Adsorption of Carbon Dioxide on Monoethanolamine (MEA)–Impregnated Kenaf Core Fiber by Pressure Swing Adsorption System (PSA)

Nabilah Zaini*, Khairul Sozana Nor Kamarudin

Faculty of Petroleum and Renewable Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

*Corresponding author: nabilahzaini88@gmail.com

Abstract

Emission of carbon dioxide (CO₂) becomes a major concern in combating issues of global warming. The strategy to reduce the concentration of CO₂ could be achieved by executing carbon capture and storage (CCS) technology such as adsorption. This study presents the used of MEA as a green source for CO₂ adsorption material. The modification of MEA on kenaf is a novelty work to enhance the capacity of adsorbent since MEA has been proved to have potential in separating CO₂ in industrial applications. In this work, 10 wt % of MEA has been impregnated on kenaf via wet impregnation method. The adsorption of CO₂ study was conducted by passing CO₂/N₂ mixture in a ratio of 30:70 in a Pressure Swing Adsorption (PSA) system with a pressure up to 1.5 bar at ambient temperature. Result obtained via SEM analysis shows that the morphology of kenaf was affected after modification with MEA. However, the presence of MEA on kenaf has improved the CO₂ adsorption capacity by 16 %. In addition, the adsorption equilibrium data for kenaf and MEA modified kenaf are well fitted in Freundlich isotherm model at low pressure and well fitted in Langmuir model at higher pressure. This study indicates that the introduction of MEA on kenaf could enhance the CO₂ adsorption process.

Keywords: Kenaf; modification; monoethanolamine (MEA); CO₂ adsorption; PSA system

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1.0 INTRODUCTION

Recently, global warming resulted from greenhouse gases has received a prime attention. Carbon dioxide (CO₂) has occupied more than 60 % of the total content of greenhouse gases that emitted in the atmosphere which induces to the global warming effects.1 As reported by Oh, the concentration of CO₂ in the atmosphere has reached up to 400 ppm which is significantly higher from a record that has been reported during pre–industrial era of about 300 ppm.2 Based on this fact, efforts to reduce the concentration of CO₂ emitted to the atmosphere should be implemented actively and vigorously. Therefore, one of the strategies to reduce the concentration of CO₂ that emitted to the atmosphere is by executing carbon capture and storage (CCS) method. The CCS that has been established in Malaysia since the Intergovernmental Panel on Climate Change (IPCC) in 2007 predicted that the average global surface temperature will rise up to 2°C between 1990 and 2100. Thus, CCS project is seen as a key technology that assists Malaysia in achieving its goal to cope with the global demand in reducing the carbon emission by 40 % in 2020 based on 2005 levels.3 The CCS technologies involved are liquid absorption,4–7 solid adsorption,8–10 cryogenic techniques11 and selective diffusion through polymer, ceramic or metallic membranes.12

It has been reported that among the CCS technologies, the sequestration of CO₂ from coal–fired power plant by using amine–based liquid absorption is the dominant technology by 2030.7,13 However, this existing technology possess several drawbacks where it requires a large absorber volume, low contact area between gas and liquid, low CO₂ loading, high energy consumption for regeneration, amine degradation and high equipment corrosion rate.14–15 Therefore, solid adsorption process has been proposed to surmount those inherent problems involving chemical absorption process since it has low energy consumption, low equipment cost, can avoid corrosion problem and ease of applicability over a relatively wide range of temperature and pressure.16–18 To improve this technology, the most important consideration is the development of a low cost adsorbent with high selectivity and high capacity of CO₂. A good adsorbent should have low–cost raw material, low heat capacity, fast adsorption/desorption kinetics, high CO₂ adsorption/desorption capacity, high selectivity towards CO₂ at high and moderate temperature, high thermal, chemical and mechanical stabilities under extensive cycle and selective at elevated temperature.19–22 A variety of adsorbents have been proposed by considering their structures and compositions as well
as adsorption and regeneration mechanisms. Currently, the selection of a green–based material as solid adsorbent is seen as an attractive method to replicate the development of the existing adsorbent technology based on its high availability, inexpensive and environmental–friendly material.

Kenaf (Hibiscus Cannabinus L.) that belongs to the family of Malvaceae and originated from western Africa is the third–world crop after wood and bamboo. This plant was introduced in Kedah, Malaysia since 2006 to replace tobacco crop which has unstable demanding and less profitable to the country. According to National Kenaf and Tobacco Board (LKTN) officer, kenaf is an environmental–friendly industrial organic material that has been recognized by Kyoto Protocol that has the ability to combat global warming issues. Since kenaf is available in Malaysia abundantly and it has fast growth rate (requires less than six months to attain a suitable size for commercial purposes), it can be used as a green–based adsorbent.

