Development of carbon dioxide adsorbent from rice husk char

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Abstract. This study was mainly concerned about the development of carbon dioxide (CO\textsubscript{2}) adsorbent from rice husk (RH). Several chemical treatments were used to produce activated rice husk char (RHAC) from RH. Initially the RH was refluxed with 3M of sodium hydroxide (NaOH) solution, activation followed by using 0.5M of zinc chloride (ZnCl\textsubscript{2}) solution and finally acidic treatment by using 0.1M of hydrochloric acid (HCl). Then, the RHAC was functionalized by using 3-chloropropylamine hydrochloride (3-CPA) and noted as RHN. RHN samples were characterized with scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), fourier transform infrared spectroscopy (FTIR). Based on the SEM, the RHN sample had a large pore diameter compared to RH sample after being treated. Based on MIP data, the average pore diameter between RH and RHAC samples were increased significantly from 0.928 microns to 1.017 microns. The RHN sample also had higher total porosity (%) compared to RHAC and RH (58.45%, 47.82% and 45.57% respectively). The total specific surface area of the sample was much increasing from RHO to RHAC (29.17 m\textsuperscript{2}/g and 62.94 m\textsuperscript{2}/g respectively) and slightly being decreasing from RHAC to RHN (58.88 m\textsuperscript{2}/g). FTIR result showed the present of weak band at 1587 cm\textsuperscript{-1} which demonstrating of the amine group present on the sample. The CO\textsubscript{2} capture result showed that the decreasing of operating temperature can increase the breakthrough time of CO\textsubscript{2} capture. On the contrary decreasing of CO\textsubscript{2} gas flow rate can increase the breakthrough time of CO\textsubscript{2} capture. The highest total amount of CO\textsubscript{2} adsorbed was 25338.57 mg of CO\textsubscript{2}/g of RHN sample by using 100 mL/min of gas flow rate at 30 °C. Based on adsorption isotherm analysis, the Freundlich isotherm was the best isotherm to describe the CO\textsubscript{2} adsorption on the sample.

1. Introduction
Carbon dioxide (CO\textsubscript{2}) gas is one of the largest contributors for the increasing of the greenhouse level in the atmosphere about 60% of global warming effects. The international panel on climate change (IPCC) predicts that, by the year 2100, the atmosphere may contain up to 570 ppmv CO\textsubscript{2} which can increase the global temperature of around 1.9°C and can increase of mean sea level about 38 m [1].

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There are several methods which have been suggested to reduce the CO₂ emission into the atmosphere, to reduce energy intensity, to reduce carbon intensity and to enhance the sequestration of CO₂. The first method would require efficient use of energy, the second one requires switching to using of non-fossils fuels such as hydrogen and renewable energy and the third one would be the development of technologies to capture and sequester more CO₂ gas from the surrounding environment [1-4]. Based on the previous researchers, the carbon which has a pore size less than 1nm is very suitable for CO₂ capture under ambient conditions [5]. It has been also found that the activated carbons (AC) with impregnation of sterically hindered amines had enhanced the CO₂ adsorption performance [6].

According to Liou and Wu [7], there are two major methods to produce rice husk (RH) activated carbon (RHAC), the physical activation and chemical activation. The physical activation is getting involved the carbonization process on the sample by using a gaseous activating agent such as steam or CO₂. While, the chemical activation is getting involved the chemical agent such as phosphoric acid (H₃PO₄), Zinc chloride (ZnCl₂) or alkali hydroxides (NaOH and KOH) plus with heating treatment to activate the RHAC. The chemical activation is provided lower reaction temperature than the physical activation method [4, 8, 9]. The surface area of RHAC can be increased by removing the ash contents inside the rice husk (RH). It is important to remove the ash from RH because the previous researchers have been mentioned that the higher the ash content, the lower the N₂ surface area [7]. One of the methods to remove ash from RH is basic leaching process by using a high concentration of base such as NaOH and KOH to leach out the silica from the sample.

Generally, the developing countries around the world produce 500 million tons of rice annually. The rice milling produces about 20% of rice husk for the total weight of rice plants [4]. Its contains an abundance of lignocellulosic biomass and ash. RH also can provide good pore structure for a functionalization process to get better CO₂ adsorbent [10-13]. However, the proper method and pre-treatment are needed to get the better pore structure. By using RH as adsorbent in industry is hopefully can reduce the production of carbon dioxide from the mill; by integrating the RH adsorbent for CO₂ from the flue gas.

Thus, the aim of this study was to produce of adsorbent from rice husk char. The char was undergone three phases of treatment with different types of chemicals before it was continued with next functionalization method by using amine functional group.

