Study of Biopolymer Modified with Arginine for CO$_2$ Adsorption

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Greenhouse gases (GHG) are not only carbon dioxide, but also methane, nitrous oxide, ozone, etc. Carbon dioxide is most concerned because it is the largest amount is mainly released into the atmosphere by anthropogenic activities, especially burning of burden fossil fuels for energy since industrialzation age. Carbon dioxide emission reduction is a global. A new type of adsorbent for carbon dioxide adsorption synthesized from biopolymer and amino acid, arginine was studied. Biopolymer-arginine was produced by reacting amino groups of biopolymer with carboxylic group of arginine.There were three effects studied to improve the degree of substitution, i.e. mole ratio of CA to biopolymer, reaction time, and mole ratio of arginine to biopolymer. The chemical structure and physical properties of biopolymer-arginine were characterized by Fourier transform infared, liquid chromatography, thermal gravimetric analysis. Result showed various degree of substitution from 5.21 to 76.41 %.

1. Introduction

Emission of GHG is a major environmental concern. The problem is worldwide and affects all living things on Earth. The greenhouse gases in the Earth's atmosphere are mainly composed of water vapor (H$_2$O), carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O), chlorofluorocarbons (CFC) and ozone (O$_3$). Among these gases, CO$_2$ is emitted into atmosphere by human activities such as food cultivation, coal mining, oil drilling, etc. According to the Kyoto Protocol and international commitment, industrialized and developed countries have to find the ways to reduce emission of CO$_2$, so that global warming and climate change can be managed. To deal with CO$_2$ emission, CO$_2$ capture and must be established.

Nowadays, there are various technologies such as absorption, adsorption, membrane separation, cryogenic separation, and chemical-looping combustion to capture CO$_2$ from industries. Carbon dioxide absorption using amine solvents is commercially available. However, there are drawbacks such as high operating cost and corrosion. Adsorption with solid adsorbents can also be used, but adsorbent still cannot cope with high concentration of CO$_2$ adsorption capacity and it has low selectivity to CO$_2$ capture. To increase CO$_2$ capture capacity of adsorption technique, effective amines are often impregnated onto a solid sorbent.

The objective of this research was to synthesize an adsorbent for CO$_2$ adsorption using an amine grafted on a biopolymer solid adsorbent, which is naturally available and an environmentally friendly material with very low cost. The reaction of biopolymer-arginine showed in Figure 1.
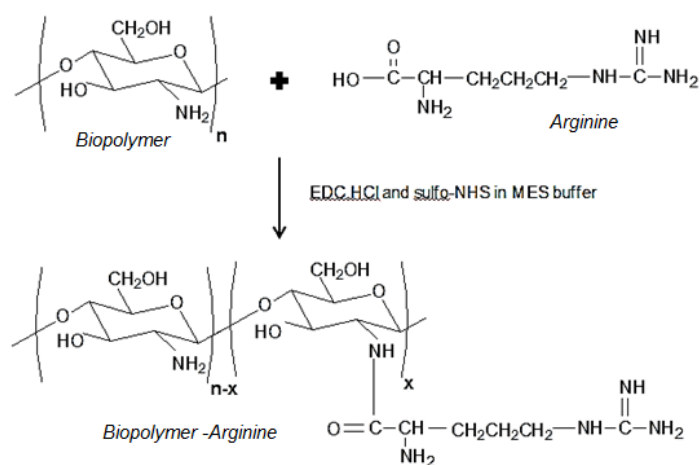
Figure 1 : Scheme of biopolymer-arginine using EDC.HCl and sulfo-NHS as coupling agents in MES buffer solution

