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# Studies of Modification of Biopolymer with Piperazine Derivative for Carbon Dioxide Adsorption

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Piperazine acetyl biopolymer (PABP), a new solid sorbent potentially used for $CO_2$ capture from industrial flue gases was synthesized by attaching chloroacetyl chloride linkage group to purified biopolymer (BP). Piperazine (PZ) was then used to functionalize so that the BP acquired amino groups essential for capturing $CO_2$.The maximum degree of PZ substitution obtained for PABP was 22 %. Purified BP was initially used to determine the optimal conditions for $CO_2$ adsorption and desorption which were also tested later on PABP. Adsorption was found the most effective using initially pre-treatment of the BP with wet $N_2$ gas prior to adsorption with dry $CO_2$ feed at 298 K. Desorption capacity yielded the best result at 403 K. $CO_2$ desorption capacity was found to decrease when the BP was repeatedly used (i.e. 2 adsorption-desorption cycles). With the optimal conditions, PABP adsorption capacity was 0.1441 mmol/g adsorbent as opposed to 0.2211 mmol/g adsorbent when dry $N_2$ pretreatment at 378 K was used.

## 1. Introduction

At present, environment issues related toglobal warming and climate change have been given the most attention by many scientists. Anthropogenic emission of greenhouse gases (GHGs) to the atmosphere is a major cause of global warming. Particularly, carbon dioxide ($CO_2$) from fossil fuel power plants and transportation known as the largest contributor is responsible for 75 % of total emitted GHGs. To reduce $CO_2$ effect, several techniques have been proposed such as absorption, adsorption, membrane separation and cryogenic. In convention technology,$CO_2$ can be separated by chemical absorption with aqueous amine solution such as momoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA). Many researches are also focused on diamines including piperazine (PZ) which is mostly used as the promoter and solvent in the amine system to increase the efficiency of absorption process. Due to PZ's two amine groups, a higher reaction rate with $CO_2$ can be achieved as compared to conventional amines (e.g. MEA, DEA, and MDEA). However, the absorption process using these amines still has some drawbacks such as corrosion, oxidative degradation, high regeneration energy and maintenance cost. Therefore, adsorption process can be used as the alternative technology for $CO_2$ capture. Since adsorption with bare solid adsorbents such as zeolite, activated carbon and mesoporous silica usually results in low $CO_2$ selectivity, thus low $CO_2$ removal concentration. A reactive amine is usually incorporated into the sorbent structure to increase the selectivity and adsorption capacity.This research will focus on the development of one of our amine

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loaded adsorbents using biopolymer derived from biological sources and modified with piperazine derivative to increase the adsorption capacity and selectivity for $CO_2$removal.

## 2. Methodology

### 2.1 Purification of biopolymer

Biopolymer (100 g) and sodium borohydride (0.5 g) were mixed in 2 L of 50 % (w/w) sodium hydroxide (NaOH) solution in an autoclave for 1 h at 393 K. The purified biopolymer (BP) was filtered and washed with deionized water until a neutral pH was reached. The BP was then dried at 80 ºC overnight in a vacuum oven and later kept in a desiccator until used.

### 2.2 Characterization of purified biopolymer (BP)

The BP was characterized with Nicolet/Nexus 670Fourier transform infrared spectrophotometer (FTIR) for determination of the functional group in the structure. Degree of deacetylation was also determined from the FTIR spectra using proposed equations by Miya *et al.* (1980). The H-NMR and element analyzer were also carried out to confirm the degree of deacetylation. The H-NMR analysis adopted from Hirai (1981) was performed on INOVA-500 Varian NMR spectrometer set at 303 K for sample dissolved in 1 % v/v $CD_3COOD/D_2O$. Elemental analysis was performed with Perkin Elmer 2400 CHN elemental analyser and calculated using proposed equations by Kasaai *et al.* (2000).

