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 CO2 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 CO2. The maximum degree of PZ substitution obtained for PABP was 22%. Purified BP was initially used to determine the optimal conditions for CO2 adsorption and desorption which were also tested later on PABP. Adsorption was found to be the most effective using initially pre-treatment of the BP with wet N2 gas prior to adsorption with dry CO2 feed at 298 K. Desorption capacity yielded the best result at 403 K. CO2 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 N2 pretreatment at 378 K was used.

1. Introduction

At present, environment issues related to global 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 (CO2) from fossil fuel power plants and transportation known as the largest contributor is responsible for 75% of total emitted GHGs. To reduce CO2 effect, several techniques have been proposed such as absorption, adsorption, membrane separation and cryogenic. In conventional technology, CO2 can be separated by chemical absorption with aqueous amine solution such as monoethanolamine (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 CO2 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 CO2 capture. Since adsorption with bare solid adsorbents such as zeolite, activated carbon and mesoporous silica usually results in low CO2 selectivity, thus low CO2 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
loaded adsorbents using biopolymer derived from biological sources and modified with piperazine derivative to increase the adsorption capacity and selectivity for CO₂ 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 °C 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 670 Fourier 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 CD₂COOD/D₂O. 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 N₂ 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 NaHCO₃ 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 N₂ environment at 333 K for 72 h. PABP was finally dried in atmospheric oven at 333 K for 24 h and used for the CO₂ 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 CO₂ 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 and 1.2 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 % CO₂ premixed gas used as a feed in this study was controlled by a rotameter respectively set at 5 mL/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 CO₂ with Agilent 6980N gas chromatograph (GC) equipped with thermal conductivity detector (TCD). The thermal regeneration of adsorbent was carried after CO₂ adsorption reaching equilibrium by flushing the reactor with pure N₂ until the CO₂ 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 CO₂ feed (i.e. dry and wet conditions), adsorption and desorption temperatures and regeneration cycle. Effect of N₂ feed condition during pretreatment step (before adsorption process) was also studied for PABP.
Figure 1: Setup for chloroacetylation and PZ functionalization: 1) Nitrogen gas cylinder  2) Reaction flask  3) By-product trap  4) Solvent flask

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$_{CH_3}$) and the sum of integral intensities of H2, H3, H4, H5, H6, and H6' protons (I$_{H2-H6'}$) 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 of PABP
The PABP adsorbent was chemically synthesized with two steps as mentioned in the previous section. Figure 5(A) shows the first step when chloroacetyl 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-) 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 CABB. 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 CABB are given in Table 1.

![Figure 5: Synthesis of PABP (A) chloroacetylation of BP and (B) PZ functionalization](image)

![Figure 6: IR spectra of (A) CABB and (B) PABP](image)

### Table 1: Elemental analysis of BP, CABB, and PABP

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>C (mmol/g)</th>
<th>Average C ± SD (mmol/g)</th>
<th>N (mmol/g)</th>
<th>Average N ± SD (mmol/g)</th>
<th>% DD</th>
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<tr>
<td>BP</td>
<td>38.15</td>
<td>38.32 ± 0.16</td>
<td>5.64</td>
<td>5.65 ± 0.01</td>
<td>94</td>
<td>96 ± 1.3</td>
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<td>38.47</td>
<td>38.32 ± 0.16</td>
<td>5.65</td>
<td>5.65 ± 0.01</td>
<td>97</td>
<td>96 ± 1.3</td>
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<td></td>
<td>38.35</td>
<td>5.65</td>
<td>N/A</td>
<td>N/A</td>
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<tr>
<td>CABB</td>
<td>37.40</td>
<td>37.58 ± 0.31</td>
<td>4.61</td>
<td>4.60 ± 0.02</td>
<td>N/A</td>
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<tr>
<td></td>
<td>37.39</td>
<td>4.61</td>
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<tr>
<td></td>
<td>40.33</td>
<td>5.97</td>
<td>N/A</td>
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<tr>
<td>PABP</td>
<td>40.38</td>
<td>40.33 ± 0.04</td>
<td>5.96</td>
<td>5.96 ± 0.02</td>
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<tr>
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#### 3.3 CO$_2$ Adsorption study

BP was initially used to establish the optimal conditions for CO$_2$ adsorption (i.e. CO$_2$ feed condition and 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 CO₂ feed as was used for CO₂ adsorption. The breakthrough curves obtained at 298, 318, and 333 K are shown in Figure 8. The CO₂ adsorption capacities of 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 CO₂ adsorption capacity was temperature dependent decreasing from 0.2969 to 0.2514, and 0.1215 mmol CO₂/g adsorbent as temperature increased from 298 K to 318 K and 333 K. Effect of temperature showed exothermic nature of CO₂ adsorption which an increase of temperature corresponded to an increase of dissociation rate constant of CO₂ 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 CO₂ desorbed to CO₂ 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 304 K.

![Figure 7: Breakthrough curves for CO₂ adsorption capacity of BP in dry and wet CO₂ feeds](image)

![Figure 8: Breakthrough curves for CO₂ adsorption capacity of BP at different adsorption temperatures](image)

![Figure 9: CO₂ adsorption capacity of BP at different adsorption temperatures](image)

![Figure 10: CO₂ desorption capacity of BP at different desorption temperatures](image)

3.3.4 Stability test of biopolymer

Adsorption-desorption efficiency of BP after repeated use was performed at the optimal condition (i.e. wet N₂ 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 CO₂/g adsorbent. The desorption capacity was also dropped from 71 % to 61 % after the second. The remaining CO₂ left on the BP active surface after the first cycle possibly reduced the availability of active sites for CO₂ during the second cycle. In conclusion, BP adsorption-desorption reactivity was considered not stable if used repeatedly for CO₂ adsorption under prolonged thermal desorption and atmospheric conditions.
3.3.5 Effect of N₂ pretreatment condition on PABP

The optimal CO₂ adsorption conditions (i.e. wet N₂ pretreatment at 298 K, dry CO₂ feed, 298 K adsorption, and 403 K desorption) obtained previously for BP was also used to test CO₂ adsorption efficiency for PABP. However, the CO₂ adsorption capacity of PABP obtained at these conditions was only 0.1441 mmol/g adsorbent as shown in Figure 12. Generally, a stoichiometric adsorption of CO₂ to amino group is 0.5 mole CO₂/mole nitrogen, but in this case, the dynamic stoichiometric adsorption of PABP obtained was a lot lower at only 0.037 mole CO₂/mole nitrogen. In order to improve CO₂ adsorption capacity of PABP, it was decided to vary N₂ pretreatment condition by running the adsorption at 298 K with dry N₂ pretreatment and 298 and 378 K with both wet and dry N₂ pretreatment. Also in Figure 12, the dynamic CO₂ 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 N₂ and 378 K conditions. The highest capacity of 0.2211 mmol/g adsorbent was found when adsorption was carried out with dry N₂ 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 nitrogen at 378 K and then adsorption with dry CO₂ at 298 K. The highest CO₂ adsorption capacity was 0.2211 mmol/g adsorbent, lower than BP and the dynamic stoichiometry of PABP was 0.037 mole CO₂/mole nitrogen, which was very low. To improve higher percentage of PABP, it is recommended to perform in the homogeneous phase reaction, which is current research.

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