

CO₂ Adsorption on Polybenzoxazine Grafted Activated Carbon: Effects of Amine Precursor

Katipot Inkong^a, Pramoch Rangsunvigit^{a,b,*}, Thanyalak Chaisuwan^{a,b},
Santi Kulprathipanja^c

^aThe Petroleum and Petrochemical College, Chulalongkorn University, 254 Soi Chulalongkorn 12, Phayathai Rd., Pathumwan, Bangkok 10330, Thailand

^bCenter of Excellence on Petrochemical and Materials Technology, 7th floor, Chulalongkorn University Research Building, Soi Chulalongkorn 12, Phayathai Rd., Bangkok 10330, Thailand

^cUOP, A Honeywell Company, Des Plaines, Illinois, U.S.A. 60017
Pramoch.r@chula.ac.th

CO₂ adsorption of polybenzoxazine-modified activated carbon prepared by grafting various polybenzoxazine (PBZ) via ring-opening polymerization of different amine precursors was investigated. Benzoxazine monomer (BZ) was synthesized from phenol, paraformaldehyde, and hexamethylenediamine (HMDA) or triethylenetetramine (TETA). The PBZ loading was varied by different benzoxazine monomer solution concentrations from 0.1 to 0.5 g/L. CO₂ adsorption isotherms were obtained at 35 °C, 50 °C, and 75 °C. Adsorbents were characterized by TG-DTA, FT-IR, and surface area and pore size analyses. The amount of PBZ grafted on activated carbon was determined by UV-Vis spectroscopy. The results showed that the CO₂ adsorption capacity of the PBZ grafted activated carbon was improved due to the synergistic effects between physical and chemical adsorption. When the adsorption temperature increased, the CO₂ adsorption capacity of the grafted adsorbent decreased because the physisorption was more dominated than the chemisorption. The decrease in the capacity due to the temperature increase was more pronounced with the unmodified activated carbon. Using TETA resulted in high CO₂ adsorption than using HMDA. It was likely that using TETA to synthesize PBZ contained secondary amine and tertiary amine whereas only tertiary amine was found in PBZ synthesized by HMDA. The secondary amine can directly react with CO₂, but the tertiary amine has only van der Waals force to attract CO₂. CO₂ adsorbed onto PBZ/AC was completely desorbed by heating at 120 °C for 24 h. There was no significant change in the CO₂ adsorption capacity of the regenerated adsorbents

1. Introduction

Nowadays, global warming is one of the most critical issues, which results from the greenhouse gas (GHG) emissions in the atmosphere. Carbon dioxide (CO₂) is the major GHG and considered as the dominant contributor to the climate change (Cox et al., 2000). The main source of CO₂ emissions arise from the combustion of fossil fuel. Therefore, CO₂ removal from flue gases is considered as the key solution to CO₂ emission problem (Keramati and Ghoreyshi, 2013).

One of the methods to solve the problem is CO₂ capture and storage (CCS). Among the CCS, the simplest is the post-combustion capture. A number of separation technologies could be employed with post-combustion capture are absorption, adsorption, membrane separation, and cryogenic separation (Pires et al., 2011). In recent years, many researches have been focused on the development of adsorption based CO₂ capture technologies. A variety of solid adsorbents has been developed and used for CO₂ capture. Lu et al. 2008 concluded that the adsorbent for competitive CO₂ capture by carbon nanotubes, activated carbons, and zeolites. Sayari et al. 2011 concluded the adsorbent for CO₂ adsorption on flue gas treatment including activated carbon, zeolites, mesoporous silica, carbon nanotube, metal-organic frameworks (2011). However, these adsorbents have limitation of their own. To overcome the limitation, the amine-functionalized adsorbents

