCR-PEHA shows adsorption capacity of CO\(_2\) at 8.816 mg/g (Figure 3 (B)) while bare SCR recorded adsorption capacity at 3.027 mg/g (Figure 3(A)). It was observed that by functionalization of the PEHA on the surface of carbonized SCR, the adsorption capacity of CO\(_2\) was improved 2.9 times as compared to bare SCR. This phenomenon can be explained from the interaction of the CO\(_2\) with the available of the amine sites provided from carbonized SCR-PEHA (Figure 4) which significantly
increased accelerated the CO\textsubscript{2} adsorption. Hence, the carbonized SCR-PEHA demonstrated as a potential adsorbent for CO\textsubscript{2} uptake.

![Figure 3. CO\textsubscript{2} adsorption capacity of (A) Bare SCR and (B) Carbonized SCR-PEHA.](image)
3.3 Comparison with reported adsorbents in the literature

The performance of the present adsorbent was compared with works in literature with respect to adsorbed CO$_2$. This study reported for the first time of the use of agricultural waste, soybean curd residues for the adsorption of CO$_2$. From Table 1, it can be seen that, the adsorption capacity of the carbonized SCR-PEHA is comparable with the other reported adsorbents. Therefore, it is good to explore the SCR waste as CO$_2$ adsorbent.

Table 1. Comparison of the developed adsorbent based agricultural waste for CO$_2$ adsorption.

| Adsorbent              | Adsorption Capacity (mg/g) | Ref.     |
|------------------------|---------------------------|---------|
| Rice husk              | 9                         | [26]    |
| Risk husk              | 10                        | [26]    |
| Cotton stalk           | 10                        | [27]    |
| Cotton stalk           | 12                        | [27]    |
| Sawdust                |                           |         |
| Soybean curd residues  | 12.18.816                 | [28]    |

4. Conclusion

The proposed adsorbent, carbonized SCR-PEHA showed a good performance as CO$_2$ adsorbent with adsorption capacity of 8.816 mg/g. The functionalization of PEHA on the surface of the carbonized SCR had improved about 2.29 times as compared to bare SCR. This result can be explained by the structure of the carbonized SCR-PEHA which consist of elemental N that provide active sites for CO$_2$ adsorption. This finding could support further investigation on the carbonized SCR-PEHA as a potential adsorbent for CO$_2$.

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Acknowledgement
We gratefully acknowledge the financial support of this project by FRGS RACER (9027-00025) from Ministry of Higher Education Malaysia.