### 2.3 Preparation of piperazine acetyl biopolymer (PABP)

The PABP was synthesized in two steps: chloroacetylation of BP and PZ functionalization. Firstly, chloroacetylation was performed under $N_2$ atmosphere as shown in Figure 1. BP (6 mmol per sugar unit) was dried in an atmospheric oven at 383°C for 24 h and slowly added with chloroacetyl chloride (62.8 mmol) in the reaction flask. Solution made of 30 mL *N,N*-dimethyl formamide (DMF) and 0.85 mL (700.06 mol) triethylamine (TEA) was then added to the mixture while being stirred at room temperature for 72 h. *N*- and O-chloroacetyl biopolymer (CABP) was precipitated from the mixture in iced water and washed with 1.0 M $NaHCO_3$ solution. CABP was kept in a desiccator until characterization. For PZ functionalization, 2 g PZ was dissolved in 80 mL DMF before adding in 1 g CABP. The mixture was stirred under $N_2$ environment at 333 K for 72 h. PABP was finally dried in atmospheric oven at 333 K for 24 h and used for the $CO_2$ adsorption study.

### 2.4 Characterization of modified biopolymer

The CABP and PABP samples were characterized by FTIR for determination the functional groups. Degree of acylation of CABP was calculated using equations proposed by Jenkins and Hudson (2001). PABP degree of PZ substitution was determined by CHN element analyzer.

### 2.5 $CO_2$ Adsorption experiment and regeneration of adsorbent

The experimental set up is shown in Figure 2. The adsorbent of 0.2 g was loaded in the fixed bed Pyrex glass rector with 4 mm inner diameter, 6 mm outer diameter and1.2 cm height of packed bed. The heating tape was used to regulate adsorption and desorption temperatures which were confirmed by a digital thermometer with an accuracy of +/- 0.5 K. The flow rate of 4 % $CO_2$ premixed gas used as a feed in this study was controlled by a rotameter respectively set at 5mL/min and 100 mL/min for adsorption and flushing the adsorption line. The flow rates were also verified by a bubble flow meter. The effluent from the reactor was continuously monitored for $CO_2$ with Agilent 6980N gas chromatograph (GC) equipped with thermal conductivity detector (TCD). The thermal regeneration of adsorbent was carried after $CO_2$ adsorption reaching equilibrium by flushing the reactor with pure $N_2$ until the $CO_2$ signal measured by GC corresponding to zero. BP was initially used to test for the optimum adsorption-desorption conditions by evaluation of the effects of moisture in $CO_2$ feed (i.e. dry and wet conditions), adsorption and desorption temperatures and regeneration cycle. Effect of $N_2$ feed condition during pretreatment step (before adsorption process) was also studied for PABP.

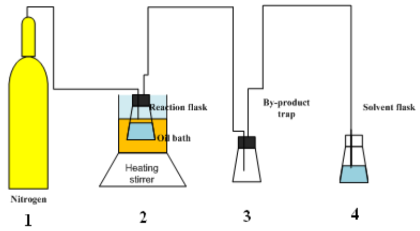


*Figure1: Setup for chloroacetylation and PZ functionalization: 1) Nitrogen gas cylinder 2) Reaction flask 3) By-product trap 4) Solvent flask*