have been investigated. Knowles et al. (2005) used aminosilane grafted on hexagonal mesoporous silica (HMS) and amorphous silica (S2). CO₂ adsorption capacity of all aminopropyl-functionalized silica materials exhibited higher adsorption capacity than silica (S2 and HMS), and the aminopropyl groups indeed enhanced the CO₂ adsorption capacity. Changa et al. (2009) used various aminosilanes grafted on SBA-15. The grafted aminosilanes on SBA-15 exhibited high adsorption capacity for CO₂ under moist as well as dry conditions. CO₂ adsorption capacity of the samples was found to be in the order of tri- > di- > mono. Then, Ko et al. (2011) studied the effect of amine type for CO₂ capture by using primary (1°), secondary (2°), and tertiary (3°) amine grafted on surface SBA-15. The CO₂ adsorption capacity for the amine type follows the sequence: 1°amine > 2°amine > 3°amine. Xu et al. (2003) used a polyethyleneimine (PEI) impregnated on MCM-41. At the PEI loading of 50 wt% in MCM-41, the CO₂ adsorption capacity was 30 times higher than the MCM-41. PBZ is a very attractive polymer for the CO₂ adsorption due to its high affinity with CO₂. Because of different amines and large amount of amines, PBZ can adsorb CO₂ via different mechanisms and enhances CO₂ adsorption performance (Ishida and Agag, 2011). In this work, Activated carbon (AC) was functionalized with BZ via ring-opening polymerization to enhance CO₂ adsorption capacity. BZ was synthesized from phenol, paraformaldehyde, and HMDA or TETA. Adsorption temperature, type of amine, and loading of PBZ were also investigated to find the optimum condition for CO₂ adsorption.

2. Experimental

2.1 Benzoxazine Monomer Syntheses

The synthesis of the BZ from HMDA (98 %, Aldrich Co., LLC) or TETA (technical grade, 60 %, Aldrich Co., LLC), phenol (99 %, Aldrich Co., LLC) and p-formaldehyde (95 %, Aldrich Co., LLC) was achieved with the 1:2:4 molar ratio. The synthesis of BZ started by first dissolving HMDA or TETA in dioxane (99.95 %, RCL Labsan Limited) in a glass bottle and stirring until a clear solution was obtained. Phenol and p-formaldehyde were also dissolved in dioxane, and stirred until a clear solution was obtained before slowly dropping the HMDA or TETA solution into the mixture. The mixture was continuously stirred in an ice bath under 10 °C for 1 h until a transparent yellow viscous liquid was obtained.

2.2 Adsorbent Preparation

AC (supported by Carbokarn Co., Ltd.) was ground and sieved to obtain a particle size of 20 - 40 mesh. Then, the AC was dried at 120 °C for 24 h. The BZ solution (0.1 - 0.5 g/L) was added to AC. The solid to liquid ratio was 1 g of ACs to 20 mL of BZ solution. The AC together with the BZ solution was stirred at 180 rpm and 80 °C for 2 h under reflux condition, before filtering and polymerization to obtain PBZ grafted AC.

2.3 Characterization

The structure of BZ was characterized by Nicolet/Nexus 670 FTIR instrument. Perkin-Elmer/DSC 7 was used to determine the cure temperature of benzoxazine monomer. The amounts of PBZ impregnated on AC were determined by a Shimadzu/UV-1800 UV-Vis Spectrophotometer (at $\lambda_{\max} = 277$ nm). Thermal stability of adsorbents was investigated by TG-DTA (Perkin-Elmer/Pyris Diamond). Surface area of adsorbents was measured by a surface area and pore size analysis (Quantachrom/Autosorb1-MP).

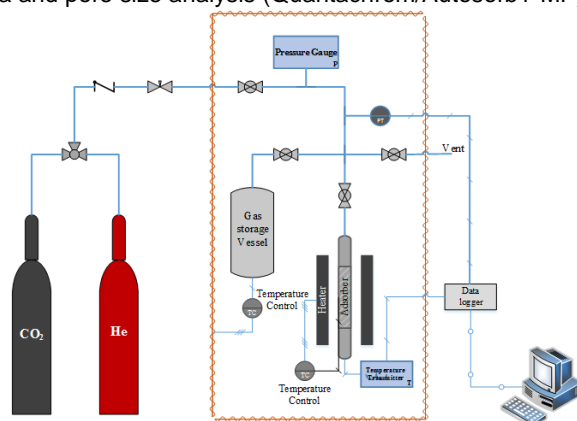


Figure 1: schematic of experimental setup

2.4 CO₂ Adsorption Measurement

One gram of an adsorbent was loaded into the adsorption chamber. He gas (99.999 %, Praxair Inc.) was used to measure the system volume by expansion principle. The adsorption processes were carried out using high

purity CO₂ gas (99.99 %, Praxair Inc.). Effects of adsorption temperature were investigated by varying the temperature from 35 to 75 °C within a pressure range of 0 - 1.1 atm.