2. Materials and Methods

2.1 Materials

Biopolymer flake (Mw 200 kDa) was purchased from Bio21 Co.,Ltd (Thailand). Purified biopolymer (PB) was created by using method (Miya *et al.,* 1980). 2-(N-morpholino) ethanesulfonic acid sodium salt (MES) (lab grade) was purchased from Calbiochem (Bangkok, Thailand). Arginine (AR) was purchased from Sigma-Aldrich. Coupling agents (CA) consist of 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimidehydrochloride (EDC.HCl) (purity 99%) and N-hydroxysulfosuccinimide sodium salt (sulfo-NHS) (purity 98%) were purchased from Suzhou Highfine Biotech Co.,Ltd. (China). Sodium hydroxide (NaOH) (lab grade) was purchased from Merck (Bangkok, Thailand). Sodium borohydride (NaBH$_4$) and Hydroxylamine (NH$_2$OH) were purchased from Labchem (Bangkok, Thailand). Hydrochloric acid (HCl, AR grade) was purchased from RCI Labscan (Bangkok, Thailand).

2.2 Purification of PB

Deacetylation was used to obtain a high purity of biopolymer by removing acetyl functional group (COCH$_3$). 100 g of PB and 0.5 g of NaBH$_4$ were immersed in 2 L of 50 % w/w NaOH solution for 1 h at 120 ºC in an auto-clave. After complete, the product was filtered and dialysed with water until the washed water was neutralized. The PB was dried at 80 ºC overnight in a vacuum oven and kept in dry place (Miya et al., 1980).

2.3 Synthesis of PB-AR
2.3.1 Effect of CA to PB

Mole ratios of PB to CA were varied, 1:1, 1:2, and 1:3 while mole ratio of PB/AR kept constant at 1:1. CA was EDC.HCl and sulfo-NHS. When the CA ratio was one, it meant 1 mole of EDC.HCl and 1 mole of sulfo-NHS, and ratio was two meant 2 moles of EDC.HCl and 2 moles of sulfo-NHS. For synthesis of modified biopolymer using CA, 0.25 g of PB was dissolved in 200 mL of MES buffer solution (25 mM) and the solution was adjusted for pH to 5.0 with an addition of 0.1 M HCl solution and left for activated AR. For activated AR, the carboxyl group of 0.271 g AR was activated for 2 h in 300 mL of MES buffer solution with the CA (EDC.HCl and sulfo-NHS) at a fixed molar ratio of PB/ AR /EDC.HCl/ sulfo-NHS of 1:1:1:1. The resultant mixture was prepared by adding the activated AR solution into the PB r solution and the reaction was allowed to take place at ambient temperature with stirring for 48 h. The final product was opaque solution, which contained white precipitate). The reaction of final product was quenched by adding of 0.259 g hydroxylamine at a fixed molar ratio of PB /hydroxylamine of 1:1, and the mixture pH was adjusted to 8.0 with 0.1 M NaOH solution. The collected products were taken

to a stirred cell for dialysis. Before dialyzing process, a part of the permeate solution (clear solution) was taken for determination of degree of substitution (%DS) of AR in PB via unreacted AR with High-performance liquid chromatography (HPLC). The collected products were dialyzed using distilled water in a stirred cell with molecular weight cut off (MWCO) of 1000 to eliminate molecules smaller than 1,000 dalton, i.e. unreacted AR and salt, CA, until the pH of permeate solution was neutral (pH7). After dialyzing, the retentate solution, which was still opaque containing unreacted PB and PB–AR was freeze-dried. The final product was solid, named PB-AR which was taken to be analysed by Fourier transform infrared spectroscopy (FT-IR).

2.3.2 Effect of reaction time
This effect used steps same effect of CA to PB at a fixed condition of the molar ratio of PB/AR/CA of 1:1:1 but varied reaction time 24, 48, and 72 h.

2.3.3 Effect of AR to PB
The mole ratio of AR was varied against PB, 1:1, 2:1 and 3:1. At a fixed condition of the molar ratio of PB/CA of 1:1 with reaction time 72h. All steps in this effect same effect of CA to PB.

