Modification of CO₂ Capture Techniques by Carbon Nanotubes: A Review

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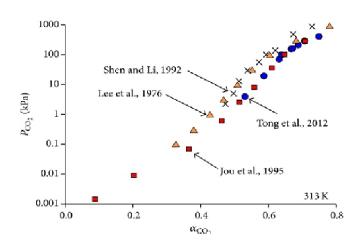
Abstract—The current scenario of global warming has gained international attention towards the research and development of CO_2 capture techniques. In the past decade, a lot of funds and time has been devoted towards developing such techniques which are feasible both financially as well as in terms of environmental standards. A number of adsorption techniques have been developed using polymers but the regeneration cost and the capture capacity has always been a point of concern. In addition, adsorption capacity of polymers has been found to increase significantly upon grafting with carbon nanotubes. Various adsorbents have been developed which upon grafting with carbon nanotubes have shown promising results. In this paper we will be discussing various techniques and their capture capacity along with the enhancement in its capture capacity upon grafting with carbon nanotubes.

1. INTRODUCTION

With the increase in the standard of living, there has been subsequent degradation in the environment. One of the important factors is global warming which continuously poses a threat to the survival of future generations of all living beings. CO₂ plays a major role in in global warming and its current status has alarmed the world. Therefore its capture from either the sources or the environment has a key role in tending to the menace of global warming. Various capture techniques have been investigated such as absorption, adsorption, cryogenics, membranes, and so forth, have been investigated [1-2]. Adsorption techniques such as development of polymer adsorbents shows promising results in the experiments. Further developments by means carbon nanotubes with polymers [3] have significantly increased the adsorption capacity of the polymers. Development of monoethanolamine [4], polyethyleneimine [5], polymer [6], polyaspartamide [7], chitosan tetraethylenepentamine [8] and the enhancement of their CO_2 capture capacity upon grafting with carbon nanotubes has shown tremendous results. Solid sorbents that consist of a supported polymeric amine can have high sorption capacities, fast adand desorption cycles and low energy consumption [9-10]

2. MONOETHANOLAMINE

Amines in which one or more hydrogen atoms are replaced by an organic radical. Monoethanolamine (MEA), is the most commonly used amines in scrubbing applications. The CO_2 absorbing capacity of amines is easily degraded by the presence of SO_2 , NO₂, HCl, HF, or O_2 in the gas stream [4]. The capacity of absorbing is a solvent property and it is defined as the maximum molar amount of pollutant absorbed per mole of solvent. Absorbing capacity is define appropriate used to the loading (pollutant/solvent molar ratio in scrubber designs. As the Low loadings result in columns with low absorbing efficiencies while high loadings lead to excessive solvent requirements and high operational costs. The CO₂ absorbing capacity of amines is dependent on the solvent capable of chemical and physical CO₂ absorption physical absorption is controlled by the thermodynamic equilibrium between O_2 molecules in the gas and aqueous phases and is described by Henry's law.



Solubility of CO2 in 30% (w/w) aqueous MEA solutions at 313 K as a function of loading (moles of CO2 per mole of MEA, α), from Tong et al.[11]

3. POLYETHYLENEIMINE

Amines have been immobilized in hollow fibers to increase their sorption capacity [12-13]. The total capacity at 1 bar is rather low with 8.3 mg/g. In comparison, the PEI-impregnated hollow fibers show a high sorption capacity of 19.9 mg/g and 47 mg/g at 2.5 wt-% and 10 wt.-% PEI, respectively, at very low CO2 pressures of 0.0035 bar or 350 ppm. For both PEIimpregnated microtubes, there is a sharp increase in CO2 sorption capacity at very low pressures up to approximately 0.03 bar. This sharp rise is followed by a linear increase of the amount of adsorbed CO2 to maximum values at 1 bar of 45.8 mg/g and 80.4 mg/g for 2.5 wt-% and 10 wt.-% PEI, respectively [5]. These results show that the PEI impregnation enhances the CO2 sorption capacity of the CNT microtubes and that the amount of PEI in the impregnation solution influences the CO2 uptake [5]. Similarly impregnating polyethyleneimine onto multi-walled carbon nanotubes (MWCNTs) increased their CO2 adsorption capacity by 200% [14]

4. CHITOSAN

The amount of CO2 adsorbed by the pure chitosan was 9 mg/g. The amount of CO2 adsorbed by the chitosan/MWCNTs was 3 mg/g. This is a 66.67 % decrease in the amount of CO2 adsorbed by the pure chitosan and a 650 % increase in the amount of CO2 adsorbed by the MWCNTs. This is a very substantial increase [6].Therefore, chitosan when impregnated onto the surface of a more suitable CNT for CO2 capture would improve the CO2 adsorption capacity of that CNT.

5. POLYASPARTAMIDE

Masayuk *et al* found that the polycondensation of polyaspartic acid in the temperature range $190^{\circ}C - 250^{\circ}C$ was used to

synthesize polysuccinimide (PSI) with a high molecular weight (>64000) [15]. PAA is a long chain PSI grafted with diamine (NH2- R-NH2) which forms amide bonds on one amine group side, and the other amine group stays available for CO2 trapping. The CO2 adsorption capacity was 12.13mgCO2/g, 25mgCO2/g, 47.1mgCO2/g and 70mgCO2/g for MWNT, PSI, PAA and MWNT-PAA, respectively [7]. The CO2 adsorption capacity and the adsorption kinetics of MWNT-PAA were enhanced compared to PAA. Regardless low CO2 adsorption capacity, PSI and MWNT have shown good regenerability at low temperature (90°C) due to the physisorption predominance during the adsorption process. Inversely, high desorption temperature (100°C) was used to regenerate PAA and MWNT-PAA due to the chemisorption predominance [7]. Thus this technique can prove beneficial for post combustion adsorption at low tempertare.