Kennaf is divided into inner layer part known as core fiber that consist of a soft and short fiber and outer fibrous bark enveloping the core named as bast fiber that consists of a long fiber. Present study focused on kenaf core that has a porous structure. Previous work conducted by Othman and Akil converted the raw kenaf core into activated carbon for capturing CO₂. Recent works also show that adsorption capacity and selectivity of CO₂ can be improved by two approaches, enhancing surface area and porous structure of the adsorbent and increasing alkalinity of the adsorbent by chemical impregnation on the surface. The impregnation of alkanolamines on various adsorbents has been widely used since it has low energy consumption for regeneration. It is important to develop a cheaper adsorbent for the separation of CO₂ from a mixture of CO₂/N₂. Therefore, this present work concentrates on kenaf as adsorbent that can effectively separate CO₂ from a mixture of CO₂/N₂. The novel adsorbent obtained by impregnating a primary alkanolamine (monoethanolamine, MEA) on kenaf surface in order to improve its adsorptive properties prior to the adsorption and regeneration study of CO₂ in pressure swing adsorption (PSA) system. PSA has been used to conduct the adsorption study of CO₂ using kenaf adsorbent.

2.0 MATERIALS AND METHODS

2.1 Preparation of the Sample

The kenaf chips of the size of 3–6 mm were obtained from National Kenaf and Tobacco Board (LKTN) Kelantan. The kenaf chips were ground and sieved into the particle size of 300 μm prior to cleaning in order to remove all the adherent extraneous impurities. After that, the cleaned kenaf sample was air–dried overnight to remove the moisture before stored in the container for further treatment.

2.2 Amine–Impregnation Method

The impregnation of amine on kenaf core as a support material was carried out through conventional method that widely known as wet impregnation method. In this study, the chemical used is monoethanolamine (MEA) with purity of 99.7 %. Initially, the kenaf core material was wetted in methanol in a solid to liquid ratio of 1 : 20 for a period of 15 minutes in two stages to accelerate the loading of MEA on sorbent. The wetting procedure was conducted at room temperature prior to be air–dried overnight. For impregnation procedure, MEA with a concentration of 10 wt % was prepared in methanol solvent and the solution was stirred for 15 minutes in order to produce an alcoholic amine solution. Then, the dried kenaf core sample were mixed with alcoholic amine solution for 15 minutes and agitated for 4 hours at room temperature. Finally, the solution was decanted and the MEA–impregnated kenaf core was allowed to air–dried overnight. Methanol is used in preparing the amine solution because it can easily vapourise at room temperature. Therefore, the loading of MEA on kenaf sorbent can be achieved in shorter period of time.

2.3 Physical Characterization Analysis

A surface characterization was carried out by using Scanning Electron Microscopy (SEM) analyzer (Philips XL–40). The physical characterization analysis is the fundamental knowledge that facilitates the understanding of the adsorbent structure for gas adsorption and regeneration process. In the current study, the physical characterization analysis has been conducted through the image of surface texture and morphology for raw kenaf and MEA–impregnated kenaf.

2.4 Adsorption Equilibrium Study

Adsorption equilibrium study was carried out to determine the amount of species adsorbed at a given condition. The initial study focused on the adsorption isotherms measurement to study the adsorption characteristics of raw kenaf and amine–impregnated kenaf at constant temperature. In this study, the CO₂ equilibrium adsorption isotherms for raw kenaf and MEA–impregnated kenaf were carried out at 0°C, 25°C and 50°C in a pressure range of 5–760 mmHg by using a static volumetric adsorption system (Micromeritics, Model ASAP 2020). Prior to the analysis, the sample was degassed at 90°C for an hour followed by 150°C for 12 hours. Then, the CO₂ analysis was conducted and water circulating bath was used to control the temperatures. The amount of CO₂ adsorbed was expressed in term of volume adsorbate (cm³) per unit adsorbent mass (g). Then, the amount of CO₂ adsorbed (cm³/g) at elevated absolute pressure (mmHg) for each constant temperature (0°C, 25°C and 50°C) was plotted and further analyzed by using two adsorption equilibrium isotherm models, Langmuir and Freundlich model.