2.4 Characterization
Infrared spectra of PB and PB-AR samples were recorded using FT-IR (Nicolet/NEXUS 670 FTIR, Massachusetts, USA). A powder sample, which was dried in an oven for 2 days, was mixed with KBr in a ratio of 3:100 (w/w) in a mortar. The sample and KBr was thoroughly ground until mixed well. The mixture was then pelletized by hydraulic pressure. The IR spectrum was obtained with DTGS detector using 4 resolutions and 64 numbers of scan. Degrees of substitution of PB -AR were determined by taking the permeate solutions from the stirred cell to analyze by high-performance liquid chromatography (HPLC) (SHIMADZU LC-20AD, Kyoto, Japan). The unreacted AR in the permeate solution was determined. The mobile phase consisting of methanol/acetonitrile/water at a volume ratio of 45:45:10. HPLC was connected to photodiode array detector (PDA) which was set at $\lambda= 190$ nm for the detection, Column (Inertsil ODS-3) with 5 um particle size and dimension of 250 mm x 4.6 mm was operated at 40 °C and the flow rate of 0.9 mL/min. The peak area of sample was measured and compared with the standard curve of AR in which the peak areas of AR were plotted against concentration, 0.1, 0.5, 1, 2, 3, 4, and 5 %wt/v.Thermal degradation of samples was monitored using a thermal analyser (METTLER TOLEDO - TGA/DSC Mode, Ohio,USA).0.03 g of sample was heated in alumina pan from ambient temperature (25 °C) to 600 °C at a constant heating rate of 10 °C/min under a nitrogen atmosphere.

3. Results and Discussion

3.1 Purification of PB
Degree of deacetylation of PB determined by FT-IR (Figure 2) and titration method (Figure 3). The PB gave spectrum quite similar to the purchased PB. However, the decrease of characteristic peak intensity at 1655 cm^{-1} corresponding to amide band I, which was used to determine the residual N-acetylglucosamine (CONH). The result of degree of deacetylation is 96.80 %. To confirm the degree of deacetylation of PB, titration was used. The degree of deacetylation calculated from the two equivalent points is 96.05 %.
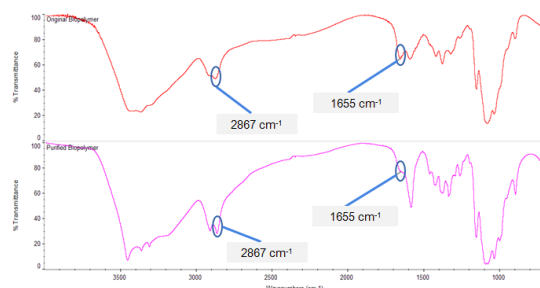

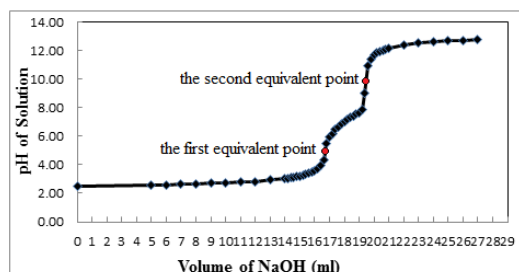Figure 2 : Comparison of infrared spectra of original biopolymer and PB.

