Carbon dioxide adsorption using biomass-based activated carbon functionalized with deep eutectic solvents

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Abstract. The biomass-based activated carbon can be synthesized into green solvent to mitigate disposal problems and enhance production efficiency. The green solvent known as deep eutectic solvents (DES), which exhibits unique characteristics can be used to enhance the performance of the activated carbon and results in high CO2 adsorption capacity. In this study, new approaches involving the modification of low-cost biomass-based activated carbon with green solvent functionalization agent is proposed. The DES produced will be characterized for their physical properties such as pH, density and viscosity. The modified adsorbents were studied for their surface morphology and element composition using field emission scanning electron microscope and energy dispersive X-ray spectroscopy techniques. Further to this, in order to evaluate the CO2 adsorption characteristic, breakthrough curve was studied in a packed-bed adsorption reactor. The effects of temperature were used as a parameter for examining the breakthrough time performance. The results revealed that, the breakthrough time decreases with increasing column temperatures. The results indicated that the breakthrough time was longer at a lower adsorption temperature (30°C) for modified activated carbon with DES, which was 5 min. Maximum high adsorption capacity of 11.05 mg/g at lower adsorption temperature was achieved using modified activated carbon with DES.

1. Introduction
The tremendous demand and consumption of energy in the world these days has caused the rise of greenhouse gases emissions, particularly carbon dioxide (CO2), which contributes to global warming [1]. It has now become a major environmental issue that need to be tackled globally. The world atmospheric CO2 concentration has increased significantly from 408.34 part per million (ppm) in July 2018 to 411.41 ppm in July 2019. The CO2 concentration is increasing mainly due to human activities including the burning of fossil fuels for power generation and transportation, as well as deforestation for agriculture purposes [2]. Carbon capture and storage/sequestration (CCS) are well-known methods, perhaps the most promising route to substantially reduce CO2 emissions and serves as a solution that can save the Earth [3-5]. CCS technology has received much attention and became the main topic among scientists and researchers globally to mitigate CO2 emissions. The four basic routes of removing CO2 are post-combustion, pre-combustion capture, oxy-fuel, and chemical looping processes [6]. Among the several CCS technologies for CO2 capture, post-combustion method using adsorption process is the effective technique preferred because of its low energy requirement, simplicity in operation, cost-effective technology and clean process [7-9].

The main difficulty faced in commercializing the adsorption method effectively is to produce the adsorbents with high adsorption capacity, low cost materials, environmental-friendly materials and easy regeneration [4,10]. Therefore, it is essential to explore and develop a cost-effective technology for CO2 capture. A new technology for the modification of adsorbents using green solvent needs to be developed to capture CO2. The green solvent known as deep eutectic solvents (DES) is a novel state-of-the-art technology, which recently has been extensively studied by many researchers for various applications. DES was recently recognized as a new type of ionic liquids with additional advantages,
specifically in terms of cost, environmental impact, and synthesis [11-14]. DESs are prepared by mixing a hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) [15]. DESs can be modified using combination of various types of HBAs and HBDs [11].

There are several literature studies which used modified adsorbent to improve their adsorption capacity. For example, Shafeeyan et al. [16] developed solid adsorbents by impregnated ammonia onto palm shell activated carbon to capture CO$_2$ and studied a modelling of CO$_2$ using various kinetic models. They showed that with increasing temperatures from 30°C to 60°C, the adsorption capacity performance of impregnated activated carbon has reduced. Li et al. [17] investigated the performance of CO$_2$ adsorption through the modification of UiO-66 type metal organic frameworks with DES (choline chloride and urea). The results indicated that the higher CO$_2$ uptake is due to extra adsorption sites from DES. Zulkurnai et al. [18] prepared an impregnation method of activated carbon from biomass activated carbon (sea mango) using DES (choline chloride and glycerol) with a 1:2 ratio to enhance the CO$_2$ adsorption capacity by functionalized with DES on the surface of the adsorbent. They found out that the modified adsorbent resulted in maximum CO$_2$ adsorption capacity as compared to the unmodified adsorbent due to the N element or additional functional group found on the surface of the adsorbent that enhance the active sites for increasing CO$_2$ capture. In addition, by modifying the activated carbon using DES, the CO$_2$ adsorption capacity will increase and enhance the surface chemistry of adsorbent as well as provide superior performance compared to that of the non-impregnated adsorbent. In this study, new approach involving the modification of low-cost biomass-based activated carbon with green functionalization agent (DES) is proposed. To date, very few studies have highlighted the modification of activated carbon with DES for CO$_2$ capture. In this work, new method of modifying activated carbon with potential ammonium-based DES (tetra-n-butyl ammonium bromide (TBAB); glycerol (Gly)) was explored for CO$_2$ capture. The morphological structures were studied by field emission scanning electron microscope and energy dispersive X-ray spectroscopy techniques (FESEM-EDX). Therefore, the study emphasized on investigating the performance of CO$_2$ adsorption using modified activated carbon with DES by evaluating the CO$_2$ breakthrough characteristics.