2.4.1 Langmuir Adsorption Isotherm

Langmuir adsorption isotherm is often applied in the processes of monolayer adsorption to describe the adsorption of gas molecules onto adsorbent surface. The model assumes that intermolecular forces decrease rapidly with distance and predicts the presence of adsorbate monolayer coverage at the outer surface of the adsorbent. The adsorption process for this isotherm equation takes place at specific homogeneous sites within the adsorbent. It means that once CO₂ molecule occupies a site, no further adsorption occurs at the site and at this stage, it is saturated. Theoretically, the adsorbent has a finite capacity for the adsorbate. The Langmuir equation is represented for the structurally homogeneous adsorbent in which all sorption sites are identical and energetically equivalent. The saturated adsorbent (Ct → ∞) can be represented as:

\[ Q_e = \frac{(Q_m K_1 P)}{(1 + K_1 P)} \quad (1) \]

P is an absolute pressure (kPa), Qₑ is the amount of gas adsorbed (cm³/g), Qₑ is Qₑ for a complete monolayer (cm³/g), K₁ is adsorption equilibrium constant. To determine the adsorption capacity for a particular range of absorbate pressure, the aforementioned Equation (1) can be used as a linear form as follows:

\[ \frac{P}{Q_e} = \frac{1}{Q_m P} + \frac{1}{(K_1 Q_m)} \quad (2) \]
The constants \( Q_e \) and \( K_f \) can be identified from a linearized form of Equation (2) by the gradient and \( y \)-intercept of the linear plot of \( P/Q_e \) versus \( P \), respectively.\(^{34,35}\)

### 2.4.2 Freundlich Adsorption Isotherm

Freundlich adsorption isotherm is an exponential equation that describes the adsorption equilibrium, based on the adsorption on heterogeneous surface. Theoretically, this model expresses for an infinite amount of adsorption.\(^{36}\)

\[
Q = K_f P^{1/n} \tag{3}
\]

\( P \) is an absolute pressure (kPa), \( Q \) is the amount of gas adsorbed (cm\(^3\)/g), \( K_f \) and \( 1/n \) are empirical constants, indicating the adsorption capacity and adsorption intensity, respectively. Equation (3) may be converted to a linear form by taking logarithms:

\[
\log Q_e = \log K_f + \frac{1}{n} \log P \tag{4}
\]

The plot of \( \log Q_e \) versus \( \log P \) for Equation (4) should result in a straight line. The values of \( n \) and \( K_f \) can be obtained from the gradient and \( y \)-intercept of the plotted graph, respectively.\(^{35}\) The favourable adsorption condition is achieved if the value of exponent \( n \) is greater than 1.\(^{37}\)

### 2.5 \( \text{CO}_2 \) Adsorption and Regeneration Study

The \( \text{CO}_2 \) adsorption and regeneration study was carried out in a single adsorption column of pressure swing adsorption (PSA) system. The principle of PSA process is to adsorb gas at high pressure and to regenerate the saturated adsorbent at low pressure.\(^{38}\) In this study, a column with a dimension of 15 cm height and 1 cm of diameter was used. The feed gases have composition of 30 v/v \% \( \text{CO}_2 \) and 70 v/v \% \( \text{N}_2 \) and were supplied by Mega Mount Industrial Gases Sdn Bhd. A schematic diagram of single–column PSA system is shown in Figure 1.

![Schematic diagram of single–column PSA system](image)

**Figure 1** Schematic diagram of single–column PSA system

In the adsorption process, the gas mixture of \( \text{CO}_2/\text{N}_2 \) with composition of 30/70 and a total flow rate of 300 cm\(^3\)/min were passed through the column containing adsorbent bed and were pressurized up to 1.5 bar. The adsorption process was allowed to take place for 5 minutes. A faster diffusion rate species were adsorbed on the adsorbent in the column. After 5 minutes, the gases that have slower diffusion rate were injected to the gas chromatography analyzer (Agilent Technologies 7820A GC) and the concentrations of the exit gases were analyzed. This process completes the half cycle operation. Another half cycle operation was completed by regenerating the saturated adsorbent by using high purity grade (99.999 \%) nitrogen gas. To carry out this step, pure nitrogen was passed through the saturated column to remove gases that trapped on the adsorbent bed. Then, the GC was switched on to analyze the concentration of the exit gases.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Physical Characterization Analysis

The scanning electron microscope (SEM) has been used to analyze the morphology of the structures and provides an image of the macrostructure of kenaf. Figure 2 (a) and (b) show the cross–sections of the raw kenaf fiber and MEA–impregnated kenaf at 1000 magnification, respectively.

