# Impregnation of Chitosan onto Activated Carbon for High Adsorption Selectivity towards $CO_2$: $CO_2$ Capture from Biohydrogen, Biogas and Flue Gas

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**Abstract**: In this study, a novel bio-based adsorbent was developed for $CO_2$ adsorption. Palm shell activated carbons were immersed in chitosan solutions at the concentrations between 0.1-2 g/L under agitation. A series of chitosan impregnated activated carbon was obtained: 0.12-0.98 wt% chitosan. The chitosan impregnated activated carbon that was the most suitable for $CO_2/H_2$ separation was the one impregnated with 0.1 g/L chitosan solution yielding 0.12 g chitosan per one hundred gram activated carbon. A lab-scale pressure swing adsorption process using the modified activated carbon as the adsorbent (adsorption pressure of 4 bar and the feed flowrate of 2 L/min 50-50 mixture of $H_2$ and $CO_2$ for a period of 2 min) yielded ultra pure $H_2$ for 8 cycles before the breakthrough of $CO_2$, while only 3 cycles were achieved with the native activated carbon. The chitosan impregnated activated carbon that was the most suitable for $CO_2/CH_4$ separation was the one impregnated with 2 g/L chitosan solution yielding 0.76 g chitosan per one hundred gram activated carbon. The lab-scale adsorption process using the modified activated carbon as the adsorbent yielded ultra pure $CH_4$ for 3 cycles before the breakthrough of $CO_2$, while only 1 cycle was achieved with the native activated carbon. For the $CO_2/N_2$ dynamic adsorption of 0.12 wt% CHI/AC, 100% nitrogen was achieved for 1-8 cycles. For the $CO_2/N_2$ dynamic adsorption of 0.76 wt% CHI/AC, 100% nitrogen was achieved for 1-9 cycles.

**Keywords:** Modified activated carbon, chitosan, impregnation, biohydrogen, biogas, flue gas, purification.

## 1. Introduction

Nowadays, our world is facing both energy and environmental problems which affect the people's living quality and a nation's economics. Carbon dioxide ($CO_2$), a green house gas that is released when burning fossil fuels, has been realized to play a crucial role in climate change [1]. The rising level of $CO_2$ can gravely affect our future. In contrast to petroleum based energy, renewable energy produced from biomass has received a special attention in recent years because it only releases the amount of atmospheric $CO_2$ that was stored in the plant during its growth. Two of the important renewable energy produced from biomass by anaerobic digestion are biogas and biohydrogen. Utilization of biogas and biohydrogen reduces $CO_2$ emissions and helps to avoid an increase of the $CO_2$ concentration in the atmosphere. Furthermore, $CO_2$ separation from biogas and biohydrogen following by a conversion of $CO_2$ to other forms or by $CO_2$ capture and storage can be a strategy for decreasing the $CO_2$ concentration in the atmosphere.

There are a number of techniques for gas separation such as absorption, adsorption and membrane. Evaluation of upgrading techniques for biogas are available and it has been reported that adsorption is a potential technology for $CO_2$ removal from biogas especially for small and middle sized upgrading plants [2]. The active part in the adsorption process is the adsorbent. There is a variety of adsorbents such as zeolite, silica gel, activated alumina and activated carbon. Activated carbon offers an attractive and inexpensive adsorbent for removing several solutes from aqueous solutions as well as from gaseous environment. In recent years, interest has been growing in the use of low-cost and abundantly available lignocellulosic materials as precursors for the preparation of activated carbon. The nature of the final product depends on both the starting material and the activation procedure. The activated carbons may differ mainly in pore size distribution and surface polarity [3].

A further development of activated carbon is to modify the pore size and/or to control the pore size distribution. Another development of activated carbon is to modify its surface polarity in order to enhance selective chelating ability. The selection is based on the chemical interactions which can preferentially attract polar molecules onto the carbons. This type of activated carbon can be prepared by oxidizing the activated carbon with acids and bases [4] such as nitric acid [5], tannic acid [6], citric acid [7], ammonia [8] or by microwave, ozone and plasma treatment [4,9]. To a lesser extent, the surface polarity can be changed by coating an adsorbent with polymers such as polyethyleneimine [4,10-12]. Yin et al. (2007) [9] impregnated palm shell activated carbon with low and high molecular weight polyethyleneimine (PEI). The impregnation with low molecular weight PEI was found to enhance $Cd^{2+}$ adsorption capacity of the activated carbon. For a gas separation application, the palm shell activated carbon impregnated with 0.26 wt% PEI was found to have higher adsorption selectivity towards $CO_2$ [13].

