Preparation and Characterization of Impregnated Commercial Rice Husks Activated Carbon with Piperazine for Carbon Dioxide (CO2) Capture

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Abstract. Development of effective materials for carbon dioxide (CO2) capture technology is a fundamental importance to reduce CO2 emissions. This work establishes the addition of amine functional group on the surface of activated carbon to further improve the adsorption capacity of CO2. Rice husks activated carbon were modified using wet impregnation method by introducing piperazine onto the activated carbon surfaces at different concentrations and mixture ratios. These modified activated carbons were characterized by using X-Ray Diffraction (XRD), Brunauer, Emmett and Teller (BET), Fourier Transform Infrared Spectroscopy (FTIR) and Field Emission Scanning Electron Microscopy (FESEM). The results from XRD analysis show the presence of polyethylene butane at diffraction angles of 21.8° and 36.2° for modified activated carbon with increasing intensity corresponding to increase in piperazine concentration. BET results found the surface area and pore volume of non-impregnated activated carbon to be 126.69 m²/g and 0.081 cm³/g respectively, while the modified activated carbons with 4M of piperazine have lower surface area and pore volume which is 6.77 m²/g and 0.015 cm³/g respectively. At 10M concentration, the surface area and pore volume are the lowest which is 4.48 m²/g and 0.0065 cm³/g respectively. These results indicate the piperazine being filled inside the activated carbon pores thus, lowering the surface area and pore volume of the activated carbon. From the FTIR analysis, the presence of peaks at 3312 cm⁻¹ and 1636 cm⁻¹ proved the existence of reaction between carboxyl groups on the activated carbon surfaces with piperazine. The surface morphology of activated carbon can be clearly seen through FESEM analysis. The modified activated carbon contains fewer pores than non-modified activated carbon as the pores have been covered with piperazine.

1. Introduction
Rice husk is the outermost layer of the paddy grain that being separated throughout the milling process which consist of 20% from overall paddy production and approximately, there are 100 million tons of rice husks generated worldwide per annum [1]. Rice husk usually categorized as agricultural waste product and often disposed by dumping or burning to produce rice husk ash [2]. The high content of hydrocarbon in the rice husk enhances its potential as the feedstock for activated carbon preparation [3].
Activated carbon usually used as adsorbent for environmental control in the form of a fixed bed due to its large internal surface area and pore volume, and its ability to adsorb organic vapors for a low cost [4]. Activated carbon was also considered as one of the highly potential adsorbent for CO₂ adsorption [5]. Adsorption is a process of mass transfer occurs from bulk of gas or liquid to adsorbents and it has been thoroughly used as separation methods in chemical and other industries [6]. Activated carbon consists of acidic and basic surfaces while CO₂ gas is an acidic gas. As the CO₂ gas interacts with activated carbon, the basic groups on the activated carbon surfaces will attract CO₂ gas. To enhance the adsorption capacity of the activated carbon, amine groups have been introduced by wet impregnation method onto the activated carbon due to their high efficiency and selectivity for CO₂ capture [7]. It has been proved that the modified activated carbon with piperazine enhanced the adsorption capacity significantly [8]. Piperazine will react with CO₂ which involves the mass transfer of CO₂ from the gas phase into the aqueous phase of amine as in (1):

\[
\text{CO}_2^\text{carbon dioxide} + 2C_4H_{10}N_2^\text{piperazine} \rightarrow C_4H_{10}NCOO^- + C_4H_{10}NH_3^+ \text{diethylamine cation}
\]

In this research work, the rice husk activated carbon was impregnated with piperazine which expected to enhance the CO₂ adsorption capacity. The research aims to study the characteristics of non-modified activated carbon and modified activated carbon with piperazine at different concentration and mixture ratio. The concentration used in this study were 2M, 4M, 6M, 8M and 10M while the mixture ratio used were 1:1, 1:2 and 2:1 of activated carbon to piperazine. The modified activated carbon then undergoes several analyses such as XRD, BET, FTIR and FESEM.

2. Materials and Methods

2.1. Materials and Chemicals
The commercial activated carbon made from rice husk ash was supplied by Sin Guan Hup Oil & Rice Mill Sdn Bhd (Penang, Malaysia). Anhydrous piperazine with a molecular weight of 86.14 g/mol was purchased from MERCK.