2.5 Regeneration

After adsorption, the regeneration of spent adsorbent was carried out by taking the adsorbent out of the reactor for heating at 120 °C for 24 h. to remove adsorbed CO₂ and volatile components. These adsorption/desorption cycles were repeated at least three times.

3. Results and Discussion

3.1 Benzoxazine Monomer Characterizations

The spectra of BZ(TETA) and BZ(HMDA) are shown in Figure 2(a). The asymmetric stretching of C–O–C at 1,254 and 1,224 cm⁻¹, the asymmetric stretching of C–N–C at 1,119-1,118 cm⁻¹ and the CH₂ wagging of oxazine at 1,367 - 1,332 cm⁻¹ can be observed. Additionally, the stretching of ortho-substituted benzene ring observed at 754 cm⁻¹ and out of plane bending vibrations of C–H at 924 - 910 cm⁻¹ are clearly present, indicating that BZ is incorporated into the structure (Thayalak et al., 2010). The curing temperature of BZ was investigated by DSC. Figure 2(b) shows the DSC thermogram of BZ. The DSC thermogram of BZ(TETA) shows the exotherm peak starts at 152 °C with a maximum peak at 184 °C, while the exothermic peak of BZ(HMDA) is starting at 124 °C with the maximum peak at 196 °C, attributed to the polybenzoxazine by ring-opening polymerization. After BZ is fully cured, the exothermic peak disappears, suggesting that the BZ is completely polymerized.

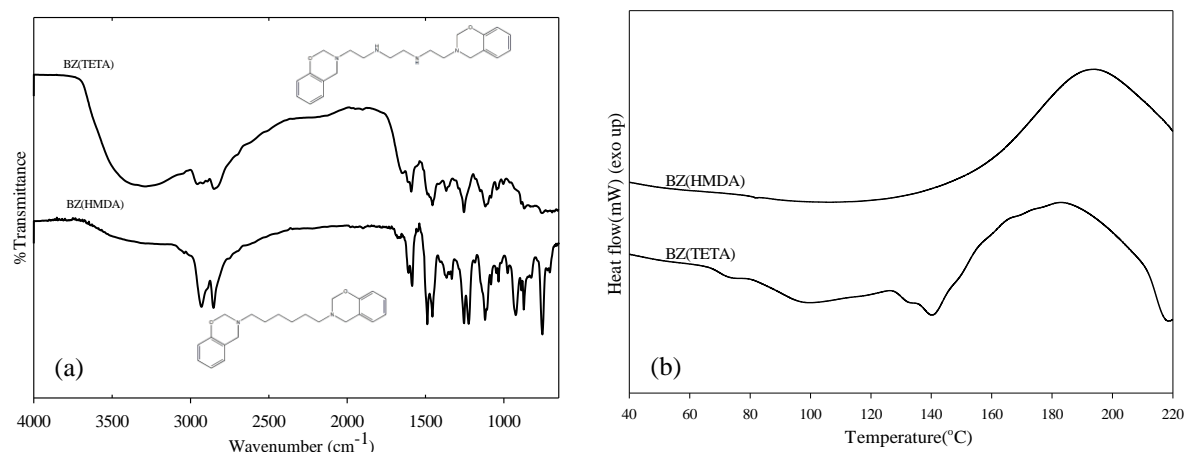


Figure 2: (a) FTIR spectra of BZ(TETA) and BZ(HMDA) and (b) DSC thermogram of the BZ(TETA) and BZ(HMDA)

3.2 Adsorbent Characterization

Table 1: Amounts of PBZ impregnated on AC and surface area of adsorbent

Initial concentration of BZ solution (g/L)	PBZ impregnated on AC (wt% PBZ)	Surface area (m ² /g)
AC	-	1,022
BZ (TETA)	0.1	964
	0.3	958
	0.5	939
BZ (HMDA)	0.1	956
	0.3	945
	0.5	928

