Surface Physicochemical Modification of Kenaf Adsorbent for Hydrogen Adsorption Study

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Abstract. In supporting the industrial kenaf plan developed by Malaysian government, this research has extended the use of kenaf as a sorbent to investigate its reliability for hydrogen adsorption system. In satisfying the objective, the effect of impregnation time and the effect of nickel nitrate concentration on hydrogen adsorption has been studied. In addition, to study the adsorption and desorption capability of the modified kenaf on hydrogen adsorption, the regeneration study was also accounted. The kenaf core with the range of particle size in between 300-500μm has been modified through the physicochemical modification by experiencing the carbonization and activation process prior to be impregnated in nickel nitrate solution (Ni(NO₃)₂). The morphological and elemental studies on the modified-kenaf sorbent have been done with the helped of Variable Pressure Scanning Electron Microscopy (VPSEM) and Energy Dispersive X-Ray (EDX) analyser, respectively. The hydrogen adsorption using the hydrogen adsorption system was controlled at the pressure of 5 bar. The results show that the modified-kenaf sorbent able to improve the hydrogen adsorption as compared to the unmodified-kenaf sorbent. Based on the morphological analysis, the modified-kenaf sorbent contain more micropores compares to the unmodified-kenaf sorbent which help in the adsorption capacity. Besides, the modified-kenaf sorbent has potential to be reused with minimum pressure drop of only 0.207 and 0.109 bar up to second regeneration cycles. This study has revealed that the modified-kenaf material has high capability to be used as hydrogen adsorbent and can be competitive technology over the existing current hydrogen storage technology.

1. Introduction
Hydrogen is light weight, renewable and can be store at a certain condition, clean with no toxic as it only produces water vapor after combustion [1]. Hydrogen can also be used in many applications or as alternative energy with zero-carbon that helps in generating electricity hence helps in sustaining current fossil fuels as it can be synthesized from many raw materials such as biomass and water [2, 8]. Therefore, the techniques for hydrogen storage needs to be further explored so that hydrogen energy can be implemented. The current techniques for hydrogen storage are pressurized gaseous, liquid hydrogen, metal hydride, and adsorption. Pressurized gaseous technique requires a tank that could withstand a high pressure of 2800 m³.N of forces, liquid hydrogen requires high energy to liquify the hydrogen and metal hydride could produce toxic [1].
The hydrogen storage by adsorption technique is always being investigated by many researchers because this technique shows high potential to be applied for storing hydrogen [3]. The exploration of adsorption for hydrogen storage technique is continuously investigating to enhance its practicality and usability for commercial applications. Most of attention was given on the enhancement of the interaction between hydrogen to the solid surfaces. The hydrogen atom interacts with each other by the hydrogen bonds, while the hydrogen adsorption by the adsorbent surface involves with the van der Waals interactions [4].

To accomplish the effectiveness of hydrogen adsorption, the adsorbent with high micropores is needed to enable the hydrogen adsorbed with maximum capacity and the adsorption capacity has a relation with pressure and temperature [5]. The adsorbent that can be used for hydrogen storage material can be categorized into three types which are organic type, inorganic type, and polymer type. Organic type adsorbent commonly came from plant waste and is relatively low cost abundant and have the potential to enhance the adsorption characteristic by modification [6].

In these studies, organic type adsorbent which is kenaf core is selected the adsorbent to adsorb the hydrogen gas. Kenaf core is classified as organic type adsorbent and is an abundant waste where 35-40% of kenaf is consist of bast fiber and other 60-65% is the kenaf core [7]. It was encouraged to utilize the kenaf as a value-added product by the government.

2. Experimental
2.1. Materials and Chemicals
The raw kenaf core has been purchased from the National Kenaf and Tobacco Board (NKTB) that located in Kelantan in the rough chips form. The kenaf core chips were grounded and sieved to the size in range of 300-500μm prior to be physically carbonized and activated under physical modification. The nickel nitrate hexahydrate, Ni(NO₃)₂·6H₂O brand Loba Chemie with molecular weight of 290.80 g/mol was obtained from VNK Supply & services.