In our viewpoint, the activated carbon with modified surface polarity can be prepared with local resource and environmentally friendly materials with similar effectiveness. One attractive alternative is chitosan biopolymer or poly [β-(1→4)-2-amino-2-deoxy-D-glucopyranose], which is mainly produced by alkaline deacetylation of chitin [14-16]. The structure of chitin and chitosan is similar to cellulose except that the C-2-hydroxyl group of cellulose is replaced by an acetamido and amino group, respectively (Figs. 1(a)-(c)). Chitosan is insoluble in most organic solvents but it dissolves in acidic solutions [17].

In this study, modified activated carbon is prepared by impregnating chitosan onto activated carbons. The modified activated carbon was produced at chitosan weight percentages of 0.12, 0.25, 0.36, 0.66, 0.76 and 0.98 wt%. The dynamic $CO_2$ adsorptions of the modified activated carbon were determined using a lab-scale adsorption column and the results were compared with those of the native activated carbon. In addition, an evaluation of carbon capture and storage by the modified activated carbon is discussed.
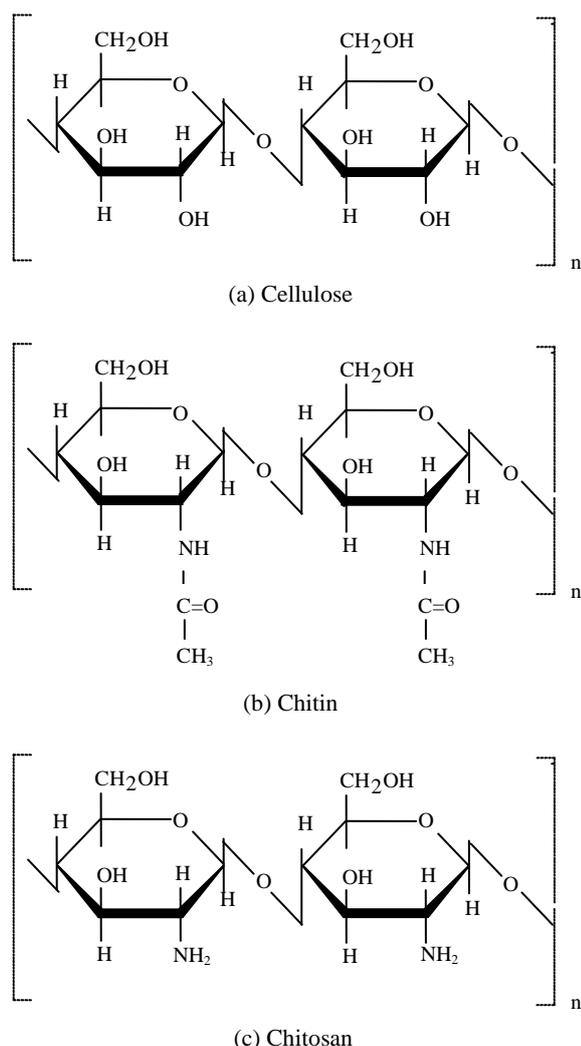
(a) Cellulose



(b) Chitin



(c) Chitosan

**Figure 1.** Structures of (a) cellulose (b) chitin and (c) chitosan.

## 2. Materials and Methods

### 2.1 Materials

Palm shell activated carbon produced by physical activation process with steam as the activating agent was obtained from C. Gigantic Carbon Co., Ltd. (Thailand). The characteristics of the activated carbon are as follow: bulk density 0.59 g/mL, particle size distribution 91% 200 mesh pass, iodine absorption 862 mg/g, pH 10.1 and ash content 6.1%.