6. TETRAETHYLENEPENTAMINE

Solid adsorbents can be prepared by either chemically bonding amine groups to a support, referred to as grafting [16] or or immobilizing liquid amines within the pores of a support, known as impregnation [17]. The MCNTs/TEPA were prepared by wet impregnation. The wet impregnation of amine-based materials is generally a physical mixture of amine-based materials and supports which results in a noncovalent introduction of amine-based materials into the pores or onto the surface of the support [1614]. An optimal TEPA loading of 75 wt% obtained the maximal CO2 sorption capacity of 5 mmol/g for a gas mixture containing 10 vol% CO2 in N2 with 1 vol% H2O [8]. Unmodified CNTs as a support showed a maximal CO2 sorption capacity of 2.5 mmol/g with an optimal TEPA loading of 50 wt% [8]. Thermal stability studies indicate that MCNTs/TEPA is stable below 110°C [8].

7. CONCLUSIONS

The modification of carbon nanotubes with the wide number of polymers is a great work as the economic cost and efficiencies of various polymers are not up to the mark in order to overcome from the increasing cost of polymers some modifications are done to the carbon nanotubes in order to reduce the cost and enhance the solubility of carbon dioxide and which enable both a more extensive characterization and subsequent chemical reactivity. It is quite clear from the review that the capture capacity of polymers increases significantly on grafting or impregnation with carbon nanotubes.

REFERENCES

- [1] Aaron, D., Tsouris, C., 2005 Separation of CO2 from flue gas :a review Separation Science Technology 40,321–348.
- [2]White,C.M.,Strazisar,B.R.,Granite,E.J.,Hoffman,J.S.,Pennline,H. W.,2003. Separation and capture of CO2 from large stationary sources and sequestration in geological formations—coal beds

and deep saline aquifers. Journal of the Air and Waste Management Association 53,645-715

- [3] P. Liu Modifications of carbon nanotubes with polymers European Polymer Journal 41 (2005) 2693–2703
- [4] José I. Huertas, Martin D. Gomez, Nicolas Giraldo, and Jessica Garzón ,CO2 Absorbing Capacity of MEA, Journal of Chemistry Volume 2015, Article ID 965015
- [5] L. Keller, B. Ohs, J. Lenhart, L. Abduly, P. Blanke, M. Wessling, High capacity polyethylenimine impregnated microtubes made of carbon nanotubes for CO2 capture, Carbon (2017), doi: 10.1016/j.carbon.2017.10.023.
- [6] K. Osler et al. Synthesis and Performance Evaluation of Chitosan/Carbonnanotube (Chitosan/MWCNT) Composite Adsorbent for Postcombustion Carbon Dioxide Capture Energy Procedia 114 (2017) 2330 – 2335
- [7] Jacob M. Ngoy et al. A CO2 capture technology using multiwalled carbon nanotubes with polyaspartamide surfactant Energy Procedia 63 (2014) 2230 – 2248
- [8] M. Irani et al. Modified carbon nanotubes/tetraethylenepentamine for CO2 capture Fuel 206 (2017) 10–18
- [9] Z. Sun, M. Fan, M. Argyle, Supported Monoethanolamine for CO2 Separation, Ind. Eng. Chem. Res 50 (2011) 11343–11349.
- [10] A. Sayari, Y. Belmabkhout, Stabilization of amine-containing CO2 adsorbents: Dramatic effect of water vapor, Journal of the American Chemical Society 132 (18) (2010) 6312–6314
- [11] D. Tong, J. P. M. Trusler, G. C. Maitland, J. Gibbins, and P. S. Fennell, "Solubility of carbon dioxide in aqueous solution of monoethanolamine or 2-amino-2-methyl-1-propanol: experimental measurements and modelling," International Journal of Greenhouse Gas Control, vol. 6, pp. 37–47, 2012
- [12] Y. Labreche, R. P. Lively, F. Rezaei, G. Chen, C.W. Jones, W. J. Koros, Post-spinning infusion of poly(ethyleneimine) into polymer/silica hollow fiber sorbents for carbon dioxide capture, Chemical Engineering Journal 221 (2013) 166–175.
- [13] Y. Fan, R. P. Lively, Y. Labreche, F. Rezaei, W. J. Koros, C. W. Jones, Evaluation of CO2 adsorption dynamics of polymer/silica supported poly(ethylenimine) hollow fiber sorbents in rapid temperature swing adsorption, International Journal of Greenhouse Gas Control 21 (2014) 61 71.
- [14] Lee, M., & Park, S. (2015). Silica-Coated Multi-Walled Carbon Nanotubes Impregnated with polyethyleneimine for Carbon Dioxide Capture under Flue Gas Condition. Journal of Solid State Chemistry, 226(2015), 17-23
- [15] Masayuk, T.; Takeshi, N.; Shigeyuki, M.; Toyoji, K. (1997). "Convenient Synthesis of high molecular weight Poly(succinimide) by acid-catalysed polycondensation of Laspartic acid." Polymer Vol. 38, Issue 18 page 4733-4736.
- [16] Grondein A, Bélanger D. Chemical modification of carbon powders with aminophenyl and aryl-aliphatic amine groups by reduction of in situ generated diazonium cations: applicability of the grafted powder towards CO2 capture. Fuel 2011; 90:2684– 93.
- [17] Ye Q, Jiang J, Wang C, Liu Y, Pan H, Shi Y. Adsorption of lowconcentration carbon dioxide on amine-modified carbon nanotubes at ambient temperature. Energy Fuels 2012; 26:2497– 504.