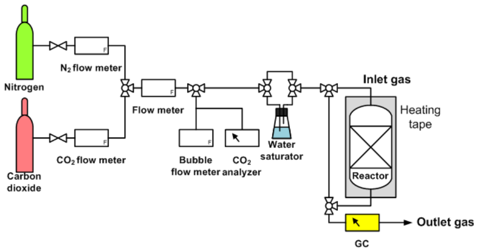


*Figure 2: Experimental setup for $CO_2$adsorption process*

## 3. Results and Discussion

### 3.1 Purification and characterization of BP

The biopolymer was purified by alkali treatment in order to obtain a higher degree of deacetylation (% DD) via hydrolysis reaction to increase amine groups in the structure. FTIR spectra obtained for original biopolymer and its modified counterpart BP are shown in Figure 3. The most noticeable difference was the decrease of the characteristic peak intensity at 1655 $cm^{-1}$ in the BP representing amide band I(C=O) of the remaining N-acetyl glucosamine units in its structure. The degree of deacetylation (DD) of BP was determined at 97 % by using the absorbance ratio of amide I (-CONH) band at 1655 $cm^{-1}$ to that of 2867 $cm^{1}$ band corresponding to C-H stretching. The NMR analysis was also used to confirm % DD using the integral intensity of $CH_3$ residue ($I_{CH3}$) and the sum of integral intensities of H2, H3, H4, H5, H6, and H6' protons ($I_{(H2\text{-}H6')}$) are shown in Figure 4. % DD obtained from NMR technique (97 %) was in a very well agreement with the FTIR method. In addition, elemental analysis summarized in Table 1 also shows similar % DD at 96 %.

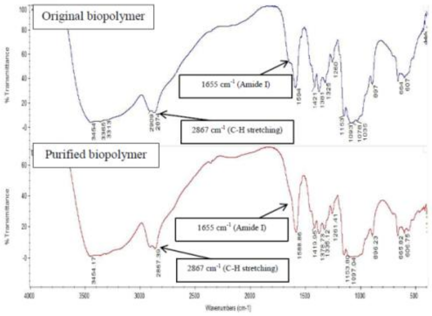


*Figure 3:The spectra of original biopolymer and BP*

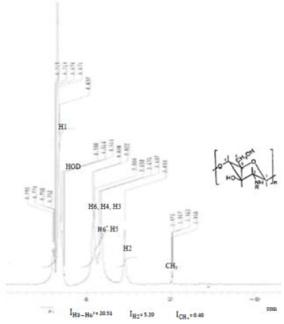


*Figure 4:NMR spectrum of BP*

### 3.2 Modification and characterization ofPABP

The PABP adsorbent was chemically synthesized with two steps as mentioned in the previous section. Figure 5(A) shows the first step when chloroactyl chloride, a medium linker reacted with either amino ($NH_2$) or hydroxyl (OH) groups of BP to form amide and ester linkage. The evidence for the *O*-chloroacetylation at OH groups and *N*-chloroacetylation at $NH_2$ groups in BP was confirmed by the IR bands at 1759 $cm^{-1}$ (assigned to C=O in ester groups of *O*-chloroacetylation), 1616 $cm^{-1}$ (assigned to C=O in amide groups of *N*-chloroacetylation; amide I), 1529 $cm^{-1}$ (assigned to N-H bending; amide II), and 783 $cm^{-1}$ (assigned to C-Cl bond) as shown in Figure 6(A). Yields of *N*-acylation and O-acylation in CABP were respectively estimated by using the absorbance ratios of the peaks at 1616 $cm^{-1}$ to 2876 $cm^{-1}$ and 1759 $cm^{-1}$ to 2876 $cm^{-1}$ for calculation in the equations proposed by Jenkins and Hudson(2001). The estimated percent yield respectively obtained for *N*-acylation and *O*-acylation were 35 % and 33 % which combined to give the total yield of acylation at approximately 68 %. Second step was functionalization of CABP with PZ. PZ was incorporated into CABP structure by replacing the chloride in the linkage (-COC-C) as illustrated in Figure 5 (B). In Figure 6(A) and (B), it is clear that PZ substitution actually occurred as shown by the disappearance of C-Cl peak at 783 $cm^{-1}$ in the IR spectrum of PABP compared to that of CABP. The elemental analysis, particularly of nitrogen in PABP was used to determine the degree of PZ substitution by comparing with a standard curve plotted between calculated degree of PZ substitution and theoretical elemental nitrogen content. The degree of PZ substitution in PABP was 22 %. Details of the elemental analysis of PABP and also CABP are given in Table 1.