Gases $CO_2$, $CH_4$ and $N_2$, were of analytical grades (99.995%). The chitosan was provided by Taming Enterprises Co., Ltd. (Thailand) and its characteristics are as follows: degree of deacetylation = 93.8%; molecular weight = 17,010 dalton; moisture content = 7%; ash content = 0.95%; protein content = 3.01%; viscosity = $27.40 \times 10^{-3}$ Pa·s. Chitosan solution (2% w/v) was prepared by mixing 2 g of chitosan in 900 mL of 1 M acetic acid. The solution was mixed at 200 rpm for 24 h. One hundred mL of 1M sodium acetate was added and agitated for 1 h.

### 2.2 Chitosan impregnation onto activated carbon

The activated carbons were washed with deionized water to remove fines and dirt and then oven dried at 378 K for 24 h before the impregnation process was conducted. The AC was sieved to sizes ranging from 3-4 mm and divided in 2 g portions and placed in separate Erlenmeyer flasks. Fifty mL of chitosan solutions with initial concentrations of 0.1-2.0 g/L

were added. The AC together with the chitosan solution was then agitated in an orbital shaker at 180 rpm at 298 K for 3 days.

The AC was separated from the chitosan solution by filtration. Chitosan concentration was indicated by an absorbance value measured by UV-vis spectrophotometer (Thermo Scientific, Genesys 10S UV-Vis, USA) at the wavelength of 202 nm. The percentage amount of chitosan impregnated onto the activated carbon was calculated by Eq. (1).

$$\%wt = \frac{(C_o - C_e)V}{m} \times 100 \qquad (1)$$

where *%wt* is the equilibrium amount of chitosan impregnated onto activated carbon; $C_0$ and $C_e$ is the initial and equilibrium concentration (g/L) of chitosan in solution; $V$ is the volume (L) of the chitosan solution; $m$ is the weight (g) of activated carbon.

The chitosan impregnated activated carbon (CHI/AC) was oven dried at 378 K for 24 h. The amount of chitosan impregnated on the activated carbon was cross-checked by a calculation of the difference between the weight of chitosan before and after the impregnation process.

### 2.3 Adsorption analysis
#### (a) Apparatus

The adsorption experimental set-up (Fig. 2) is comprised of a single stainless steel column with a diameter of 1.9 cm, height of 80 cm and total volume of 200 $cm^3$ packed containing 160 g of the adsorbent. The column pipeline was made of polyurethane with an outside diameter of 1 cm. The column was equipped with three automatic solenoid valves which were controlled via Visual Basic interface. Two temperature detectors were positioned at the column inlet and outlet to measure any temperature variation due to the adsorption process. Two flowmeters (Dwyer, measuring ranges 0-10 L STP/min and 0-5 L STP/min) was installed at the inlet and outlet to record the flowrate and a pressure gauge (a maximum pressure of $10^3$ kPa) was installed at the column to measure the pressure variation. A vacuum pump (30 kPa, GAST Manufacturing Corp., USA) was employed to desorb the gas before and after each experiment.
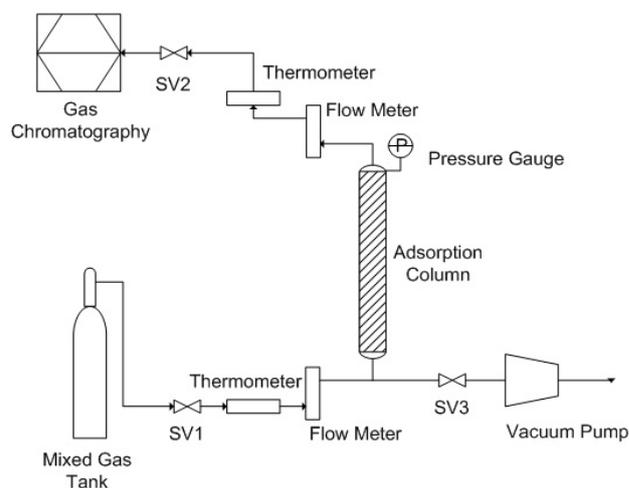