2. Materials and methods

2.1 Raw materials
The biomass-based activated carbon from palm shell source was used as an adsorbent and purchased from Bravo Green Sdn. Bhd., Malaysia. The adsorbent was formed by the physical activation with steam process. The adsorbent was then washed with distilled water to remove impurities and dried in oven at 105°C overnight.

2.2 Synthesis of deep eutectic solvents
The synthesis of DESs were carried out by mixing two components between HBA (tetra-n-butyl ammonium bromide (TBAB)) and HBD (glycerol (Gly)) at different ratios (1:1 to 1:4) at 80°C with stirring rate of 350 rpm for 3 h until the DESs mixture was a homogenous solution without any precipitate.

2.3 Impregnation of activated carbon with deep eutectic solvents
The activated carbon was functionalized with DES at 70°C for 3 h using ultrasonic bath sonicator. The functionalized activated carbon was repeatedly washed, filtered and dried at 110°C overnight.

2.4 Experimental procedure – CO$_2$ adsorption
The packed bed CO$_2$ adsorption column is made of stainless-steel reactor with 1.5 cm inner column diameter and 30 cm long, surrounded with an insulator (heater) to maintain a constant column temperature during the experiment process. The CO$_2$ adsorption study was conducted using the packed bed CO$_2$ adsorption column to determine the breakthrough curve and maximum CO$_2$ adsorption capacity of the adsorbent by varying the operating temperatures. Two types of gases (N$_2$ & CO$_2$) were introduced. The N$_2$ and CO$_2$ flow rates were controlled accurately by digital mass flow controllers. To
attain 15% inlet composition of CO₂, the CO₂ and N₂ flow rates were controlled and set using mass flow controllers. The adsorbent (50 g) was transferred into the packed bed column for breakthrough study. Then, purging process was performed with flow of N₂ at room temperature and atmospheric pressure for 15 minutes. Subsequently, the column was heated to desired adsorption temperature using temperature controller. Once the desired adsorption temperature had been reached, the adsorption breakthrough study was carried out at the temperatures of 30°C and 60°C, at a fixed CO₂ inlet flow rate of 85 ml/min. A CO₂ analyzer (Alpha Omega series 9610) with measuring capacity of 15% CO₂ was applied to analyze the CO₂ concentration released from the adsorption packed bed reactor. The amount of CO₂ adsorbed was analyzed by data logger system (GRAPHTEC GL820) with a temperature controller system. The breakthrough time results were recorded using data logger system for every experiment.

2.5 Characterization of adsorbent
A field emission scanning electron microscope (FESEM), Model: Quanta FEG 450 coupled with an energy dispersive X-ray spectroscopy (EDX) system, Model: EDX-Oxford were used to analyze the surface morphology and element composition of the adsorbent.

3. Results and discussion

3.1 Textural structure and carbon content
The FESEM analysis was studied to observe the textural morphology and porosity development of raw activated carbon and functionalized activated carbon at various magnification sizes. Figures 1(a), (b), (c) at a magnification size of 1000x, 5000x, and 10000x and Figures 2(a), (b), (c) depict the FESEM micrographs of raw activated carbon and functionalized activated carbon at magnification sizes of 1000x, 5000x and 10000x. As shown in Figure 1b, the analysis revealed a porous structure with an appearance in the form of a highly porous material ‘sponge-puff’, large pores and had irregular-shaped particles found on the raw activated carbon. However, the surface texture of impregnated activated carbon showed noticeable changes and well-developed pores which result in a good surface for CO₂ adsorption. After the functionalized-DES (Figure 2b and 3c), a honeycomb form and slightly hexagonal shape with a high pore structure was obviously seen in the morphology structure.
Figure 1. Surface morphology of raw activated carbon at a magnification size of (a) 1000x, (b) 5000x, and (c) 10000x.

Figure 2. Surface morphology of modified activated carbon with DES at a magnification size of (a) 1000x, (b) 5000x, and (c) 10000x.

3.2 Energy dispersive X-ray spectroscopy (EDX) analysis

Based on the result of energy dispersive X-ray spectroscopy (EDX) analysis, the raw activated carbon exhibited a relatively high composition of carbon (98.5%). The composition of carbon slightly increased with the impregnated activated carbon from 98.5% to 98.78% (Table 1).