2. Materials and methods

2.1 Materials

RH was collected from Seri Dusun Rice Mill, Kota kinabalu, Sabah, Malaysia. All the chemicals were supplied by Sigma Sdn Bhd., Malaysia. The RH undergoes several chemical treatments before being functionalized by using 3-chloropropylamine hydrochloride (3-CPA).

2.2 Preparation of functionalised AC

2.2.1 Base treatment

The RH was refluxed with 3M of sodium hydroxide (NaOH) solution at a ratio of 10ml of NaOH over 1 gm of RH char for 2 h. Then, the refluxed RH was being heated, stirred and washed by using distilled water till the washing solution was changed into a range of pH 8 to 9. After that, the washed RH was dried in oven at 105°C for 24 h.

2.2.2 Activation of RH

The activation of RH was done by using 0.5 M of zinc chloride (ZnCl₂) solution. Firstly, the RH and ZnCl₂ were mixed in a beaker in ratio of 1g of treated NaOH rice husk with 8 mL of 0.5 M of ZnCl₂ in the
form of mixture. Then, this mixture was mixed and stirred for 2 h in a beaker with a temperature range between 50°C to 60°C. Finally, the mixture was impregnated in oven at 105°C for 24 h.

2.2.3 Acidic treatment
The NaOH treated rice husk was refluxed with 0.1M hydrochloric acid (HCl) in ratio of 10 ml/g for 2h at a temperature of 100 °C. Then, the RH were stirred, heated and washed with distilled water until the pH of mixture solution change to pH 5 to 6. Lastly, the mixture solution was drained and the AC was dried in an oven at 105 °C for 24h.

2.2.4 Functionalization of sample
0.003M 3-chloropropylamine hydrochloride (3-CPA) and 0.02M of potassium hydroxide (KOH) was mixed in a ratio of 1:1 volume. A weight of 1g of the rice husk activated carbon (RHAC) was refluxed with 25 mL mixture of 3-chloropropylamine hydrochloride (3-CPA) and KOH for 6h at 40°C. Then, the solution was dried in an oven for 24h by using the impregnation method to functionalize the AC at temperature 105 °C. This functionalised AC was labelled as RHN.

2.3 Characterisations of functionalised AC

2.3.1 Scanning electron microscopy (SEM)
The surface morphology of the sample was determined by using SEM. The setting was chosen as follows; working distance (WD) was 6.0 mm, 6.5 mm and 7.0 mm and electron high tension (EHT) was 10 kV.

2.3.2 Mercury intrusion porosimetry (MIP)
The sample porosity and surface area were determined by using automated MIP model Pascal 440 series. The external pressure was applied to the sample to force the liquid into a pore against the opposing force of the liquid’s surface tension. The pressure was created by the intrusion of a non-wetting liquid such as mercury. Then, the chosen parameter value was inserted into Washburn’s equation to find the pore diameter (“Porosimetry,” 2013).

2.3.3 Fourier transform infrared spectroscopy (FTIR)
The determination of the sample’s functional group was determined by using FTIR and the model which was used is “Perkin Elmer Spectrum”. Before starting the analysis, the sample analysis was cleaned with acetone to ensure that no others impurities present during the analysis run. The scan ranges were from 650 cm⁻¹ to 4000 cm⁻¹ with a resolution of 4cm⁻¹. The result data was saved as an ASCII file and was plotted again by using Microsoft Excel.

2.4 CO₂ capture experimental setup
For CO₂ capture experiment, 7 gm of RHN sample were used for every set of experiment. So, there are 9 sets of CO₂ capture experiment. The parameters were used to capture of CO₂ shown in Table 1. Initially, the surrounding temperature was measured by using a thermometer which was used for CO₂ meter setting. After that, the N₂ gas was purged into setup until CO₂ meter showed a 300 ppm reading and started the CO₂ capture experiment. The CO₂ capture experiment was stopped immediately once the CO₂ concentration was achieved their saturated concentration based on the calibration data. Then, The CO₂ concentration value from the CO₂ meter was recorded. Figure 1 shows the schematic diagram for CO₂ capture experiment
Table 1. The parameters for CO\textsubscript{2} capture experiment

| Gas flow rate (mL/min) | Temperature (°C) | Pressure (atm) |
|------------------------|------------------|----------------|
| 100                    | 30               | 1              |
|                        | 60               |                |
|                        | 90               |                |
|                        | 30               |                |
| 150                    | 60               | 1              |
|                        | 90               |                |
|                        | 30               |                |
| 170                    | 60               | 1              |
|                        | 90               |                |