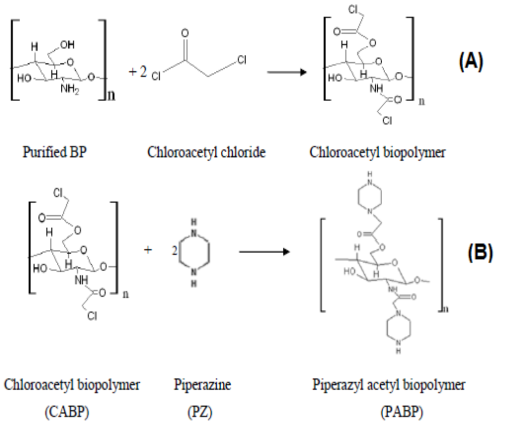


*Figure 5: Synthesis of PABP (A) chloroacetylation of BP and (B) PZ functionalization*

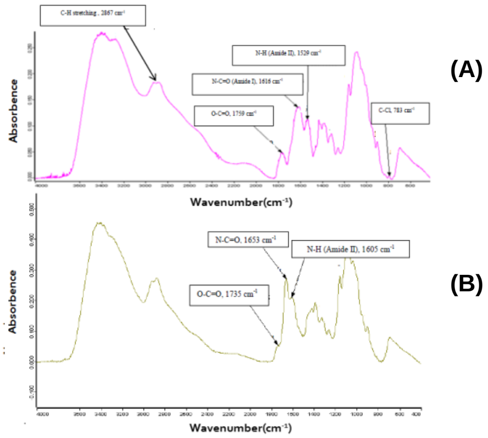


*Figure 6: IR spectra of (A) CABP and (B) PABP*

*Table 1: Elemental analysis of BP, CABP, and PABP*

| Adsorbent | C (mmol/g) | Average C (mmol/g) | N (mmol/g) | Average N (mmol/g) | % DD | Average %DD |
|---|---|---|---|---|---|---|
| BP | 38.15 | 38.32±0.16 | 5.64 | 5.65±0.01 | 94 | 96±1.3 |
| | 38.47 | | 5.65 | | 97 | |
| | 38.35 | | 5.65 | | 96 | |
| CABP | 37.93 | 37.58±0.31 | 4.58 | 4.60±0.02 | | N/A |
| | 37.40 | | 4.61 | | | |
| | 37.39 | | 4.61 | | | |
| PABP | 40.33 | 40.33±0.04 | 5.97 | 5.96±0.02 | | N/A |
| | 40.38 | | 5.96 | | | |
| | 40.29 | | 5.94 | | | |

### 3.3 $CO_2$ Adsorption study

BP was initially used to establish the optimal conditions for $CO_2$ adsorption (i.e. $CO_2$ feed conditionand adsorption and desorption temperatures) which were later used to test PABP. Adsorption-desorption efficiency of BP after repeated use (i.e. 2 cycles) was also evaluated. In addition, effect of $N_2$ condition during pretreatment step was also studied for PABP.

### 3.3.1 Effect of moisture in $CO_2$ feed

The experiment was carried using initially wet $N_2$ (passed through a water saturator) at 298 K to pretreat the BP. The actual $CO_2$ adsorption test was then followed by using dry or wet ($CO_2$ stream being passed through the water saturator before entering the reactor) $CO_2$ feed gas. Breakthrough curves for $CO_2$ adsorption of BP in dry and wet $CO_2$ feeds are shown in Figure 7. The dynamic $CO_2$ adsorption capacity of BP calculated based on the curves in Figure 7 respectively for dry and wet $CO_2$ feed conditions were 0.2969 and 0.1597 mmol $CO_2$/g adsorbent. The $CO_2$ adsorption with dry feed showed a longer saturation time than that of wet feed condition. The results indicated a stronger affinity and more competitive to BP amino groups of water than that of $CO_2$.Therefore the dry $CO_2$ feed for the $CO_2$ adsorption was a suitable condition on BP.

