

Polyethyleneimine Supported Mesoporous Silica for CO₂ Capture: Adsorption Kinetics and Degradation Problems

Dang Viet Quang^a, Thosmas Nelson^b, and Mohammad R.M. Abu-Zahra^{a,*}

^aMasdar Institute of Science and Technology, P.O. Box 54224, Masdar city, Abu Dhabi, United Arab Emirates

^bRTI International, Research Triangle Park, NC 27709-2194, USA

Abstract

Polyethyleneimine supported mesoporous silica (PEI-MPS) has widely been investigated as solid sorbents for CO₂ adsorption in laboratory. However, the adsorption kinetics of CO₂ on this sorbent is still a disputed problem and the sorbent degradation could be a cause that hinders the sorbent from industrial application. In this study, the PEI-MPS sorbent was prepared by impregnating PEI onto mesoporous silica and then the adsorption kinetics was investigated using the pseudo-first order model, pseudo-second order model and intraparticle diffusion model. Results indicated that the CO₂ adsorption kinetics on the sorbent occurred in a 2 stage process. In early stage, it is well fitted by the pseudo-first order model, but in later stage, it is well fitted by the intraparticle diffusion model. The pseudo second-order model proved to be the most suitable one to describe the adsorption of CO₂ on the sorbent for the whole adsorption period with less than 5% absolute deviation. The sorbent with a CO₂ adsorption capacity of 144.9 mg/g was calculated based on the fitting of the pseudo-second order model. The major degradation issues and their potential effects on the CO₂ capture process were also discussed. The degradation significantly impacts on the performance and efficiency of CO₂ capture process. The chemical degradation, however, can be considerably minimized by humidification.

Keywords: CO₂ adsorption; CO₂ capture; Polyethyleneimine; Adsorption/regeneration; Kinetic.

1. Introduction

Polyethyleneimine supported mesoporous silica (PEI-MPS) has widely been investigated as solid sorbents for CO₂ adsorption. The PEI-MPS sorbent possesses a high CO₂ adsorption capacity, low CO₂ adsorption heat, and multi adsorption/regeneration cyclability. However, beside these advantages, there are some degradation issues that may hinder the sorbent from industrial application. The most severe issue associated with PEI-MPS sorbent is chemical degradation in which amine reacts with CO₂ and oxygen to form components that are not thermally regenerated [1-3]. The degradation usually occurs rapidly in dry environment at a high temperature [4, 5]. Previous studies indicated that CO₂ loading of PEI-MPS sorbent began decreasing after 3 and 2 cycles at adsorption/regeneration temperature of 75/105 °C and 75/120 °C, respectively [3]. Each regeneration cycle was conducted in pure N₂ for 30 min indicating that the sorbent started degradation after 1.5 h and 1h treatment at 105 °C and 120 °C in dry N₂. In another research, Nelson et al. aged the sorbent in dry pure CO₂ for 10 h at 120°C after regeneration at 105 °C in N₂ with 5.65% humidity,

which resulted in 20% CO₂ loading reduction after the first treatment [5]. The CO₂ adsorption kinetic behavior of adsorbent is of great importance for industrial application.

Understanding the adsorption kinetic helps predict the operating time of an adsorption process. It is particularly helpful information for engineers to design and predetermine the performance of CO₂ capture process. The kinetic behaviors of CO₂ adsorption on different porous sorbents varies depending on their specific porous structure and the conformation of active CO₂ adsorption sites. There are some reports on the kinetics of CO₂ adsorption on amine containing mesoporous silica, but silicas used in those studies, SBA-15 [6] and MCM-41 [7, 8], have ordered porous structures which are much different with the disordered porous structure of silica using in this study.

The objective of this study is to prepare PEI-MPS sorbent by impregnating PEI onto mesoporous silica and then investigate the adsorption kinetics using the pseudo first-order model, pseudo second-order model and intraparticle diffusion model. The degradation of the sorbent is also discussed.