2.2. Activated Carbon Preparation
The activated carbon particle’s size was sifted using 500nm sieve. The prepared activated carbon particles were rinsed with deionized water followed by heating in a 70°C oven for 6 hours. The sample was then being kept in a desiccator at room temperature to avoid moisture effect.

2.3. Impregnation Process
Impregnation of activated carbon was conducted with the presence of piperazine. Concentrations of piperazine being used in this work were 2M, 4M, 6M, 8M, and 10M. 50g of activated carbon was used for preparation of each sample. Ratio of the mixture was based on the weight percent of the activated carbon to piperazine (ie: 1:1, 1:2 and 2:1). Firstly, the mixture was mixed in a beaker and mechanically stirred at 60 rpm for one hour at room temperature before being heated at 70°C for 6 hours to ensure complete drying without any trace of moisture left within its particles obtained. The sample then being kept in a desiccator at room temperature.
2.4. Activated Carbon Characterization

2.4.1. X-Ray Diffraction (XRD). Rigaku Miniflex X-Ray Diffractometer of the CuKα radiation filtered by a Ni filter was used in this research with a wavelength of 1.54 Å at 30 kV and 15 mA. The activated carbon samples were initially crushed to a fine powder (< 200 µm) to minimize inducing extra strain (surface energy) that can offset peak positions, and to randomize orientation. The specimens were placed on the glass specimen holder and pressed using a glass slide. Scanning of sample was performed starting from 3° to 80° at a speed of 1° min\(^{-1}\). The peaks obtained from the analysis were identified using PDLX software.

2.4.2. Fourier Transform Infrared Spectroscopy (FTIR). Analysis of FTIR was conducted by FTIR (Thermo Scientific Nicolet iS10) using Attenuated Total Reflectance (ATR), Nujol and thin film. Enough samples were needed to obtain an absorption spectrum during FTIR analysis. The first step was to collect background spectra to subtract from the test spectra. Next, the sample was analysed by LTI’s fully-computerized Fourier Transform Infrared Spectroscopy system which produces the absorbance spectra showing the unique chemical bonds and the molecular structure of the sample material. This profile was either in the form of an absorption/transmittance spectrum which shows peaks representing the components concentration. The wavelength used was in range of 500 – 4000 cm\(^{-1}\). The software used to interpret the data was OMNIC.

2.4.3. Brunauer, Emmett and Teller Analysis (BET). Physical adsorption of a gas on solid surface will results in a formation of a thin layer that covers the entire solid surfaces. Analysis using BET instrument provides single sample surface area as well as pore size distribution. Firstly, around 0.3g of activated carbon was packed in the U-sample tube, and degassed at 70°C overnight and cool down to ambient temperature. The nitrogen (N\(_2\)) adsorption or desorption process was done using Thermo Scientific (Surfer) equipment. Once the TCD signal has stabilized, the sample tube was immersed in a flask fill up with liquid N\(_2\). When the adsorption has reached the equilibrium, the sample was shifted back to ambient temperature for 15 minutes. Surface area was calculated and the effect of surface porosity and pore size was determined.

2.4.4. Field Emission Scanning Electron Microscopy (FESEM). The activated carbon was analysed by using JEOL field emission scanning electron microscope at the magnifications of 60x and 50,000x. The accelerating voltage was 5.0 kV during image capture using secondary electron and dark field detectors.

3. Results and Discussions

3.1. X-Ray Diffraction (XRD)

X-Ray diffraction analysis was used to determine the crystallographic structure and chemical composition of the non-modified activated carbon and modified activated carbon with piperazine. Figure 1 shows the difference between diffraction peaks for the non-modified and modified activated carbon. The presence of pyrazole in non-impregnated activated carbon can be seen clearly at the diffraction angle of 21.66° and 36.25° in Figure 1(A). There is pyrazole chain presence on the non-modified activated carbon surface [9]. The peaks obtained for modified activated carbon with piperazine can be observed through Figure 1(B) and Figure 1(C). Figure 1(B) shows the results for concentration of 4M of piperazine impregnated sample while Figure 1(C) shows the peaks for concentration of 10M of piperazine impregnated sample. The diffraction angle for lower concentration piperazine shows the presence of polyethylene butane at 21.86° and 36.28° while at higher concentration of piperazine which is 10M, there is presence of silicon oxide at 21.89° and polyethylene butane at 36.12°. The differences in peak height for both samples explain that there is
higher content of polyethylene butane in low concentration of piperazine while the silicon oxide appears in high concentration piperazine. The intensity of the peak is higher when the amine loading on the surface of activated carbon is higher [10]. In this case, the peak of silicon oxide shows the highest intensity compared to the polyethylene butane peak, thus proved the statement made by the previous researchers.