### 3.3.2 Effect of adsorption temperature

Effect of temperature was studied using similar pretreatment condition as used in the previous section. Dry $CO_2$ feed as was used for $CO_2$ adsorption. The breakthrough curves obtained at 298, 318, and 333 K are shown in Figure 8. The $CO_2$ adsorption capacitiesof BP corresponding to each breakthrough curve in Figure 8 are presented in Figure 9. Adsorption at 298 K was the best showing the longest saturation time followed by those of 318 and 333 K The $CO_2$ adsorption capacity was temperature dependent decreasing from 0.2969 to 0.2514, and 0.1215 mmol $CO_2$/g adsorbent as temperature increased from 298 K to 318 K and 333 K. Effect of temperature showed exothermic nature of $CO_2$ adsorption which an increase of temperature corresponded to an increase of dissociation rate constant of $CO_2$ and amino group of BP.

### 3.3.3 Effect of desorption temperature

The desorption temperature was studied at 383, 393, 403 and 423 K. The desorption efficiency calculated based on equations proposed by Sonia and Abdelmottaleb (1981) was defined as a mole ratio of $CO_2$ desorbed to $CO_2$ adsorbed. Effect of desorption temperature was found opposite to that of the adsorption temperature described previously.As shown in Figure 10, the desorption efficiency increased from 47 % to 57 % and 71 % when temperature was increased from 383 K to 393 K and 403 K, respectively. The increase of temperature significantly improved the extent of regeneration because the desorption rate was more favorable thermodynamically at higher temperature. Exception was only applied to 423 K run when the desorption capacity dropped to 55 % due to thermal degradation of BP. Based on the results, the optimal adsorption temperature of BP was 403 K.

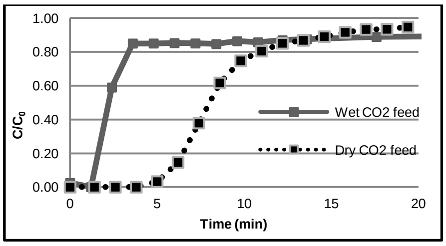


*Figure 7: Breakthrough curves for $CO_2$ adsorption capacity of BP in dry and wet $CO_2$ feeds*

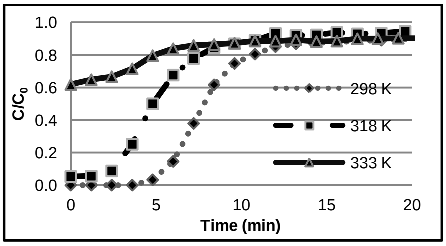


*Figure 8: Breakthrough curves for $CO_2$ adsorption capacity of BP at different adsorption temperatures*

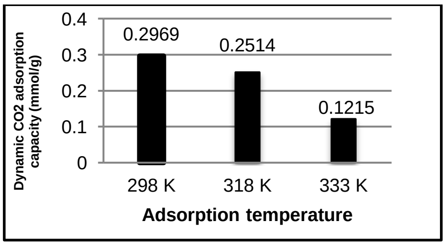


*Figure 9: $CO_2$ adsorption capacity of BP at different adsorption temperatures*

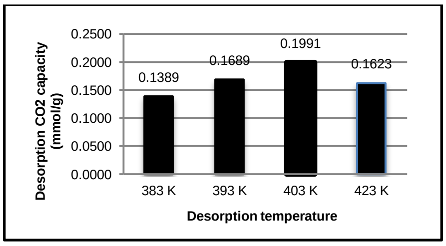
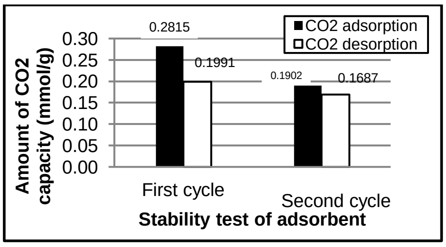