The amount of PBZ grafted on the AC is shown in Table 1. Interestingly, the higher concentration of the BZ solution increases the amount of grafted BZ. Figure 3(a) shows the TGA thermograms of PBZ(TETA), PBZ(HMDA), AC, and grafted AC. The AC shows about 7 wt% loss between 100 °C and 250 °C, corresponding to the removal of volatile and moisture. The thermograms of both PBZ(TETA) and PBZ(HMDA) start to lose weight at 250 °C, and the maximum weight loss can be observed between 250 °C and 700 °C, where the decomposition products, like a combination of benzene derivatives, amines, phenolic compounds,

and mannich base compounds, were reported (Hemvichian et al., 2002). The thermograms of modified AC show the weight loss in two steps. The first step is around 100 °C, which is from the removal of volatile and moisture. The second step of the impregnated AC is around 250 °C, which is from the PBZ degradation. Figure 3(b) shows the nitrogen adsorption-desorption isotherms of the adsorbents, which exhibit type I isotherm according to the IUPAC classification. This indicates that the adsorbents exhibit both meso- and microporosity (Pevida et al., 2008). Surface areas of the adsorbents are shown in Table 1. The results show that, after grafting of PBZ on the AC, the BET surface area of the samples confirms that PBZ is successfully introduced on the support (Xu et al., 2003).

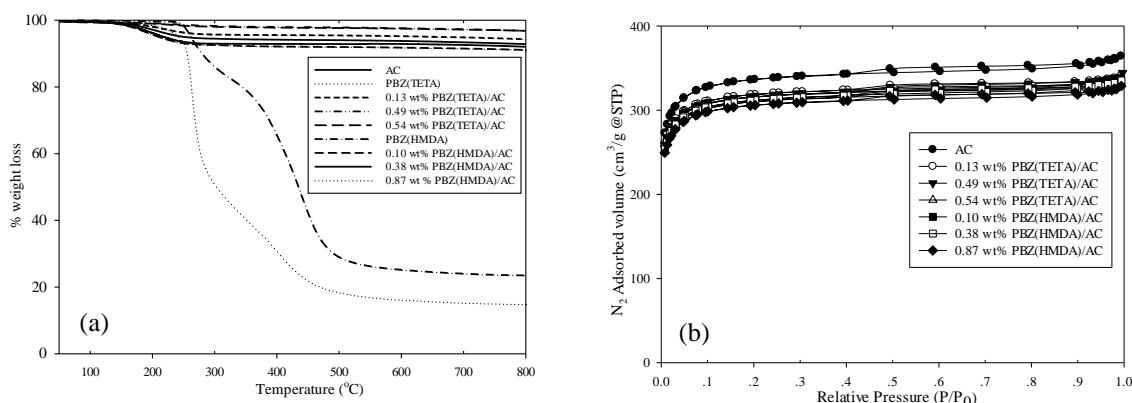


Figure 3: (a) TGA thermograms of PBZ, AC, and modified AC and (b) Nitrogen adsorption/desorption isotherms of AC and modified AC at -196 °C