Figure 3 : Titration curve for determining degree of deacetylation of PB

3.2 Characterization of PB -AR

3.2.1 Effect of CA to PB

The role of CA is to facilitating a change of carboxylic group of AR to amides by bonding with amine group of PB (Hermanson, 2008). The first CA, EDC.HCl reacts with carboxylic acid in AR to form an active ester intermediate, which is not stable. The second CA, Sulfo-NHS replaces EDC.HCl in the intermediate, which makes the new intermediate more soluble, stable, and available for a reaction with amine. FT-IR spectrum of PB exhibits the characteristic bands of C=O stretching of the amide I at 1667 cm-1, NH2 bands of PB at 1600 cm-1, and C-O stretching vibrations of the pyranose ring at 1083-1038 cm-1. For AR, the absorption band at 1645 cm-1 is assigned to the guanido group, and the band at 1419 cm-1 is attributed to COO- symmetric bending. The C-C-N asymmetric bending and COO-scissoring modes are found at 1131 and 790 cm-1, respectively (Figure 4). If PB bond with AR, it can be seen that there appear characteristic bands of AR around 1630 cm-1 (guanido group). The new band around 1530 cm-1 is most likely due to an amide bond linking between PB and AR that showed in Figure 5. For calculating %DS, percentage of unreacted AR was determined by comparing the peak area with the AR standards curve and the result are shown in Table 1.

3.2.2 Effect of Reaction Time

The purpose of this study was to find the most suitable reaction time that gives the highest %DS. The condition used was at the mole ratio PB / AR / CA of 1:1:1. The results from the infrared spectra shown in Figure 6 illustrate the increase of peak intensity as the reaction time increases. The HPLC analysis shown in Table 1 determine the highest %DS of 76.41 % at a reaction time of 72 h.

3.2.3 Effect of AR to PB

Arginine in PB /AR/CA was varied at 1:1:1, 1:2:1, and 1:3:1. The experiment was studied at a reaction time of 72 h. The infrared spectra are shown in Figure 7 and %DS analyzed by HPLC method, is shown in Table 1. The %DS was independent of the mole ratio of AR to PB.
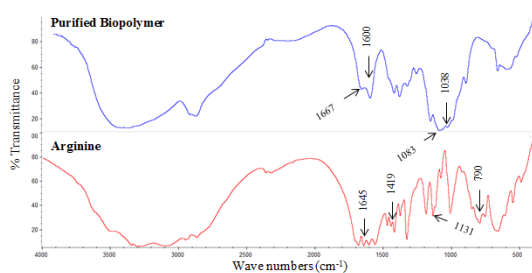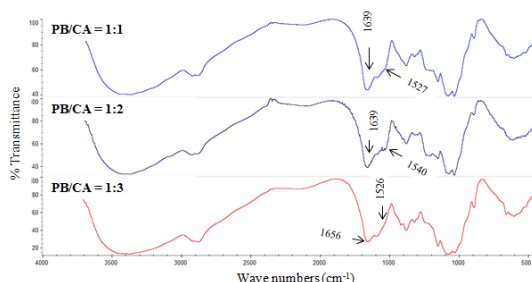

Figure 4 : Infrared spectra of PB and AR.

Figure 5 : Infrared spectra of PB/AR/CA used at ratio 1:1:1, 1:1:2 and 1:1:3 with reaction time of 48 h.
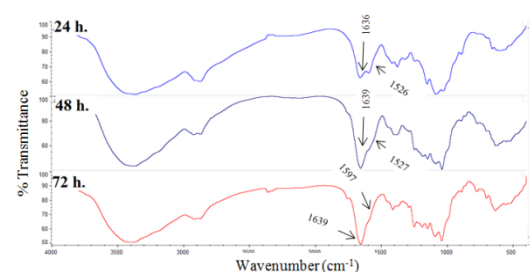

Figure 6 : Infrared spectra of PB-AR at reaction time 24 h, 48 h and 72 h, while the ratio of PB/AR/CA was constant at 1:1:1.
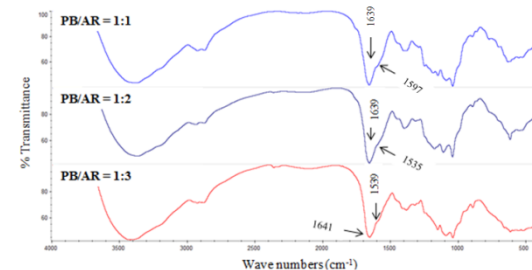

Figure 7 : Infrared spectra of PB-AR used at ratio 1:1, 1:2 and 1:3, while PB/CA was kept constant at 1:1 at a reaction time 72 h.