* Corresponding author

E-mail: mabuzahra@masdar.ac.ae

© 2016 International Association for Sharing Knowledge and Sustainability

DOI: 10.5383/ijtee.11.02.001

2. Experimental

2.1. Sorbent Preparation

Typical preparation procedure is described as follows. First, a desired amount of PEI was dissolved in a designated solvent in a 1-L flask before adding a desired amount of silica under vigorous mixing in order to produce homogeneous slurry. The flask was then mounted to a rotary evaporator (IKA RV 10 Rotovapor, USA) to evaporate the solvent. The resulting PEI-impregnated silica was dried in a vacuum oven at 80 °C over night to remove moisture and the solvent.

2.2. CO₂ Adsorption

CO₂ adsorption performance of adsorbent was investigated using a packed bed reactor. Approximate 2 g of sorbent was mixed with silicon carbide as a support material and charged into 1.27 cm inner diameter and 20 cm length stainless steel reactor. The experiment began by activating sorbent at 110 °C for 30 min in N₂ flow and then the reactor was cooled to a desired temperature followed by flowing simulated flue gas including CO₂ 15 vol% in balance with N₂ at 150 ml/min for 90 min. Before entering reactor, the simulated flue gas was blown through a humidifier. The outlet gas was directed to CO₂ analyzer for continuously measurement of CO₂ concentration. The use of support material help spread fine sorbent in support media and therefore significantly reduce the mass transfer resistance in the packed bed reactor, which allows to investigate the kinetic behavior of the sorbent using pseudo-first and second order model and intraparticle diffusion model.

3. Adsorption Kinetic Model

To investigate the CO₂ adsorption kinetic on the PEI-MPS adsorbent, pseudo-first and second order model and intraparticle diffusion model were considered.

3.1. Pseudo-First Order Model

The pseudo-second order model is based on the assumption that the adsorption rate is proportional to the number of vacant adsorption sites in the sorbent and can be expressed as equation (1).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

where, q_t (mg/g) and q_e (mg/g) are CO₂ loading at time (t) and at equilibrium, respectively. k_1 (min⁻¹) is the pseudo-first order rate constant.

Boundary conditions: $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$
Integration with the boundary condition:

$$\ln(q_e - q_t) = \ln q_e - kt \quad (2)$$

3.2. Second Order Kinetic

The pseudo-first order model is based on the assumption that the adsorption rate is proportional to the square of the number of vacant adsorption sites in the sorbent and can be expressed as equation (3).

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where, k_2 (g/mg·min) is the pseudo-second order rate constant

Boundary conditions: $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$
Integration with the boundary conditions:

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{1}{q_e} t \quad (4)$$

Intraparticle Diffusion Model

The intraparticle diffusion model given in equation (5) is based on the Fick's second law, this model considers the intraparticle diffusion as an element that governs adsorption process. According to this model, if the plot of q_t versus $t^{1/2}$ is linear and passes the origin, the intraparticle diffusion should be sole-limiting step of adsorption process. If the plot is multi-linear, other processes also have significant role in the CO₂ adsorption process.

$$q_t = k_{int} t^{1/2} + C \quad (5)$$

where, k_{in} (mg/g·min^{1/2}) is the intraparticle diffusion rate constant and C is the intercept which is associated with the boundary layer thickness.

The linear fitting of equation 2, 4 and 5 provide the kinetic parameters of the corresponding kinetic models. To evaluate the accuracy of the model, the coefficient of determination (R^2) and the average absolute deviation (%) between experimental data and calculated data which is defined by equation (6).

$$AAD(\%) = \frac{\sum_{i=1}^N \left| \left(\frac{q_{exp} - q_{cal}}{q_{exp}} \right) \right|}{N} \times 100\%$$

Where, q_{exp} and q_{cal} are the experimental and calculated CO₂ loading, respectively, and N is the total number of experimental points.

4. Results and Discussion

4.1. CO₂ Adsorption Kinetics

The experimental CO₂ adsorption kinetics of the sorbent are shown in Figure 1 A (solid lines). The adsorption occurred with high rate at the first 10 min and then it slowed down until reaching equilibrium; this trend was seen at both investigated temperatures, 50 and 80 °C. The fast adsorption rate at early stage can be attributed to the readily-accessible active sites, they collided and reacted with CO₂ molecules once CO₂ was being introduced into reactor. At the later stage, it is likely that the adsorption involved a diffusion of CO₂ molecules into the pores of the adsorbent. Closer to the thermodynamic adsorption capacity, the reduction in vacant adsorption sites and increase in diffusion resistance caused the adsorption kinetics slowdown. The CO₂ adsorption kinetic of PEI-MPS is similar to that observed in previous studies, which reported the CO₂ adsorption kinetics of mesoporous adsorbents [6, 9].