2.2. Pre-Preparation Procedure
2.3. Kenaf core chip was grounded into small particle size and sieved to the size in range of 300-500μm by sieving process. The sieved kenaf core was dried in the oven at the condition of 70ºC for 24 hours to remove the extra moisture contents of the kenaf core. After drying process, the kenaf core was cleansed by using formaldehyde (HCHO) with 37% solution to reduce the metal precursor in kenaf dispersion. Finally, sodium hydroxide (NaOH), formaldehyde (HCHO), and ethanol (C₂H₆O) were mixed and stirred for 4 hours prior to be filtered and dried at room temperature.

2.4. Physical and Chemical Modification Procedure
The physical modification of kenaf (size range: 300-500μm) was executed by activate it with KOH solution. The activated carbon kenaf core sample was immersed to nickel nitrate solution via wetting impregnation method to create active sites that lead to the enhancement of the adsorption capacity. The wetting impregnation procedure was carried out by varying the time for the impregnation and the concentration of nickel nitrate. All the prepared samples were stirred using a magnetic stirrer for 15 minutes at 1000 rpm.

2.5. Carbonization Preparation
Raw kenaf core sample was placed in the furnace before it was closed tightly. The airflow rate into the furnace was set to be at 1 L/min and the pressure of the nitrogen has that was purged into the furnace was set to be at 2 bars. The temperature of the reactor was set to be at 700ºC. After the temperature reached 700ºC, the furnace was turned off and the sample was let cooled.

2.6. Activated Carbon Preparation
The activated carbon preparation was prepared by switching the nitrogen gas to the CO₂ gas after the temperature of furnace reached at 700ºC before it maintained for the next 2 hours. After 2 hours, the
CO₂ gas channel was switched back to N₂ gas and the furnace was turned-off for cooling process. The N₂ gas was let to be purged in 4 hours then. Finally, the sample was placed in a container for the adsorption study.

2.7. Manipulation of Impregnation Time.
0.4M of Ni(NO₃)₂ was prepared and be poured into 6 beakers and labelled with TK-01, T02, TK-03, TK-04, TK-05, and TK-06 where TK stand for Treated Kenaf. To study further about the effect of impregnation time, 6.5g of cleansed kenaf core was weighed and be immersed into labelled beakers containing the solution prior to be stirred by using a magnetic stirrer at 1500 rpm for 15 minutes. Table 1 lists impregnation time used for each label.

| LABEL   | TIME OF IMPREGNATION (HOURS) |
|---------|-----------------------------|
| TK-01  | 0.5                         |
| TK-02  | 01                          |
| TK-03  | 3                           |
| TK-04  | 5                           |
| TK-05  | 7                           |
| TK-06  | 24                          |

After achieving the desired time of impregnation, the sample was filtered using vacuum filtration technique to separate the sample and solution. The filtrated sample then was dried in the oven at 70°C for 5 hours to remove any excess moisture contain in the sample. After dried, the samples were placed in a labelled container for the adsorption process.

2.8. Manipulation of Ni(NO₃)₂ concentration.
The Ni(NO₃)₂.6H₂O crystal was diluted into 1M concentration with volume 250 ml before impregnating it into kenaf core. The solution was stirred using a magnetic stirrer for 15 minutes at 1000 rpm. Eq. 2.1 was used to calculate the desired concentration from the 1M concentration of Ni(NO₃)₂ solution.

\[ C_1V_1 = C_2V_2 \] (Eq. 2.1)

The prepared 1M Ni(NO₃)₂ solution was diluted into the desired concentration and poured into a beaker that was labelled with MK-Ni01, MK-Ni-02, MK-Ni03, MK-Ni04 and MK-Ni05 where MK- Ni stands for Modified Kenaf with Nickel. The concentration of each beaker was controlled as shown in Table 2.

| LABEL     | CONCENTRATION (M) |
|-----------|-------------------|
| MK-Ni01   | 0.003             |
| MK-Ni02   | 0.1               |
| MK-Ni03   | 0.25              |
| MK-Ni04   | 0.4               |
| MK-Ni05   | 0.65              |

The cleansed kenaf were weighted to 6.5g and were placed inside the beaker with Ni(NO₃)₂ solution. Then, it was stirred using a magnetic stirrer at 1500 rpm for 15 minutes. The samples were let immersed according to the time selected from impregnation time studies.
After achieving the time of impregnation, the sample was filtered using vacuum filtration system to separate the sample and solution. The filtrated sample then was dried in the oven at 70°C for 5 hours to remove any excess moisture contain in the sample. After dried, the samples were placed in a labelled container for the adsorption process.