Figure 2. Schematic diagram for CO\textsubscript{2} capture experiment

2.5 Adsorption isotherms

Langmuir model is based on the assumption that adsorption energy is constant and independent of surface coverage where the adsorption occurs on localized sites with no interaction between adsorbate molecules and that maximum adsorption occurs when the surface is covered by a monolayer of adsorbate. The mathematical expressions of Langmuir equation can be written as follows,

\[
\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0 C_e}
\]  

(1)

where, C\textsubscript{e} = Equilibrium concentration (mg/L); q\textsubscript{e} = Amount adsorbed per unit mass (mg/g); Q\textsubscript{0} = Langmuir constant related to adsorption capacity (mg/g); K\textsubscript{L} = Langmuir constant related to rate of adsorption (L/mg)

In order to find the value of \( R^2 \), Q\textsubscript{0} and K\textsubscript{L} for the Langmuir isotherm for the adsorption of CO\textsubscript{2} on RHN samples, the graph of \( \frac{C_e}{q_e} \) against C\textsubscript{e} was plotted.

The Freundlich equation was calculated by using equation below,

\[
q_e = K_f C_e^{1/n}
\]  

(2)
\[
\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}
\]

where, \(K_f\) and \(n\) are the Freundlich constants with \(n\) as a measure of the deviation of the model from linearity of the adsorption and \(K_f\) indicates the adsorption capacity of the adsorbent. In order to find the value of \(R^2\), \(n\) and \(K_f\) for the Freundlich isotherm for the adsorption of CO\(_2\) on the RHN samples, the graph of \(\log q_e\) against \(\log C_e\) was needed was plotted.

Temkin isotherm assumes that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent-adsorbate interaction and the adsorption is characterized by a uniform distribution of binding energies. Temkin model is expressed as,

\[
q_e = \left( \frac{R T}{b} \right) \ln(A_T C_e) \tag{4}
\]

where \(\frac{R T}{b} = B\) (J/mol), is the Temkin cons’ant related to heat of sorption whereas \(A_T\) (1/g) is the equilibrium binding constant corresponding to the maximum binding energy. In order to find the value of \(R^2\), \(A_T\) and \(B\) for the Temkin isotherm for the adsorption of CO\(_2\) on RHN samples, the graph of \(q_e\) against \(\ln C_e\) was plotted.

3. Results and discussions

3.1 Surface morphology

Figure 2 shows the SEM images of samples at 1000x magnification: (a) RH (b) RHAC (c) RHN. Based on the manual calculation, the average pore diameter of RH sample was 9.1 microns, RHAC sample was 11.7 microns and RHN sample was 14.6 microns. The pore diameter of RH sample looks very small and likely has been clogging with some materials on the sample’s pore. The clogging material might be caused by ash and metal impurities which were also being reported by previous researchers. This problem can reduce the cumulative volume sample. The RH sample also consists of large particles which contribute to the decreasing surface area value on the MIP result. The RHAC sample consists of small particles after being treated with three chemical treatments. The increasing of surface area value has been proven by using MIP characterization method which had been done to support this result data. Based on manual calculation, the average pore diameter of RHAC sample is 11.7 microns. This result value is only applicable for the sample’s pore diameter, which can be seen through 1000x magnification. The largest pore diameter is 15 microns and the smallest is 1 microns. Based on the manual calculation, the average pore diameter of RHN sample is 14.6 microns. This result value is only applicable for the sample’s pore diameter, which can be seen through 1000x magnification. Based on the SEM image result, the largest pore diameter for RHN was 20 microns and the smallest was 1 micron.
3.2 Surface area and porosity

Table 2 shows the surface area, porosity and pore diameter of RH, RHAC and RHN samples.

| Sample | Total specific surface area (m²/g) | Average pore diameter (µm) | Total cumulative volume (mm³/g) | Total porosity (%) |
|--------|-----------------------------------|-----------------------------|-------------------------------|-------------------|
| RH     | 29.17                             | 0.928                       | 410.50                        | 45.57             |
| RHAC   | 62.94                             | 1.017                       | 983.00                        | 47.82             |
| RHN    | 58.88                             | 1.225                       | 988.50                        | 58.45             |

Based on Table 2, the total specific surface area of the sample was much increasing from RHO to RHAC and slightly being decreasing from RHAC to RHN. The decreasing of total surface area between
RHAC and RHN was a natural phenomenon which had been proven by Bhagiyalakshmi et al. [9]. The average pore diameter between RH and RHAC samples were increased significantly from 0.928 microns to 1.017 microns after being treated with several chemical treatments. The treatments could remove the metal and ash impurities on the sample especially on the basic and acidic chemical treatments. The result also shows the increasing of total cumulative volume of samples which corresponding to the increasing of sample’s pore diameter after being treated with several chemical treatments. The total porosity of samples also becomes increasing from RH to RHN. The functionalization of 3-CPA on the RH sample can increase its total porosity value which is much better than using basic and acidic treatment.