Table 1 : Degree of substitution of PB-AR from three effects studied

Molar ratio			Reaction time (h)	% DS	SD
PB	AR	CA			
1	1	1	48	34.84	0.060
1	1	2	48	7.04	0.171
1	1	3	48	5.21	0.131
1	1	1	24	29.10	0.111
1	1	1	72	76.41	0.260
1	2	1	72	69.69	0.331
1	3	1	72	72.25	0.176

3.2.4 Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis of PB- AR obtained from the highest %DS, i.e.at the ratio of PB to AR to CA of 1:1:1 at reaction time 72 h is shown in Figure 8.
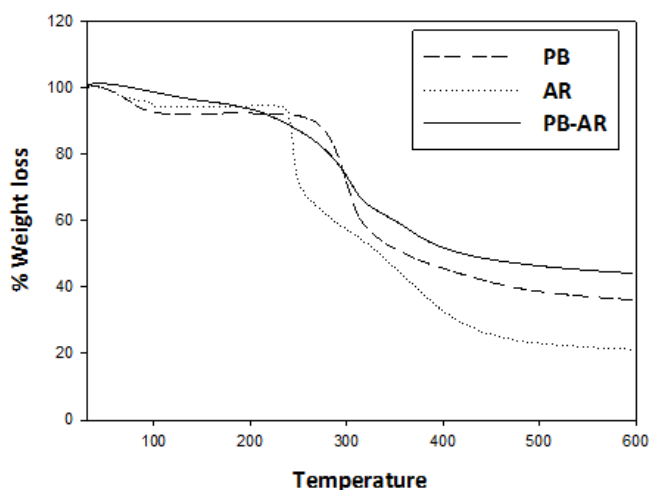

Figure 8 : Thermograms of a) PB, b) AR and c) PB-AR with 76.29 %DS, from 25 °C to 600 °C at a constant heating rate of 10 °C/min under a nitrogen atmosphere.

The thermogram of PB indicated two weight loss stages. The first stage corresponds to the loss of bound water in the sample. The second one corresponds to depolymerisation of polymeric chains, decomposition of pyranose rings through dehydration and degradation of the samples (Bo Xiao *et al.*, 2011). For the thermogram of AR, it indicated three weight loss stages, the first stage corresponds to the loss of loosely bound water in the samples. The second stage corresponds to the guanido group. The third stage corresponds to the degradation of main carbon chain (Mallik and Kar, 2005). PB - AR indicated two weight loss stages. The first stage ranging between 30.21 °C and 150.34 °C (extrapolated temperature 100.52 °C) was accounted for 6.23 % loss in weight which corresponds to the evaporation of adsorbed and bound water. The second one which started at 220 °C and continued up to 400 °C (extrapolated temperature 352.68 °C) was accounted for about 39.8 %, the degradation of PB -AR together with the breakage of the amide linkage of PB-AR (Bo Xiao *et al.*, 2011).

4. Conclusion

The purpose of this research was to synthesize a new type of adsorbent for CO_2 adsorption by grafting amine function of AR on PB. The best condition that gave the highest %DS was the mole ratio of PB /AR/CA of 1:1:1 with reaction time 72 h. The optimal %DS was 76.41 %.

Acknowledgement

References

Hermanson G.T., 2008, Bioconjugate techniques, Elsevier, 19-220

Mallik T., Kar T., 2005, Growth and characterization of nonlinear optical L-arginine dihydrate single crystals, Journal of Crystal Growth, 285, 178–182

Miya M., Reikichi I., Susumu Y. and Seiichi M., 1980. I.R. spectroscopic determination of CONH content in highly deacylated chitosan, International Journal of Biological Macromolecules, 323-324

Xiao B., Wan Y., Zhao M., Liu Y., Zhang S., 2010, Preparation and characterization of antimicrobial chitosan-N-arginine with different degrees of substitution, Carbohydrate Polymers, 83, 515-523