2.9. Sample Characteristics Procedure
The characteristics of the raw kenaf core and nickel nitrate modified-kenaf core sample was determined using Thermogravimetric Analysis (TGA), Energy Dispersive X-ray (EDX), and Variable Pressure Scanning Electron Microscopy (VPSEM). Table 3.3 describes the selected structural and morphological characterization analysis used in this study.

2.10. Hydrogen Adsorption Study
The adsorption process using solid material need proper and efficient adsorbent surface characteristic. A large surface area was needed for high adsorption process. For this study, Hydrogen Gas Adsorption System will be used to interpret the data. The system flow diagram was shown in Figure 1. The hydrogen adsorption system was designed for laboratory scale to measure the amount of hydrogen adsorbed by the modified kenaf. An inert gas that was nitrogen gas was purged to the system before running the experiment to test the leakage along the line of system. Digital pressure gauge was used to observe any small changes inside the reactor during the adsorption process. The reactor lid was covered with a piece of rubber and wire gauze in between the cover and the reactor to ensure that the reactor was in air-tight condition, pressure-resistant, and preventing the kenaf sample from spreading throughout the system during the experimental work. The hydrogen storage reactor is shown in Figure 1.

![Figure 1. Hydrogen adsorption system.](image)

The hydrogen adsorption system was designed for laboratory scale to measure the amount of hydrogen adsorbed by the modified kenaf. An inert nitrogen gas was purged to the system before running the experiment to test the leakage along the line of system. Digital pressure gauge was used to observe any small changes inside the reactor during the adsorption process. The reactor lid was covered with a piece of rubber and wire gauze in between the cover and the reactor to ensure that the reactor was in airtight condition, pressure-resistant, and preventing the kenaf sample from spreading throughout the system during the experimental work. At first, valves V01, V02, V03, V06, V07, V09, V10 and V13...
were opened. Then, the hydrogen cylinder regulator (GR01) need to be opened until it reaches the required pressure which was 5 bar. The hydrogen was fill up the reservoir before being flow to the reactor. The reactor cap was opened, and the sample was poured inside the reactor. The reactor’s cap was placed on the reactor to close the reactor. The bolts were placed inside the holes on the reactor’s cap and was tightened to prevent any leakage during the adsorption process as shown in Figure 1. Then, V13 was opened.

3. Main Results

The capacity of hydrogen that was adsorbed into the kenaf was calculated by determining the pressure drop between the initial pressure at 5 bar range and the pressure was the pressure started to constant. Then, the pressure drop of each sample was compared where the higher the pressure drop, the higher the capacity of hydrogen was adsorbed.

3.1. Effect of Nickle Concentration

Using 5 hours of impregnation time as it has better adsorption based on the effect of impregnation time studies, different concentration of nickel was studied for the adsorption capability. In this study, the size range of the Modified Kenaf with Nickel was 300-500μm and the pressure of the reactor is set up to 5 bar. The results were tabulated, and Figure 2 is the graph plotted to compare the adsorption capacity.

![Graph showing effect of nickel concentration](image)

**Figure 2. Effect of nickel concentration**

From Figure 2, initially the pressure was at 0 ~ 0.002 bar and as the hydrogen gas was filling up the reactor, the pressure increased. At 5bar, the valve was closed, and no hydrogen is filling up the reactor. The pressure started to drop as the hydrogen was being adsorbed into the kenaf’s pore. It is shown that MK-Ni04 has a greater pressure drop compared to other which the value was 0.098 bar. The pressure drops for MK-Ni01, MK-Ni02, and MK-Ni05 is 0.004 bar, 0.015 bar, and 0.015 bar respectively. While MK-Ni03 is the second-highest pressure drop value, which is 0.018 bar. This shows that MK-Ni04 adsorbed more hydrogen gas compared to the other. This is because MK-Ni04 has a greater attraction toward hydrogen.