From these cross–section images, the raw kenaf Figure 2 (a) has a rigid open cylindrical pore of honeycomb shape with irregular trend. However, the impregnation of MEA on kenaf yields highly heterogeneous pores of honeycomb shape structures (Figure 2 (b)). The channels exhibit different morphological trend and form a rough and perforated surface due to amine impregnation procedure. However, the presence of these open cylindrical and heterogeneous pores provide sites for adsorbates (\( \text{CO}_2 \)) to be trapped and adsorbed on kenaf surface.\(^{31}\) Moreover, the impregnation of MEA on kenaf provides an active adsorption sites that facilitate the formation of covalent bonding between the surface and \( \text{CO}_2 \) molecules.

Hence, it increases the adsorption of \( \text{CO}_2 \) on kenaf adsorbent. The morphological changes observed after the impregnation of MEA on kenaf suggests that the impregnation process has a significant effect to its cylindrical surface channels.

![Scanning electron microscopy of cross–section of kenaf fiber at 1000 magnification](image)

**Figure 2** Scanning electron microscopy of cross–section of kenaf fiber at 1000 magnification (a) before treatment (b) after impregnated by 10 wt % of MEA.
3.2 Adsorption Equilibrium Study

Adsorption equilibrium study provides a fundamental physicochemical data for measuring the applicability of the sorption process. The adsorption isotherm describes the interaction of adsorbates with adsorbent. The correlation of equilibrium data either by theoretical or empirical equation is necessary to the practical design as well as to the adsorption system operation. In the present study, the adsorption isotherm of adsorbate molecules (CO₂) on raw kenaf and 10 wt % MEA–impregnated kenaf were plotted by the Langmuir and the Freundlich isotherm models at three different temperatures (0°C, 25°C and 50°C). The constants of these equations are tabulated in Table 1. Then, the equilibrium data of CO₂ adsorption were plotted and compared with Langmuir and Freundlich equations (Figure 3). The most appropriate model is based on the values of the correlation coefficient (R²).

Based on Table 1 and Figure 3, Freundlich isotherm model fitted well with the experimental data up to the relative pressure of 0.6, whilst Langmuir isotherm is fitted the experimental data at a relative pressure greater than 0.6. It is suggested that the adsorption mechanism at P/P₀ up to 0.6 occurs on the surface heterogeneity of the prepared kenaf adsorbent. Meanwhile, at P/P₀ pressure greater than 0.6, a monolayer adsorption of CO₂ onto the homogeneous surface of kenaf adsorbent occurred. Adsorption of CO₂ adsorbate has equal activation energy for the binding sites. Moreover, the separation factor (K_L) is less than 1, indicating that the adsorption of CO₂ onto raw kenaf and MEA–impregnated kenaf is favourable. Besides, the magnitude of Freundlich adsorption capacity (n) gives an indication of adsorption favourability since all values are greater than 1. Thus, it suggests that the adsorption forces of CO₂ exerting on the surface of kenaf adsorbent are stronger. Consequently, it was inferred that the adsorption of equilibrium data for raw kenaf and MEA–impregnated kenaf are well represented by Freundlich and Langmuir isotherm models.

**Table 1** Langmuir and Freundlich model constants and correlation coefficients for adsorption of CO₂ on raw kenaf and 10 wt % MEA–impregnated kenaf

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Sample</th>
<th>T (°C)</th>
<th>Parameters</th>
<th>Parameters</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Q_max</td>
<td>K_L</td>
<td></td>
</tr>
<tr>
<td>Langmuir</td>
<td>Raw kenaf</td>
<td>0</td>
<td>9.346</td>
<td>7.576</td>
<td>0.022</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>50</td>
<td>0.011</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>7.752</td>
<td>0.004</td>
<td>0.004</td>
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<tr>
<td></td>
<td>10 wt % MEA–impregnated kenaf</td>
<td>0</td>
<td>7.874</td>
<td>6.289</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>50</td>
<td>0.012</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>6.803</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Freundlich</td>
<td>Raw kenaf</td>
<td>0</td>
<td>1.471</td>
<td>1.233</td>
<td>0.319</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>50</td>
<td>1.089</td>
<td>0.036</td>
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<td></td>
<td></td>
<td>50</td>
<td>1.233</td>
<td>1.263</td>
<td>0.122</td>
</tr>
<tr>
<td></td>
<td>10 wt % MEA–impregnated kenaf</td>
<td>0</td>
<td>1.233</td>
<td>1.263</td>
<td>0.122</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>50</td>
<td>1.089</td>
<td>0.036</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>1.263</td>
<td>1.075</td>
<td>0.098</td>
</tr>
</tbody>
</table>