Figure 1. XRD pattern for (A) non-impregnated activated carbon, impregnated activated carbon with (B) 4M piperazine and (C) 10M piperazine.

3.2. Fourier Transform Infrared Spectroscopy (FTIR)
Based on the FTIR results, the transmission range for the samples are from 4000 – 500 cm\(^{-1}\), however the sensitive transmission regions of the samples were detected in a few different regions. Amides regions were found across 3500 – 1500 cm\(^{-1}\). The reaction between carboxylic acids presence on the surface of activated carbon with amine has formed amide. Figure 2 shows the difference of transmittance peaks between non-impregnated activated carbon and impregnated activated carbon. The presence of amide on the impregnated activated carbon at wavelength 3278.28 cm\(^{-1}\) with the transmittance percentage of 64% while for the non-modified activated carbon, no presence of amide’s
peaks observed on the sample. This results were strengthen with the research carried out which discovered the presence of NH\textsubscript{2} surface groups at band 3365 cm\textsuperscript{-1}, described as amide region [11]. The presence of amide in impregnated activated carbon is linked with presence of nitrogen functional group in the amine solution [12]. Figure 3 shows the transmittance peak for modified activated carbon with different piperazine concentration. The lowest transmittance percentage indicates the highest piperazine concentration (10M) while the lowest concentration (2M) shows a very slight curve in transmittance peak at band 1541.28 cm\textsuperscript{-1}. The presence of several functional groups including –OH stretch and –NH stretch on commercial activated carbon has improved CO\textsubscript{2} binding process onto the surface of activated carbon [13]. From Figure 4, the mixture ratio parameter shows that the modified activated carbon with high piperazine ratio which is 1:2 forms a transmittance peak at band 3278.28 cm\textsuperscript{-1}. The lowest quantity of piperazine used which is 2:1 has almost no peak formed at the amide region.

![Figure 2. FTIR spectrum for non-impregnated activated carbon and impregnated activated carbon with piperazine.](image)

![Figure 3. FTIR spectrum of impregnated activated carbon with different concentration of piperazine.](image)
3.3. Brunauer, Emmett and Teller Analysis (BET)

Table 1 shows the summary of the surface area and pore volume of the non-modified activated carbon and impregnated activated carbon with 4M and 10M piperazine concentration. The BET total surface area of the non-impregnated activated carbon is 126.69 m$^2$/g. The result obtained is higher compared to the total surface area of the impregnated activated carbon with piperazine which is 6.77 m$^2$/g for 4M sample and 4.48 m$^2$/g for 10M sample. This suggested that the pores were blocked by the piperazine molecules and decreased the pore volume. The pore volume and surface area decreased because of the alkanolamine being filled inside the inner pores of activated carbon [14]. There was a large difference between the pore sizes of the non-impregnated activated carbon and impregnated activated carbon. The non-modified activated carbon has the highest pore size which is 0.081 cm$^3$/g while the impregnated activated carbon with 4M and 10M of piperazine has 0.015 cm$^3$/g and 0.0065 cm$^3$/g of pore volume respectively. High concentration of adsorbate tend to fill more pores on the adsorbent and resulting in narrow and small pore volume and surface area [15]. The surface area and pore volume become smaller with the increase of piperazine loading hence will increase the active sites for CO$_2$ bonding during CO$_2$ adsorption process. The modified adsorbent surface with piperazine has increased the capacity of CO$_2$ captured [16]. From the BET results, it can be concluding that the activated carbon impregnated with high concentration piperazine is a better adsorbent as the surface area and pore volume are the smallest, indicates that it has largest active sites for CO$_2$ adsorption.