3.3 Functional groups

Figure 3 shows the FTIR spectra of RH, RHAC and RHN.

![Figure 3. The FTIR spectra of RH, RHAC and RHN](image)

Figure 3 shows the FTIR data between RH, RHAC and RHN. This data was used to determine of the presenting of the amine functional group on the RH sample by comparing the present of weak band between RHAC and RHN. The result shows the RHN’s demonstrate a weak band at 1587 cm\(^{-1}\) to represent of the presence of the amine functional group in RHN sample. The large band between 3300 and 3600 cm\(^{-1}\) was represented to the -OH stretching frequency of the silanol group in the inorganic framework due to formation of hydroxyl groups from the adsorbed water. The spectrum of RHN also showed the weak band at 3700 cm\(^{-1}\) which indicating as the presents of –OH group in on the sample. Then, the two stretches weak bands of RHN’s spectra at 2840 cm\(^{-1}\) and 2880 cm\(^{-1}\) was represented as the present of N-H stretching vibration. The peaks at 2370 cm\(^{-1}\) may be because of the existence of ammonium ions on the RHN sample. Probably, the amine group was attached to C instead of Si due to the presence of vibration peak at 1020 cm\(^{-1}\).

3.4 Amount of CO\(_2\) adsorbed

Table 4 shows the amount of CO\(_2\) adsorbed by using 100, 150 and 170 mL/min of flow rate

| Gas flow rate (mL/min) | Temperature (°C) | Amount of CO\(_2\) adsorbed (mg of CO\(_2\)/g of sample) | Breakthrough time to achieve saturated CO\(_2\) conc. (min) |
|-----------------------|------------------|----------------------------------------------------------|----------------------------------------------------------|
| 30                    | 25338.57         | 110                                                      |

Table 4. Amount of CO\(_2\) adsorbed by using 100, 150 and 170 mL/min of flow rate
Based on Table 4, the amount of CO₂ adsorbed was increased with the decreasing of the operating temperature of CO₂ capture. The breakthrough time of CO₂ capture also was increased with the decreasing of temperature by using 100, 150 and 170 mL/min of gas flow rate.

### 3.5 Adsorption isotherms

On the basis of the $R^2$ value, Freundlich isotherm seemed to represent the equilibrium adsorption data with better fit as compared to other isotherms. The reason is because the $R^2$ value for the Freundlich isotherm is higher than that of Langmuir and Temkin isotherms except for the CO₂ capture data which used 150 mL/min at 30°C operating temperature; the adsorption data was fit to Temkin isotherm model which has higher regression correlation value than others isotherm model. Most of the results show that the $\frac{1}{n}$ values of adsorption data were higher than one. These values represent a concave, curved upward, solvent affinity type isotherm, where the marginal sorption energy increases with increasing surface concentration. It can be interpreted also with strong adsorption of the solvent, strong intermolecular attraction within the adsorbent layers, penetration of the solute in the adsorbent, and mono-functional nature of the adsorbate. The value of $\frac{1}{n}$ represents a joint measure of both the relative magnitude and diversity of energies associated with a particular sorption process. A $\frac{1}{n} = 1$ indicates linear adsorption and, therefore, equal adsorption energies for all sites. Linear adsorption generally occurs at very low solute concentrations and low loading of the sorbent.

### 4. Conclusion

The RH with amine functionalized can adsorb high capacity of CO₂ with a suitable parameter chosen. The CO₂ adsorption capacity could be increased by the decreasing of the operating temperature in CO₂ capture experimental setup. On contrary, the decreasing of operating temperature can increase the total amount of CO₂ adsorbed. The highest total amount of CO₂ adsorbed was 25338.57 mg of CO₂/g of RHN sample by using 100 mL/min of gas flow rate at 30°C operating temperature. The breakthrough time of CO₂ capture also was increased with the decreasing of temperature. Based on SEM result obtained and being supported by BET result it could be concluded that the chemical treatments on the RH increases the average pore diameter, total specific surface area and porosity of sample. The Freundlich adsorption isotherm was the best isotherm to describe CO₂ adsorption on the adsorbent.

### References

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