Figure 1B, C, and D show the linear fitting of the pseudo-first order, second order, and intraparticle diffusion models. From these figure, it is not difficult to recognize that the pseudo-second order model is the only one that fits the experimental data for the whole investigated period. The kinetic parameters for the pseudo-second order model are exhibited in the Table 1. The coefficients of determination are 0.996 and 0.997 for 50 and 80 °C, respectively. In addition, the average absolute deviations at 50 and 80 °C are 3.71% and 4.51%, respectively. The curve of CO₂ loading versus time based on the calculated value from the model presented in the Figure 1 A (dash line) is relatively fitted the experimental curve. The results indicated that the pseudo-

second order model well describes the CO₂ adsorption of the PEI-MPS sorbent.

Whereas, both the pseudo-first order and intraparticle diffusion models does not fit the experimental data. The pseudo-first order model only fits for the first 10 min. Previous studies indicated that reaction of CO₂ with amines in aqueous solution is well described by the pseudo-first order model [10, 11].

Therefore, it is likely because, at the early stage, the adsorption is governed by the reaction between CO₂ and the readily-accessible amino groups. Since at the early stage, the adsorption is governed by the chemical reaction, it does not fit the intraparticle diffusion model. However, at the later stage, it requires time for CO₂ molecules to diffuse in to the pores, the adsorption fits very well the intraparticle diffusion mode

Table 1. Parameters of the pseudo-second order model

Temperature	Experimental q_e (mg/g)	Calculated q_e (mg/g)	k_2 (g/mg.min)	R^2	ADD (%)
50	132.40	144.93	0.00059	0.996	3.71
80	115.18	120.48	0.00126	0.997	4.51

From the pseudo-second order model, the q_e was calculated and shown in Table 1. The calculated q_e at 50 and 80 °C are 144.9 and 120.5 mg/g, respectively, which are higher than experimental q_e at corresponding adsorption temperature. This is understandable because experimental q_e were determined after 90 min while the adsorption requires more time to reach equilibrium.

Therefore, this model allows to determine the q_e value of the sorbent with the limited experimental time. Higher CO₂ loading was obtained at 50 °C in both experiment and calculation indicating its reduction with the increase in the adsorption temperature. This is likely due to the effect of thermodynamic equilibrium on the adsorption that is favorable to CO₂ desorption at higher temperature.