3.2. Effect of Impregnation Time

For this study, the adsorption study was done to determine the adsorption capacity of each sample using the size range 300 - 500μm with rig pressure up to 5 bar. The
results were tabulated, and the graph was plotted in Figure 3.

![Pressure vs. Time Graph](image)

**Figure 3.** Effect of impregnation time

From Figure 3, the graph plotted shows that the pressure increased in the early experiment. This is due to the hydrogen was being supplied to the reactor and it started to decline after it reached range 5 bar. As for TK02 and TK05, the graph shows that the pressure increased, then started to decline before it reached 5 bar and started to increase back to 5 bar. This is due to the valve that was not be fully open thus slowed down the gas to enter the reactor. The decline graph shows that the hydrogen has started to occupy the pore on the kenaf’s surface.

TK05 has the highest pressure drop compared to others with a value of 0.020 bar differences. While TK01, TK02, TK03, TK04, and TK06 shares the same value which is 0.016 bar. The time for TK05 which is 5 hours was the ideal time for impregnation time.

3.3. Adsorption and Desorption. The sample used in this study was modified kenaf with nickel with a concentration of 0.4M (MK-Ni04), carbonized treated kenaf (CTK04), and activated carbonized modified kenaf with nickel (ACK-Ni04). The size of the kenaf and reactor’s pressure was controlled at 300-500μm and up to 5 bar, respectively. Each of the samples was studied for 2 cycles. After the first cycle, the hydrogen gas was removed from the reactor. A vacuum pump was used to remove the hydrogen inside the reactor and the kenaf’s pore.
In the first cycle (Figure 4), the hydrogen entering the reactor was 5.127 bar at minute 1.00 and the pressure slowly drop until it started to constant at minutes 4.00 with pressure 5.029 bar. As for the second cycle, the hydrogen entering the reactor was 5.132 bar at minute 1.00 and drop until constant at minute 10.00 with pressure 5.113 bar. At minute 60.00, the pressure suddenly rises to 5.114 and 5.116 at minute 120.00. This is due to the change of the ambient temperature from 27°C to 30°C. The pressure drop for the first cycle was 0.098 bar while the second cycle was 0.019 bar.

3.4. Surface Characterization. Kenaf has porous surface structure where the porous structure and the micropores on the surface helps for the adsorption. The morphological analysis was carried to observe the surface structure and the topography of the samples. the analysis was carried on by using VPSEM analyzer.

Figure 4. Modified kenaf with nickel (MK-Ni04)

Figure 5. Surface Structure and topography of ACK-Ni04
Figure 5 shows the morphological structure and topology of ACK-Ni04. From the figure, the sample consist a lot of porous structure with a uniform shape. The uniform shape of the structure may help in the effectiveness of the adsorption process. Micropores were observed on the surface of the structure. The sample contain a lots micropores where it was arranged uniformly on the surface. The carbonization process increased the number of pores that help to enhance the adsorptive characteristic. The average size of the micropores was 2μm.

4. Conclusion
This study has proved that the ideal impregnation time is 5 hours as it achieves the highest adsorption capacity with small pressure drop of 0.020 bars. Result obtained in this research shows that hydrogen was adsorbed with greater capacity when impregnating nickel metal in 0.4M of Ni (NO₃)₂ solution with pressure drop of 0.098 bars. This study shows that the capacity of hydrogen adsorption is greatly affected by the amount of metal impregnated into the pore of the kenaf. Finally, the adsorption and desorption processes were successfully achieved for two consecutive cycles. The result shows that ACK-Ni04 has the highest adsorption and desorption capability as compared to TK04 and MK-Ni04 the pressure drop achieved of 0.207 bar for the first cycle and reduced to 0.109 bar for the second cycle. This adsorption and desorption capabilities were due to the presence of highly porous properties. The impregnation of nickel has also enhanced the adsorption capability by increasing the attractive forces between the kenaf core adsorbent and gas. Finally, the adsorption and desorption ability provide evidence that the modified-kenaf core sorbent can be reusable.

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