**Figure 2.** Diagram of the adsorption system.

#### (b) Dynamic adsorption

The dynamic adsorption was carried out by passing the standard binary gas mixtures (50/50% $CO_2/CH_4$, $CO_2/H_2$ and $CO_2/N_2$ v/v) through the adsorption column at 298 K. The controlled room temperature was chosen because most of the pressure swing adsorption (PSA) systems were operated at an ambient condition. Before each experiment, the gas was evacuated to 30 kPa by the vacuum pump during the vacuum step. The three-step adsorption cycle was operated: (1) pressurization, (2)

adsorption and (3) depressurization, via three automatic solenoid valves operated according to Table 1. The pressure during the pressurization and adsorption steps was 400 kPa. The feed flow rate during the pressurization step was 2 L STP/min for 2 min. During the adsorption step, the system was holding constant for 15 min to ensure that equilibrium was achieved. During the depressurization, the gas exits at the end of the column and the gas composition was determined by a gas chromatograph (GC) equipped with a thermal conductivity detector (GC-2014; SHIMADZU, Japan), a stainless steel packed column and an argon carrier gas with a flow rate of 50 mL/min. The accuracy of the GC at high $CH_4$ concentrations was tested with 99.9% $CH_4$ (Thai Special Gas Co., Ltd.). During the depressurization step, the gas was desorbed by a reduction in pressure from the adsorption pressure to atmospheric pressure. The cycle was repeated until a breakthrough of $CO_2$ was reached.

**Table 1.** Valve Operation System.

| Valve Operation | SV1 | SV2 | SV3 |
|---|---|---|---|
| Pressurization | Open | Close | Close |
| Adsorption | Close | Close | Close |
| Depressurization | Close | Open | Close |
| Vacuum | Close | Close | Open |

## 3. Results and Discussion

In this study, the adsorption dynamics of the activated carbon bed was investigated by using the binary gas mixtures of $CO_2/CH_4$, $CO_2/H_2$ and $CO_2/N_2$ feed (50:50 v/v) to the adsorption column. The adsorption cycle was described in section 2.3 (b) and each cycle lasted approximately for 20 min. A typical pressure profile in the adsorption column for an operating cycle is shown in Fig. 3.
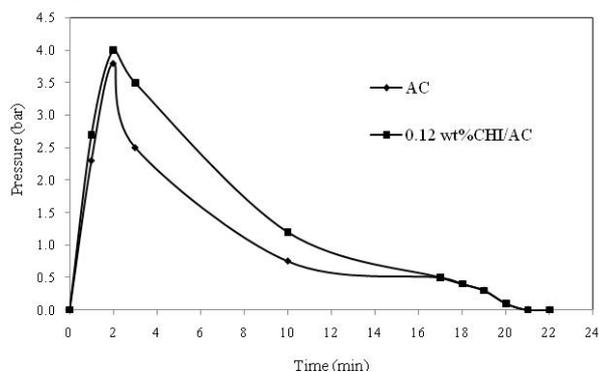


**Figure 3.** Pressure profile in the adsorption column during $CO_2/H_2$ dynamic adsorption.

### 3.1 Biogas upgrading

Biogas is produced by anaerobic digestion, the process in which biomass is converted by microorganisms to biogas under absence of oxygen. Biogas is a mixture of $CH_4$ 50-70%, $CO_2$ 30-50% and small traces of $N_2$, ammonia ($NH_3$) and hydrogen sulfide ($H_2S$). Biogas is currently most commonly used for electricity and/or heat production by combined heat and power technology. Upgraded biogas is increasingly used as natural gas substitute in natural gas grids or used as vehicle fuel especially in European and Scandinavian countries [18]. Besides the removal of $NH_3$ and $H_2S$, the removal of $CO_2$ is the main step for upgrading biogas to natural gas quality. Adsorption is one of the widely employed technology for removing $CO_2$ from biogas and for converting biogas to high purity methane (>96%).

Biogas upgrading was studied using a synthetic mixture of 50-50 (v/v) $CH_4/CO_2$ mixture. Based on the data on