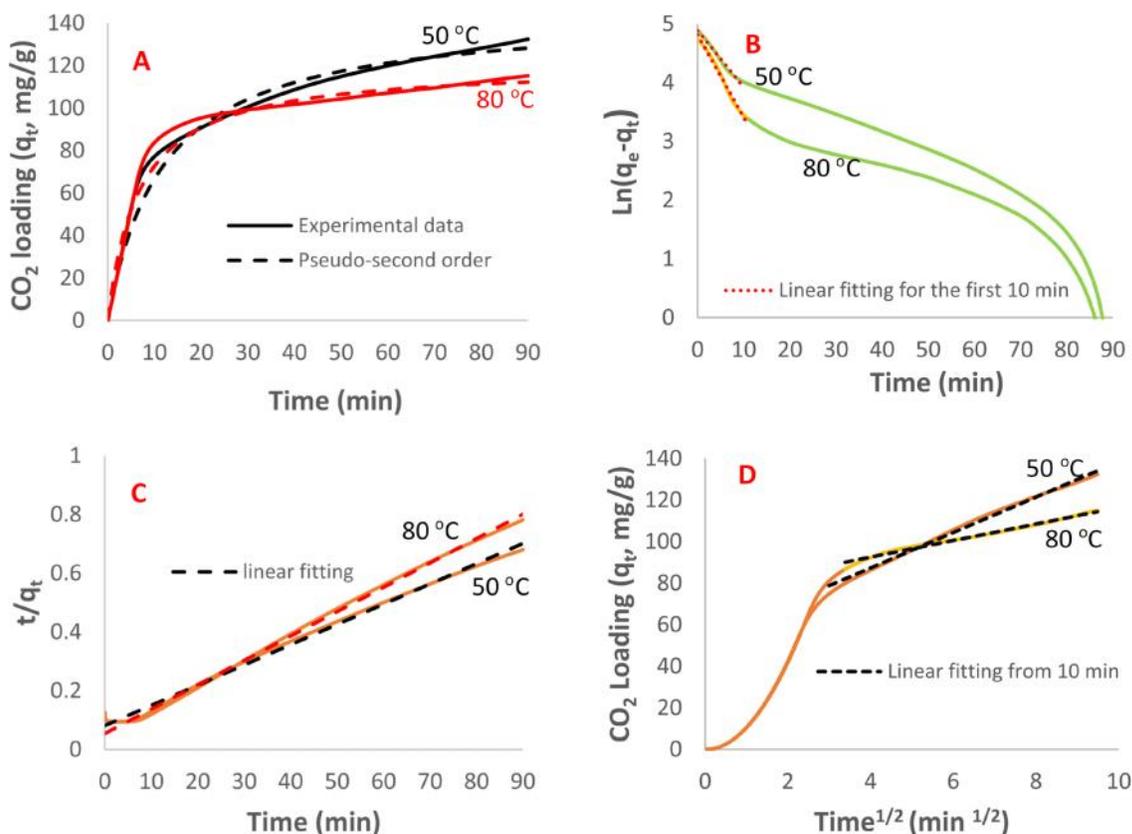


Figure 1. CO₂ Adsorption Kinetic: the experimental and predicted CO₂ adsorption based on pseudo-second order model (A), linear fitting of the pseudo-first order (B), the pseudo-second order (C) and the intraparticle diffusion model (D)

4.2. Sorbent Degradation

To investigate effect of the regeneration condition on its stability, adsorption was conducted in pure CO₂ at 75 °C in a micro reaction calorimeter and then the sorbent was regenerated in the air at 90, 100, and 110 °C in oven working under atmosphere as described in Quang et al. 2014 [12]. The results are shown in Figure 2 suggesting that the sorbent was relatively stable when regenerating at temperature below 100 °C, however, it was rapidly degraded at a temperature above 100 °C. The sorbent lost 15% loading capacity for 20 adsorption/regeneration cycles at the regeneration temperature of 100 °C. As regenerating at 110 °C, the loading capacity reduced 16% after 7 cycles and the loading capacity loss began after 3 cycles being equivalent to 1.5 h treating in the air at 110 °C. Apparently, the sorbent was rapidly degraded with increasing regeneration temperature. The PEI-MPS sorbent, however, can keep its CO₂ loading constant during regeneration by adding moisture to the sweep gas. A test carried using a packed bed reactor indicated that PEI-MPS sorbent was stable for multiple cycles at adsorption/regeneration temperature of 65/110 °C; it lost only 16.6% of CO₂ loading capacity after 335 cycles with regeneration in humid N₂ (5.6% humidity). In a previous study, Sayari and Belmabkhout revealed that CO₂ loading of the sorbent reduced 41% after 22 cycles regenerated in dry N₂ at 105 °C, but it was constant for 22 cycles regenerated in humid N₂ at the same temperature [4]. Nelson et al. found that the sorbent lost approximately 15% for 14 cycles combining with the 10h aging in humid CO₂, while the sorbent was nearly completely deactivated after the same number of cycles aging in dry CO₂. This confirms that moisture has an extremely important role in PEI-MPS sorbent-based CO₂ capture process.