3.3 CO₂ Adsorption

i) Effect of PBZ loading on CO₂ adsorption

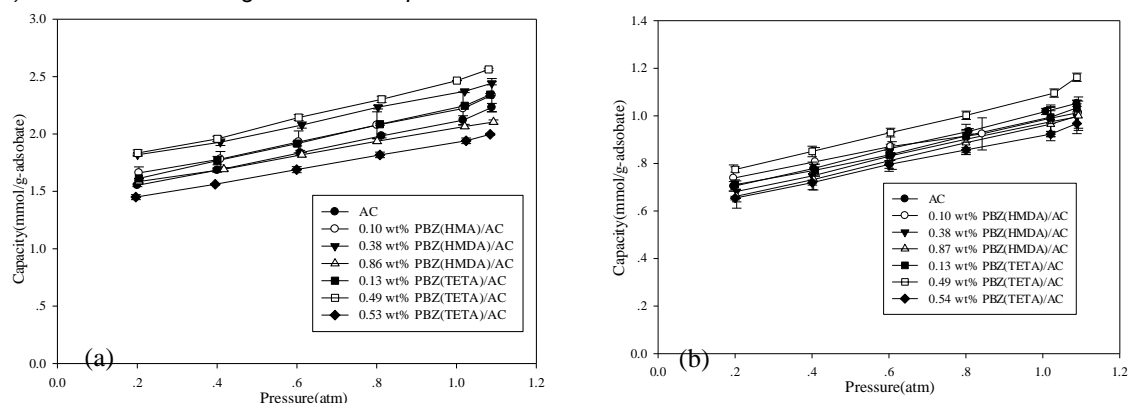


Figure 4: Adsorption isotherms of AC and modified AC at (a) 35 °C and (b) 75 °C

Table 2: CO₂ adsorption capacity of adsorbents at 35 °C, 50 °C and 75 °C and 1 atm

Adsorbent	CO ₂ adsorption capacity (mmol/g adsorbent)		
	35 °C	50 °C	75 °C
Activated Carbon (AC)	2.12 ± 0.04	1.61 ± 0.01	1.02 ± 0.01
0.10 wt% PBZ(HMDA)/AC	2.22 ± 0.14	1.63 ± 0.09	0.99 ± 0.06
0.38 wt% PBZ(HMDA)/AC	2.37 ± 0.01	1.66 ± 0.06	0.98 ± 0.06
0.87 wt% PBZ(HMDA)/AC	2.07 ± 0.02	1.48 ± 0.15	0.96 ± 0.07
0.13 wt% PBZ(TETA)/AC	2.26 ± 0.01	1.72 ± 0.02	0.99 ± 0.03
0.49 wt% PBZ(TETA)/AC	2.46 ± 0.01	1.86 ± 0.04	1.09 ± 0.02
0.53 wt% PBZ(TETA)/AC	1.94 ± 0.02	1.53 ± 0.02	0.92 ± 0.01

The influence of PBZ loading on the CO₂ adsorption of PBZ grafted AC was investigated in the range of 35 - 75 °C and up to 1.1 atm. Figure 4 shows the adsorption isotherms at 35 °C and 75 °C. As observed, all adsorbents show low adsorption capacity at the low pressures. In other words, the adsorption capacity

increases at higher pressures. The CO₂ adsorption capacity at 35 °C, 50 °C and 75 °C and 1 atm is shown in Table 2.

The CO₂ adsorption capacity of both PBZ(TETA) and PBZ(HMDA) grafted AC at 35 °C, 50 °C, and 75 °C shows the same trend. After grafting PBZ(TETA) or PBZ(HMDA) on the AC, the adsorption capacity increases with the increase of the amount of PBZ. The CO₂ adsorption capacity reaches the maximum capacity with the 0.49 wt% and 0.38 wt% of PBZ(TETA) and PBZ(HMDA), respectively. However, the adsorption capacity decreases when the amount of grafted was higher than 0.49 wt% PBZ(TETA) or 0.38 wt% PBZ(HMDA).

The results show that the CO₂ adsorption capacity of 0.13, 0.49 wt% PBZ(TETA)/AC and 0.10, 0.38 wt% PBZ(HMDA) is higher than that of the AC, whereas the surface area of PBZ grafted on the AC decreases (as shown in Table 2). The increase in the CO₂ adsorption capacity of the grafted AC is because of the affinity between CO₂, a Lewis acid, and -NH- group, a Lewis base, in PBZ structure. Therefore, a combination of physical and chemical adsorption may result in the significant increase in the CO₂ adsorption. The adsorption capacity of 0.54 wt% PBZ(TETA)/AC and 0.87 wt% PBZ(HMDA) has lower capacity than the AC may be due to PBZ blocks the pore size of AC, substantiated by the decrease in the surface area.