Table 1. EDX elements of raw activated carbon and modified activated carbon with DES

| Adsorbents              | Carbon (%) | Oxygen (%) | Nitrogen (%) | Bromine (%) |
|-------------------------|------------|------------|--------------|-------------|
| Raw activated carbon    | 98.5       | 1.50       | -            | -           |
| Impregnated activated carbon | 98.78     | -          | 0.69         | 0.53        |

3.3 CO2 Breakthrough analysis

CO2 breakthrough curves plotted for raw activated carbon and impregnated activated carbon with DES at different adsorption temperatures (30°C and 60°C) and at a fixed CO2 flow rate (85ml/min) and CO2 concentrations (15%) are shown in Figure 3 and 4. The trend of the breakthrough curves obtain in this study were similar to those reported in the literature for ammonia-impregnated activated carbon [16], amine-impregnated commercial activated carbon [18] and DES-functionalized activated carbon [18]. It was observed that the breakthrough time decreased and became faster with the increase in adsorption temperatures. It can be observed that, saturation time became shorter with an increase in temperatures from 30°C to 60°C. In addition, it is also revealed that breakthrough time for the functionalized activated carbon with DES is longer compared to the breakthrough time of the raw activated carbon. The longest breakthrough time was observed in the impregnated activated carbon with DES at 30°C,
whereby the adsorption breakthrough occurred at 5 min. On the other hand, the CO$_2$ breakthrough curves of the impregnated activated carbon with DES at 60°C showed a lower breakthrough time, which occurred only at 2 min. For raw activated carbon at 30°C, the adsorption breakthrough occurred at 2 min. However, at 60°C, the breakthrough time for raw activated carbon slightly decreased to 1 min. Based on the findings, it can be concluded that the CO$_2$ breakthrough time decreases with increasing adsorption temperatures because of the exothermic condition of the adsorption process [16]. Moreover, low adsorption temperature resulted in longer saturation time. Based on Table 2, when the temperatures decreased from 60°C to 30°C, the time needed to achieve equilibrium condition increased from 18 to 22 mins for the impregnated activated carbon.

![Figure 3. Breakthrough curves of CO$_2$ adsorption at 60°C](image)

![Figure 4. Breakthrough curves of CO$_2$ adsorption at 30°C](image)

**Table 2.** Breakthrough time and saturation time of the raw activated carbon and impregnated activated carbon with DES

| Adsorbents         | Temperature (°C) | Breakthrough time | Saturation time |
|--------------------|------------------|-------------------|-----------------|
| Raw activated carbon | 30°C             |                  |                 |
| Impregnated activated carbon with DES | 30°C             |                  |                 |
|                    | 60°C             |                  |                 |

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3.4 Adsorption capacity

The maximum CO₂ adsorption of impregnated activated carbon with DES at 30°C and 60°C were 11.05 mg/g and 9.04 mg/g, respectively (Table 3). Whereas, for the raw activated carbon at 30°C and 60°C, the maximum adsorption capacities were 10.05 mg/g and 9.04 mg/g, respectively. These findings were supported by Shafeeyan et al. [16] who claimed that there is a decrease in CO₂ adsorption capacity when the bed temperature increased. This is due to the exothermic nature of the adsorption process. The highest CO₂ adsorption capacity was found in impregnated activated carbon with DES at 30°C because of its high pH (12.6), high pore size (observed from morphology) and the availability of carbon and N elements on the surface, which enhanced CO₂ adsorption performance.

Table 3. CO₂ adsorption capacities of the raw activated carbon and impregnated activated carbon with DES

| Adsorbents                | Temperature (°C) | Breakthrough adsorption capacity, (mg/g) | Maximum adsorption capacity, (mg/g) |
|---------------------------|------------------|------------------------------------------|------------------------------------|
| Raw activated carbon      | 30               | 1.00                                     | 10.05                              |
|                           | 60               | 0.50                                     | 9.04                               |
| Impregnated activated carbon | 30               | 2.51                                     | 11.05                              |
|                           | 60               | 1.00                                     | 9.04                               |

3.5 CO₂ desorption

Easy regeneration is one of the important characteristics of effective adsorbent for CO₂ capture. In this work, the maximum adsorption capacity of impregnated activated carbon was selected to test the regeneration performance at 30°C for five adsorption/desorption cycles. The results showed that, all five cycles indicate the impregnated activated carbon were easily regenerated for CO₂ desorption and hence indicating it is good to be reused. Hence, the new modified adsorbents produced using green solvents are effective in reducing CO₂ emissions and suitable for use in large applications.

4. Conclusion and future work

In this study, new approaches involving the modification of activated carbon with the potential ammonium-based DES (tetra-n-butyl ammonium bromide (TBAB) with glycerol (Gly) were explored for CO₂ capture. The adsorbents showed a significant improvement in the surface morphology with the DES impregnation method. The adsorption process was under exothermic reaction and showed a physisorption nature. The impregnated activated carbon showed high maximum CO₂ capacity of 11.05 mg/g at 30°C. Moreover, the adsorbent showed it is good for reuse and can be recycled over five adsorption-desorption cycles and thus it cost-effective for CO₂ capture process. It can be concluded that, the adsorbent used in this study has great potential to enhance CO₂ adsorption performance and can be used as an alternative to commercial activated carbon.

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