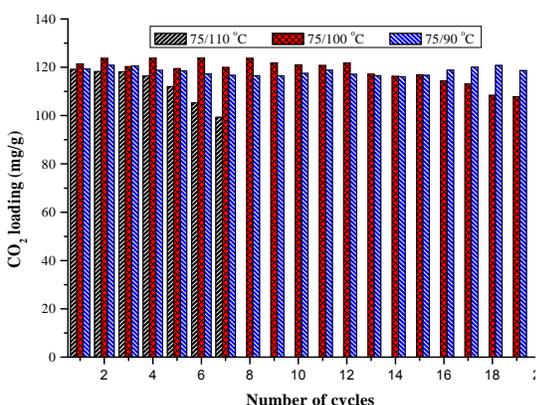


Figure 2. Adsorption/Regeneration Performance in Atmosphere at Different Regeneration Temperatures

In PEI-MPS sorbent, PEI is impregnated into porous channels and has weak physical interaction with silica substrate, therefore, it may face other degradation problems including leaching and vaporization. The degradation has a great effect on the performance of sorbent and selecting adsorption technology. Here the impacts of degradation on temperature swing adsorption processes based on PEI-MPS sorbent for CO₂ capture i.e. packed bed reactor (PBR) and fluidized bed reactor.

Operation of PBR begins with heating sorbent bed to adsorption temperature, it is normally below 100 °C and then flue gas is directed into reaction vessel until the adsorption saturated. This stage works at a low temperature (<100 °C) with a certain moisture content in the flue gas and therefore the degradation is negligible. The regeneration begins with raising temperature from adsorption to regeneration stage (110-130 °C) and following by flowing steam as a stripping gas. Since this stage works at temperature above 100 °C, the sorbent has high potential to be degraded, particularly before flowing steam. As discussed earlier, the sorbent begins degradation after few hours treated in dry air (2-3 cycles), therefore, to prevent the severe degradation, the regeneration stage should begin with increasing temperature combining with flowing humid CO₂ before replacing by steam. This help humidify sorbent during raising temperature while avoiding the dilution of CO₂ at effluent. Flowing humid gas at a low temperature, however, would increase the moisture of sorbent causing higher sorbent specific heat capacity (C_p). The dry sorbent usually containing approximately 3% moisture, which has a C_p of 1.9 J/°C·g, but the C_p of 10% moisture sorbent is 2.2 J/°C·g. The moisture causes increasing in sensible heat and heat of water vaporization, which result in the rise of the total energy requirement for sorbent regeneration.

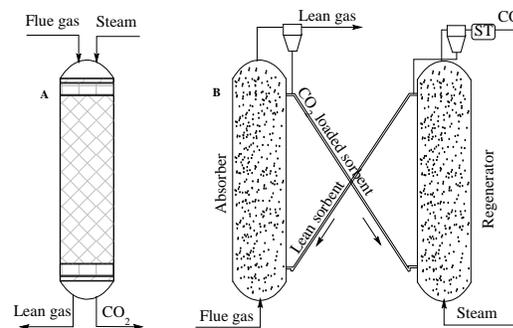


Figure 3. Schematic Illustration of CO₂ Capture Process: Packed Bed Reactor (A) and Fluidized Bed Reactor (B)

Previous result revealed that the regeneration energy required for dry sorbent was 2096 kJ/kg of CO₂, but that required for 10% moisture sorbent was 2967 kJ/kg of CO₂ [13]. Evidently, flowing humid gas helps maintain adsorption performance of sorbent but potentially raises the regeneration energy. As discussed, by adding 5.6% humidity to regeneration gas, sorbent lost only 16.6% after 335 cycles operating in a PBR. Therefore, to maintain optimal adsorption performance and regeneration energy requirement, humid CO₂ should be flown with a slow rate and the humidity should not higher than 5.6%.

In the FBR (Figure 3 B), the adsorption and regeneration stages are occurred in two different vessels and sorbent is continuously circulated between two vessels. Sorbent adsorbs CO₂ in absorber, is transferred to regenerator for regeneration. (FBR) will be discussed. The PBR (Figure 3 A) is usually filled with sorbent in the form of pellets and operates as a batch process with two typical stages: adsorption and regeneration.