ii) Effect of amine type on CO₂ adsorption

Table 2 shows the effect of amine precursor to synthesize BZ. The results show that the CO₂ adsorption capacity of PBZ(TETA) is higher than PBZ(HMDA) because of the different amine type in PBZ after polymerization. It was likely that using TETA to synthesize PBZ contains 2° amine and 3° amine. The 2° amine can react directly with CO₂ to produce carbamates through the zwitterionic mechanism and also adsorb CO₂ by electrostatic or van der Waals forces. In contrast, using HMDA contained only 3° amine. The 3° amine cannot react with CO₂ directly without H₂O. In this study, the CO₂ adsorption test was carried out under dry condition; therefore, CO₂ is adsorbed on tertiary amine through electrostatic or van der Waals forces only (Ko et al., 2011)

iii) Effect of temperature on CO₂ adsorption

Figures 6(a) and 6(b) show the effects of adsorption temperature on the CO₂ adsorption of PBZ-grafted AC and AC. The corresponding CO₂ adsorption capacity is listed in Table 2. It can be observed that the CO₂ adsorption capacity decreases with the increase in the operating temperature. It is likely that PBZ, a thermosetting polymer is produced from BZ by curing reaction, has a three dimensional structure that cannot be changed. Hence, when the adsorption temperature increases, PBZ cannot move to adsorb CO₂. As the result, CO₂ adsorption capacity decreases. It further implies that the physisorption is more dominant than the chemisorption or the adsorbent is predominantly determined by the thermodynamic effect rather than the kinetic effect. In the contrary using PEI, which is a thermoplastic, as the temperature is increased, PEI becomes more flexible and CO₂-affinity sites are more exposed to CO₂; thus, CO₂ adsorption capacity increases (Wang et al., 2012). Another reason for the decrease in the capacity is explained by the interaction between CO₂ and tertiary amine. Because the 3° amine attaches with CO₂ by van der Waals forces, the van der Waals forces can be broken easily by increasing the temperature.

3.4 CO₂ Adsorption after Regeneration

Figure 5 shows the CO₂ adsorption isotherms at 50 °C of regenerated samples of 0.49 wt% PBZ(TETA)/AC and 0.38 wt% PBZ(HMDA)/AC. During the three cycles, the CO₂ adsorption capacity of the 0.49 wt% PBZ(TETA)/AC and 0.38 wt% PBZ(HMDA)/AC is not significantly changed, confirming the reproducibility and stability of the material.

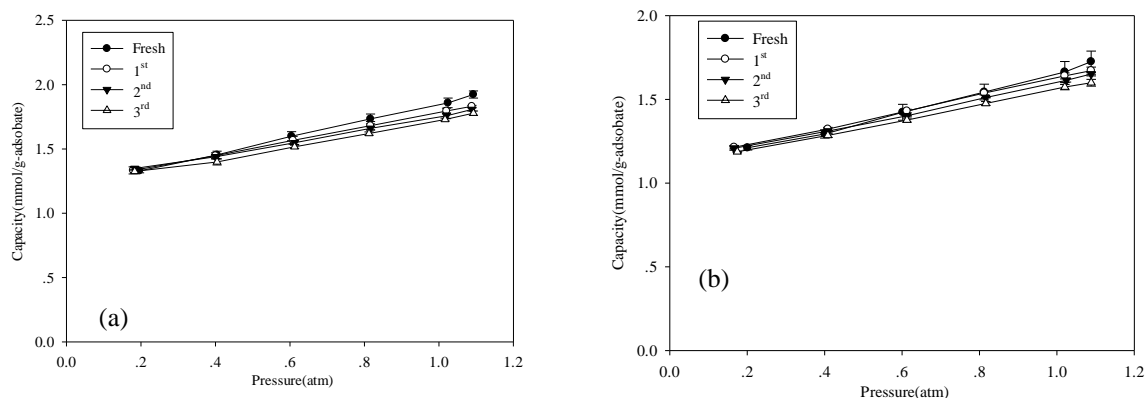


Figure 5: CO₂ adsorption isotherms at 50 °C of (a) 0.49 wt% PBZ(TETA)/AC and regenerate sample and (b) 0.49 wt% PBZ(HMDA)/AC and regenerate sample