equilibrium and kinetic selectivity, the 0.76 wt% CHI/AC was selected for dynamic gas separation in comparison with the native activated carbon [19]. When using the native activated carbon as the adsorbent, high purity methane in the range of 93-100% was achieved during cycle 1-2. As the gas separation was processed to cycle 3, the methane purity dropped to the range between 72-84%. The shape of $CO_2$ concentration profile was broad as shown in Fig. 4 (a). When using the 0.76wt% CHI/AC as the adsorbent, 100% methane was achieved during cycle 1-2. It should be noted that the methane purity can be maintained at 100% during the operating cycle when using the 0.76 wt% CHI/AC, but not by the native activated carbon. The breakthrough of $CO_2$ occurred at cycle 3 where the methane purity dropped lower to nearly 90%. (Fig. 4 (b)). It is evident that the 0.76 wt% CHI/AC had higher affinity for $CO_2$, resulting in ultra pure $CH_4$ as the raffinate, which cannot be achieved by using the native activated carbon.
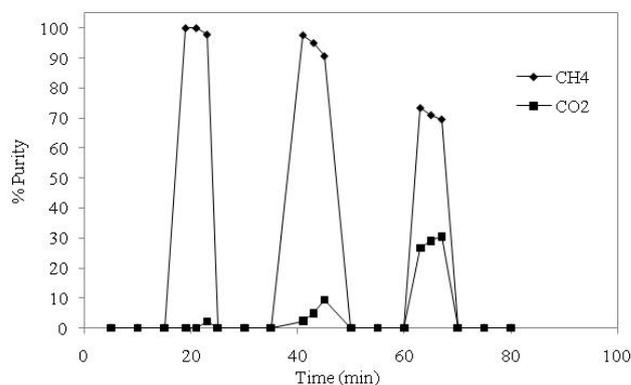


(a) The native activated carbon
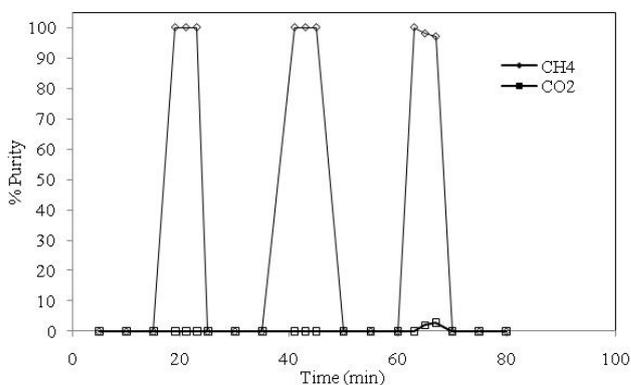


(b) The 0.76 wt% CHI/AC

**Figure 4.** Dynamic adsorption profile of 50-50 mixture of $CO_2/CH_4$ (a) the native activated carbon (b) the 0.76 wt% CHI/AC.

### 3.2 Biohydrogen upgrading

A well known method for hydrogen production is a steam reforming process which yields a gas mixture with a typical composition of $H_2$ 87%, $CO_2$ 11%, carbon monoxide (CO) 0.5-1% and $CH_4$ 1-2%. An alternative hydrogen production is by a biological process which yields a gas mixture with a typical composition of $H_2$ 50-60% (v/v), $CH_4$ 10-20%, $CO_2$ 30-40% and few percentages of water. The separation of carbon dioxide from hydrogen is a necessary step to upgrade biohydrogen. Purified hydrogen can be acquired by a gas separation process such as pressure swing adsorption. There are variety types of adsorbent for the adsorption process. Some of them are available naturally while the others are synthesized such as zeolite, silica gel, activated alumina and activated carbons. Activated carbon has been illustrated to be a potential adsorbent for the separation

of $CO_2$ from $H_2$ [20].

Biohydrogen upgrading was studied using a synthetic mixture of 50-50 (v/v) $H_2/CO_2$ mixture. When using the native activated carbon as the adsorbent, high purity hydrogen in the range of 93-100% was achieved during cycle 1-3. However, during cycle 4-7, the hydrogen purity dropped significantly to the range of 72-84%. The $CO_2$ concentration increased slowly as shown in Fig. 5 (a).