| Adsorbing Bed                        | Surface Area (m$^2$/g) | Pore Volume (cm$^3$/g) |
|--------------------------------------|------------------------|------------------------|
| Non-modified activated carbon        | 126.69                 | 0.0810                 |
| Modified activated carbon with 4M piperazine | 6.77                   | 0.0150                 |
| Modified activated carbon with 10M piperazine | 4.48                   | 0.0065                 |

Figure 4. FTIR spectrum of piperazine impregnated activated carbon with different mixture ratio.
3.4. Field Emission Scanning Electron Microscopy (FESEM)

Figure 5 shows the surface morphology of non-impregnated activated carbon and impregnated activated carbon with piperazine at different concentration. At magnification of 60 times, a major difference can be seen in the pore size and surface structure of the macropores. The non-modified activated carbon has largest pore size while the impregnated activated carbon has a stacking of piperazine on its surface. Lower concentration piperazine impregnated activated carbon shows less stacking than higher concentration piperazine impregnated activated carbon. At 50,000 times magnification, there is slight difference in the surface morphology of the mesopores. A higher concentration of piperazine causes the coating on the activated carbon to be thickened. It also causes the increment in amount of piperazine loaded in the macropores which in agreement with the previous work stated that there was a formation of octahedral stack on the surface of activated carbon impregnated with amine [17].

Figure 6 shows the morphology for different mixture ratio of impregnated activated carbon with piperazine. Figure 6(A), (B) and (C) show the surface structure for magnification of 60 times while Figure 6(D), (E) and (F) show the morphology for magnification 50,000 times. At magnification of 60 times, the mixture ratio for activated carbon to piperazine which is 1:2 has the highest piperazine loading on its surface followed by ratio of 1:1 and 2:1. At magnification of 50,000 times, the mixture ratio of 1:2 activated carbon to piperazine has slightly more covered pores compared to the other two ratios. The mesopores for 1:2 ratio activated carbon to piperazine also shows a better attachment and coating compared to ratio of 1:1 and 2:1. Higher ratio of piperazine shows the increase of amide loading on the activated carbon surface as the carboxyl groups on the activated carbon surface reacts with amine groups present in piperazine to form surface of amide [18].
Figure 5. The FESEM images for (A) non-impregnated activated carbon, (B) 60 times magnification for 4M impregnated activated carbon with piperazine, (C) 60 times magnification for 10M impregnated activated carbon with piperazine, (D) 50,000 times magnification for 4M impregnated activated carbon with piperazine and (E) 50,000 times magnification for 10M impregnated activated carbon with piperazine.
Figure 6. The FESEM images for impregnated activated carbon with piperazine at (A) 60 times magnification at ratio 2:1, (B) 60 times magnification at ratio 1:1, (C) 60 times magnification at ratio 1:2, (D) 50,000 times magnification at ratio 2:1, (E) 50,000 times magnification at ratio 1:1 and (F) 50,000 times magnification at ratio 1:2.

4. Conclusions

Preparation of rice husk activated carbon impregnated with piperazine was successfully performed in this research. The effects of concentration and mixture ratio are investigated by using several analytical equipments which were XRD, FTIR, BET and FESEM. In XRD analysis, diffraction angle around 21.66° and 36.25° are linked for pyrazole in non-modified activated carbon sample while in piperazine modified sample, the polyethylene butane and silicon oxide are discovered at angle 21.86° and 21.89° respectively. For FTIR analysis, amide regions are detected for all impregnated activated carbon at band 3278.28 cm\(^{-1}\) while there is an absent of amide reagent on the non-modified activated carbon sample. The higher concentration and mixture ratio have a lower transmittance percentage compared to a lower concentration and mixture ratio of impregnated activated carbon. The BET results show that the non-modified activated carbon contains large surface area and pore volume than the modified activated carbon with piperazine. The lower concentration piperazine has a higher surface area and pore volume as there is less fillings inside the pores compared to high concentration piperazine. FESEM analysis shows that the morphology of non-impregnated activated carbon contains more pores compared to modified activated carbon with piperazine. The stacking of piperazine on the activated carbon surfaces increase with the increase of concentration and mixture ratio. With all the results obtained, we can now perform the testing on the adsorbent for CO\(_2\) capture experiment, which will be in our future work.
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