4. Conclusions

The grafting of PBZ improved the CO₂ adsorption capacity due to the synergistic effects between physical and chemical adsorption. The increase in the adsorption temperature reduced the CO₂ adsorption capacity due to the strong influence of physisorption. Using TETA as an amine precursor resulted in the higher CO₂ adsorption capacity than using HMDA as the precursor to synthesize BZ because of the different amine types in the PBZ structure. The results also showed that the CO₂ adsorption capacity depended on the amount of PBZ loading, and the 0.49 wt% PBZ(TETA) or 0.38 wt% PBZ(HMDA) loadings were the optimum amounts. The decrease in the adsorption capacity was observed when the AC was loaded with PBZ(TETA) or PBZ(HMDA) higher than 0.54 wt% or 0.86 wt% because of the pore filling effect. The CO₂ adsorption capacity of the regenerated adsorbents showed no significant change in the capacity.

Acknowledgements

The authors would like to sincerely thank The 90th Anniversary of Chulalongkorn University Fund and Grant for International Integration: Chula Research Scholar, Ratchadaphiseksomphot Endowment Fund, Chulalongkorn University, Thailand; The Petroleum and Petrochemical College, Chulalongkorn University, Thailand; Center of Excellence on Petrochemical and Materials Technology, Thailand; and UOP, A Honeywell Company, USA, for providing support for this research work.

References

- Chaisuwan T., Komalwanich T., Luangsukrer S., Wongkasemjit S., 2010, Removal of heavy metals from model wastewater by using polybenzoxazine aerogel, *Desalination*, 256, 108–114.
- Changa F.Y., Chao K.J., Cheng H.H., Tan C.S., 2009, Adsorption of CO₂ onto amine-grafted mesoporous silicas, *Separation and Purification Technology*, 70, 87-95.
- Cox P.M., Betts R.A., Jones C.D., Spall S.A., Totterdell I.J., 2000, Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model, *Nature*, 408,184-187.
- Hemvichian K., Laobuthee A., Chirachanchai S., Ishida H., 2002, Thermal decomposition processes in polybenzoxazine model dimers investigated by TGA–FTIR and GC–MS, *Polymer Degradation and Stability*, 76, 1-15.
- Ishida H., Agag T., 2011, *Handbook of Benzoxazine Resins*, Elsevier, New York.
- Keramati M., Ghoreyshi A.A., 2013, Improving CO₂ adsorption onto activated carbon through functionalization by chitosan and triethylenetetramine, *Physica E*, 57, 161-168.
- Knowles G.P., Graham J.V., Delaney S.W., Chaffee A.L., 2005, Aminopropyl-functionalized mesoporous silicas as CO₂ adsorbents, *Fuel Processing Technology*, 86, 1435-1448.
- Ko Y.G., Shin S.S., Choi U.S., 2011, Primary, secondary, and tertiary amines for CO₂ capture: Designing for mesoporous CO₂ adsorbents, *Journal of Colloid and Interface Science*, 362, 594-602.
- Lu C., Bai H., Wu B., Su F., Hwang J.F., 2008, Comparative study of CO₂ capture by carbon nanotubes, activated carbons, and zeolites, *Energy and Fuels*, 22, 3050-3056.
- Pevida C., Plaza M.G., Arias B., Feroso J., Rubiera F., Pis J.J., 2008, Surface modification of activated carbons for CO₂ capture, *Applied Surface Science*, 25, 7165-7172.
- Pires J.C.M., Martins F.G., Alvim-Ferraz M.C.M., Simões M., 2011, Recent developments on carbon capture and storage: An overview, *Chemical Engineering Research and Design*, 89, 1446-1460.
- Sayari A., Belmabkhouta Y., Serna-Guerrero R., Flue gas treatment via CO₂ adsorption, 2011, *Chemical Engineering Journal*, 171, 760-774.
- Wang J., Chen H., Zhou H., Liu X., Qiao W., Long D., Ling L., 2012, Carbon dioxide capture using polyethylenimine-loaded mesoporous carbons, *Journal of Environmental Sciences*, 25 124-132.
- Xu X., Song C., Andresen J.M., Miller B.G., Scaroni A.W., 2003, Preparation and characterization of novel CO₂ “molecular basket” adsorbents based on polymer-modified mesoporous molecular sieve MCM-41, *Microporous and Mesoporous Materials*, 62, 29-45.