Based on the data on equilibrium and kinetic selectivity, the 0.12 wt% CHI/AC was selected for dynamic gas separation in comparison with the native activated carbon [21]. When using the 0.12 wt% CHI/AC as the adsorbent, 100% hydrogen was achieved during cycle 1-8, and the breakthrough of $CO_2$ occurred at cycle 9 with a relatively steep concentration profile as shown in Fig. 5 (b). It is evident that the 0.12 wt% CHI/AC adsorbed $CO_2$ more effectively, leading not only to the higher $H_2$ purity in the early cycles, but also the longer effective operating cycles. However, in contrast to physical adsorption of $CO_2$ onto the native activated carbon, chemisorption is the underlying mechanism for $CO_2$ adsorption onto the chitosan impregnated activated carbon and desorption of $CO_2$ from the modified adsorbent requires heat regeneration.
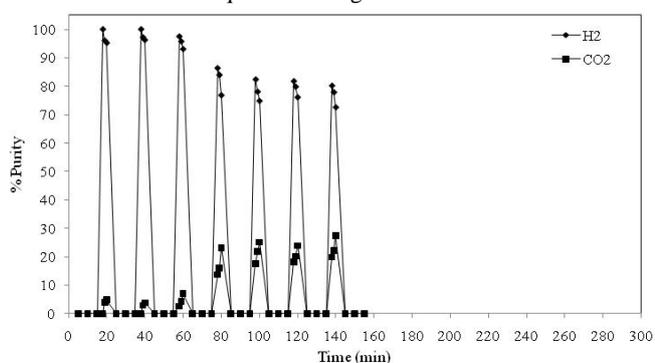


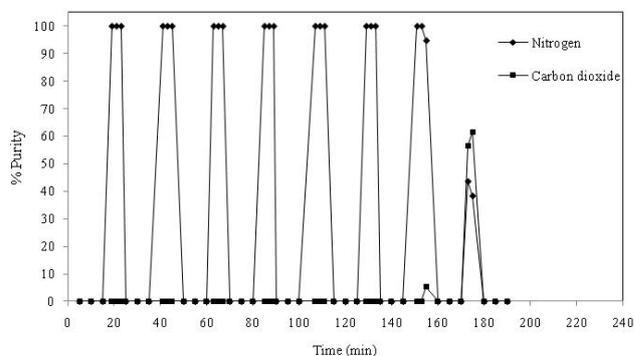(a) The native activated carbon
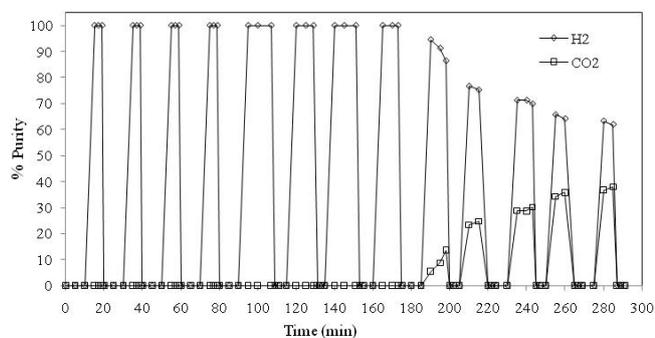


(b) The 0.12 wt% CHI/AC

**Figure 5.** Dynamic adsorption profile of 50-50 mixture of $CO_2/H_2$ (a) the native activated carbon (b) the 0.12 wt% CHI/AC.

**3.3 $CO_2$ removal from flue gas**

Typical flue gases consist of approximately 17% $CO_2$, 79% $N_2$, 4% $O_2$ and trace amounts of $SO_2$ and $NO_x$ [22]. Since the beginning of industrial revolution, flue gases have been released to the atmosphere from industries and it has been estimated that the amount of carbon dioxide in the atmosphere increases globally about six billion tones per year [22]. Therefore, one important strategy to reduce $CO_2$ emission is to recover carbon dioxide from the flue gases.

$CO_2$ removal from flue gas was studied using a synthetic mixture of 50-50 (v/v) $N_2/CO_2$ mixture. Activated carbon has been investigated as an adsorbent for the separation of $CO_2$ from $N_2$ [23]. Similar to the $CO_2/H_2$ dynamic adsorption, the $CO_2/N_2$ dynamic adsorption of the activated carbon yielded ultra pure nitrogen during cycle 1-7. After cycle 7, the nitrogen

purity dropped rapidly to the range between 30-50%. The carbon dioxide concentration increased rapidly with additional operating cycles as shown in Fig. 6 (a). For the $CO_2/N_2$ dynamic adsorption of 0.12 wt% CHI/AC, 100% nitrogen was achieved for 1-8 cycles. Nitrogen purity dropped 10-15% at cycle 9 (Fig. 6 (b)). For the $CO_2/N_2$ dynamic adsorption of 0.76 wt% CHI/AC, 100% nitrogen was achieved for 1-9 cycles. Nitrogen purity dropped 40-50% at cycle 10 (Fig. 6 (c)).