5. Conclusion

Investigation on the CO₂ adsorption kinetics indicated that the CO₂ adsorption occurred with a 2 stage process in which neither the pseudo-first order nor intraparticle diffusion model could correctly describes the adsorption kinetic behavior of the PEI-MPS sorbent. The pseudo-second order model only fitted in the early stage, while the intraparticle diffusion model only fitted in the later stage. The pseudo-first order model is the most fitting model with the coefficient of determination of 0.99 and average absolute deviation less than 5%. Based on this model, the CO₂ loading at equilibrium were calculated; they are 144.9 and 120.5 mg/g at 50 and 80 °C, respectively. PEI-MPS sorbent has serious degradation problem when operating in dry condition at a high temperature. The degradation significantly impacts on the performance and efficiency of CO₂ capture process. The chemical degradation, however, can be considerably minimized by humidification. FBR causes less chemical degradation than PBR due to a constant adsorption and regeneration temperature but it may face more leaching and evaporation problems.

References

- [1] R.A. Khatri, S.S.C. Chuang, Y. Soong, M. Gray, Thermal and Chemical Stability of Regenerable Solid Amine Sorbent for CO₂ Capture, *Energy & Fuels*, 20 (2006) 1514-1520.
- [2] T.C. Drage, A. Arenillas, K.M. Smith, C.E. Snape, Thermal stability of polyethylenimine based carbon dioxide adsorbents and its influence on selection of regeneration strategies, *Microporous and Mesoporous Materials*, 116 (2008) 504-512.
- [3] A. Heydari-Gorji, A. Sayari, Thermal, Oxidative, and CO₂-Induced Degradation of Supported Polyethylenimine Adsorbents, *Industrial & Engineering Chemistry Research*, 51 (2012) 6887-6894.
- [4] A. Sayari, Y. Belmabkhout, Stabilization of Amine-Containing CO₂ Adsorbents: Dramatic Effect of Water Vapor, *Journal of the American Chemical Society*, 132 (2010) 6312-6314.
- [5] T.O. Nelson, L.J.I. Coleman, A. Kataria, M. Lail, M. Soukri, D.V. Quang, M.R.M.A. Zahra, Advanced Solid Sorbent-Based CO₂ Capture Process, *Energy Procedia*, 63 (2014) 2216-2229.
- [6] A. Zhao, A. Samanta, P. Sarkar, R. Gupta, Carbon Dioxide Adsorption on Amine-Impregnated Mesoporous SBA-15 Sorbents: Experimental and Kinetics Study, *Industrial & Engineering Chemistry Research*, 52 (2013) 6480-6491.
- [7] R. Serna-Guerrero, A. Sayari, Modeling adsorption of CO₂ on amine-functionalized mesoporous silica. 2: Kinetics and breakthrough curves, *Chemical Engineering Journal*, 161 (2010) 182-190.
- [8] A. Heydari-Gorji, A. Sayari, CO₂ capture on polyethylenimine-impregnated hydrophobic mesoporous silica: Experimental and kinetic modeling, *Chemical Engineering Journal*, 173 (2011) 72-79.
- [9] G. Qi, Y. Wang, L. Estevez, X. Duan, N. Anako, A.-H.A. Park, W. Li, C.W. Jones, E.P. Giannelis, High efficiency nanocomposite sorbents for CO₂ capture based on amine-functionalized mesoporous capsules, *Energy & Environmental Science*, 4 (2011) 444-452.
- [10] N.E.L. Hadri, D.V. Quang, M.R.M. Abu-Zahra, Study of Novel Solvent for CO₂ Post-combustion Capture, *Energy Procedia*, 75 (2015) 2268-2286.
- [11] A. Sadiq, A.V. Rayer, A.A. Olanrewaju, M.R.M. Abu Zahra, Reaction Kinetics of Carbon Dioxide (CO₂) Absorption in Sodium Salts of Taurine and Proline Using a Stopped-Flow Technique, *International Journal of Chemical Kinetics*, 46 (2014) 730-745.
- [12] D.V. Quang, A. Dindi, A.V. Rayer, N.E. Hadri, A. Abdulkadir, M.R.M. Abu-Zahra, Impregnation of Amines Onto Porous Precipitated Silica for CO₂ capture, *Energy Procedia*, 63 (2014) 2122-2128.
- [13] D.V. Quang, A. Dindi, A.V. Rayer, N.E. Hadri, A. Abdulkadir, M.R. Abu-Zahra, Effect of moisture on the heat capacity and the regeneration heat required for CO₂ capture process using PEI impregnated mesoporous precipitated silica, *Greenhouse Gases: Science and Technology*, (2014).