*Figure 10: $CO_2$ desorption capacity of BP at different desorption temperatures*

### 3.3.4 Stability test of biopolymer

Adsorption-desorption efficiency of BP after repeated usewas performed at the optimal conditions (i.e. wet $N_2$ pretreatment, 298 K adsorption, and 403 K desorption) for two cycles. As shown in Figure 11, it is clear that adsorption-desorption capacity of BP reduced after in the second cycle. The adsorption capacity decreased from 0.2815 to 0.1902 mmol $CO_2$/ g adsorbent. The desorption capacity was also dropped from 71 % to 61 % after the second. The remaining $CO_2$ left on the BP active surface after the first cycle possibly reduced the availability of active sites for $CO_2$ during the second cycle. In conclusion, BP adsorption-desorption reactivity was considered not stable if used repeatedly for $CO_2$ adsorption under prolonged thermal desorption and atmospheric conditions.



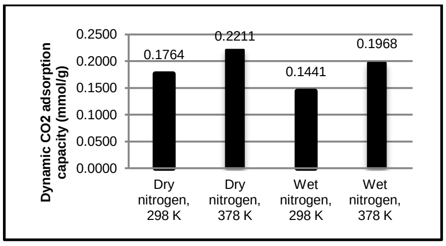


*Figure 11: Dynamic $CO_2$ adsorption and desorption capacity of BP during cyclic operation*

*Figure 12: Dynamic $CO_2$ adsorption capacity of PABP at different condition*

### 3.3.5 Effect of $N_2$ pretreatment condition on PABP

The optimal $CO_2$ adsorption conditions (i.e. wet $N_2$ pretreatment at 298 K, dry $CO_2$ feed, 298 K adsorption, and 403 K desorption) obtained previously for BP was also used to test $CO_2$ adsorption efficiency for PABP. However, the $CO_2$ adsorption capacity of PABP obtained at these conditions was only 0.1441 mmol/g adsorbent as shown in Figure12. Generally, a stoichiometric adsorption of $CO_2$ to amino group is 0.5 mole $CO_2$/mole nitrogen, but in this case, the dynamic stoichiometric adsorption of PABP obtained was a lot lower at only 0.037 mole $CO_2$/mole nitrogen. In order to improve $CO_2$ adsorption capacity of PABP, it was decided to vary $N_2$ pretreatment condition by running the adsorption at 298 K with dry $N_2$ pretreatment and 298 and 378 K with both wet and dry $N_2$ pretreatment. Also in Figure 12, the dynamic $CO_2$ adsorption capacity at 298 K was improved to 0.1764 mmol/g adsorbent when pretreating the PABP with dry nitrogen. The capacity was further boosted up to 0.1968 mmole/g adsorbent with wet $N_2$ and 378 K conditions. The highest capacity of 0.2211 mmol/g adsorbent was found when adsorption was carried out withdry $N_2$ pretreatment at 378 K. This indicated that the amount of water adsorbed on PABP was an important parameter affecting the adsorption capacity.

## 4. Conclusion

The present work demonstrated preparation of the new adsorbent (PABP) using biopolymer (BP) functionalized with piperazine derivative which the reactions were two steps and in the heterogeneous phase. The degree of PZ substitution was 22 %.Adsorption of BP was studied to obtain the optimal condition and then tested with PABP.However, the best adsorption of PABP was obtained after being pretreated with dry nitrogenat 378 K and then adsorption with dry $CO_2$ at 298 K. The highest $CO_2$adsorptioncapacitieswas 0.2211 mmol/g adsorbent, lower than BPand the dynamic stoichiometry of PABP was 0.037 mole $CO_2$/mole nitrogen, which was very low. To improve higher percentage of PAPB, it is recommended to perform in the homogeneous phase reaction, which is current research.

### Acknowledgement

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