![Figure 3](image_url) Experimental, Langmuir and Freundlich equilibrium isotherm models for CO₂ adsorption on raw kenaf and 10 wt% MEA kenaf at temperature of 0°C, 25°C and 50°C
3.3 CO₂ Adsorption and Regeneration Study

CO₂ adsorption and regeneration study was conducted in a pressure swing adsorption (PSA) system at pressure of 1.5 bar. The gas mixture of CO₂/N₂ was passed through the adsorbent bed containing a raw kenaf sample. Similar procedure was repeated for 10 wt % MEA–impregnated kenaf sample. The results obtained are presented in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO₂ adsorption (%)</th>
<th>g CO₂ adsorbed / g adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw kenaf</td>
<td>9.560</td>
<td>0.007</td>
</tr>
<tr>
<td>10 wt % MEA–impregnated kenaf</td>
<td>11.090</td>
<td>0.009</td>
</tr>
</tbody>
</table>

According to the results tabulated in Table 2, the raw kenaf without having amine–impregnation process could adsorb up to 9.560 % of CO₂ or 0.007 g CO₂ adsorbed per 1 g of adsorbent. The result indicates that the raw kenaf has a capability in capturing CO₂ since it is a porous structure with large pore diameter (in range of 20 to 40 µm) as shown in Figure 2 (a). The presence of porous structure with different sizes and open cylindrical channels may allow the adsorbates (CO₂) to penetrate easily and trap and adsorb on the adsorbent surface.²¹,²⁰

After kenaf has been impregnated with 10 wt % of MEA, the percentage of CO₂ adsorption has slightly increased to 11.090 % or 0.009 g CO₂ adsorbed per g of adsorbent. This result shows that the presence of primary amine (MEA) on the adsorbent surface has improved the CO₂ adsorption capacity of kenaf by 16 %. The reaction of MEA with CO₂ is presented in the Equation (5) below.⁴¹

\[ R\text{NH}_2 + \text{CO}_2 \rightarrow R\text{H}_2\text{OHHNCOO}^- + \text{H}^+ \] (5)

MEA is represented by R₁NH₂ where R₁ = CH₃OH. The presence of MEA on the adsorbent surface provides additional basic active sites to interact with acidic CO₂ molecules through the formation of covalent bonding. This study clearly proves that the impregnation of MEA on large porous structure could improve the interaction between adsorbent and the adsorbate molecules; thus enhancing the adsorbent capacity. Yu and co-workers also reported that the use of adsorbent with large pore size as a support material for amine–impregnation process enhanced the adsorption capacity.³ Similar result was also obtained in this study where the amount of CO₂ adsorbed on MEA–impregnated kenaf is relatively higher than the raw kenaf.

Two consecutive cycles of adsorption have been done to observe the regenerating performance of kenaf. During the regeneration process, the adsorbed gases on kenaf adsorbent were removed by passing the adsorbent bed with pure nitrogen at atmospheric pressure. A comparison was carried out between the performance of raw kenaf and MEA–impregnated kenaf. Figure 4 shows that the adsorption capacity of kenaf adsorbent in capturing CO₂ adsorbate molecules has reduced after second cycle of adsorption.

The percentage of CO₂ adsorption for raw kenaf showed an abrupt reduction (34.91 %) after second cycle; whilst the percentage of CO₂ adsorption for MEA–impregnated kenaf at second cycle only shows 2.41 % reduction. The significant differences between both samples are due to the presence of amine (MEA) on kenaf surface. The presence of amine (MEA) could maintain the adsorption capacity of kenaf in cyclic operation. This study suggested that amine impregnation on kenaf not only influence the adsorbent–adsorbates interaction, but it may also contribute to the cyclic operation of the adsorption and desorption process.

4.0 CONCLUSION

This study reveals that the adsorption of CO₂ on kenaf increases in the presence of MEA. The presence of MEA improved the CO₂ adsorption capacity of kenaf by 16 % as compared to the raw kenaf in PSA system. At P/Po less than 0.6, the adsorption equilibrium data for raw kenaf and MEA–impregnated kenaf is well fitted by Freundlich isotherm model but P/Po higher than 0.6, it is best described by Langmuir isotherm model. It can be inferred that the presence of amine (MEA) could maintain the adsorption capacity of kenaf in cyclic operation. The future work will involves the effect of amine concentration and the operating pressure of PSA system on CO₂ separation using kenaf.

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