(a) The native activated carbon
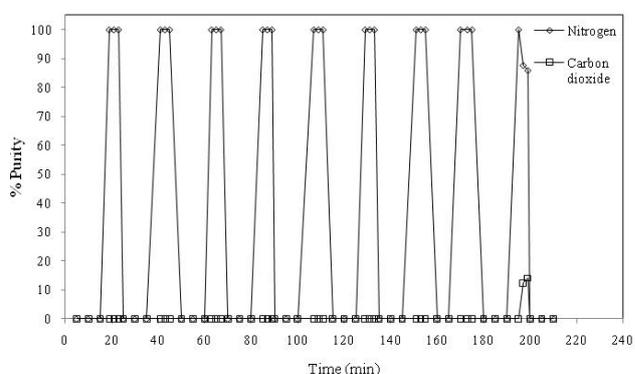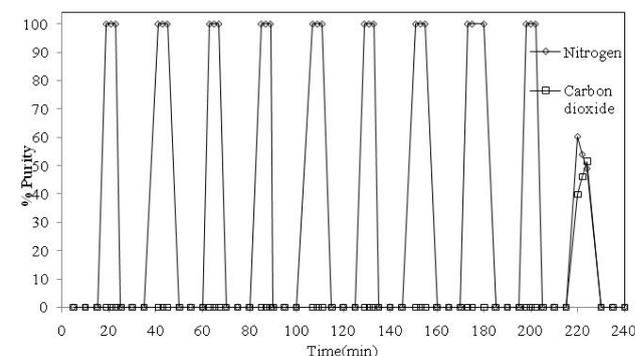


(b) The 0.12 wt% CHI/AC



(c) The 0.76 wt% CHI/AC

**Figure 6.** Dynamic adsorption profile of 50-50 mixture of $CO_2/N_2$ (a) the native activated carbon (b) the 0.12 wt% CHI/AC (c) the 0.76 wt% CHI/AC

For an integrated process of both gas purification and carbon dioxide capture and storage, regeneration of the adsorbent may not be necessary as the adsorbent also works as carbon storage, but the affinity of an adsorbent for carbon dioxide should be maximized. The modified activated carbon developed in this study would serve this purpose because it has higher adsorption capacity and higher carbon dioxide selectivity compared to the native activated carbon without modification. The storage of $CO_2$ in adsorbent can reduce the container volume substantially. For example, consider the $CO_2$ storage at 4 bar and 298 K in a tank volume of 1 $m^3$. Using the ideal gas (PV = $nRT$), the amount of $CO_2$ in the tank is calculated to be

164 mole. If this amount will be adsorbed on the chitosan impregnated activated carbon, the required amount of the adsorbent is calculated based on the adsorption capacity of 3.76 mole of $CO_2$ adsorbed per kg to be 43.62 kg (obtained from 164/3.76). Based on the bulk density of the adsorbent (0.59 g/mL or 590 kg/m$^3$), the required volume is estimated to be 0.074 m$^3$. Therefore, when comparing $CO_2$ storage in a tank with and without containing the modified activated carbon under the same pressure, $CO_2$ storage on the modified activated carbon can reduce a tank volume by 14 folds.

## 4. Conclusions

In this study, $CO_2$ separation from biogas, biohydrogen and flue gas is presented and a combined $CO_2$ separation and storage is proposed to be a strategy for decreasing the $CO_2$ concentration in the atmosphere. Dynamic adsorption of 50-50 mixture of $CH_4/CO_2$ and $H_2/CO_2$ by the chitosan impregnated activated carbon yielded ultra pure methane and hydrogen, respectively, which cannot be achieved by the native activated carbon. In addition, dynamic adsorption of 50-50 mixture of $N_2/CO_2$ by the chitosan impregnated activated carbon yielded ultra pure nitrogen. The modified activated carbon has higher adsorption capacity and higher carbon dioxide selectivity compared to the native activated carbon without modification. When comparing $CO_2$ storage in a tank with and without containing the modified activated carbon under the same pressure, $CO_2$ storage on the modified activated carbon can reduce a tank volume by 14 folds.

## Acknowledgments

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