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CO_2 CAPTURE USING POLYETHYLENEIMINE FUNCTIONALIZED SILICA XEROGELS

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ABSTRACT: CO_2 capture technologies using solid adsorbents are promising approach to reduce environmental pollution resulting from CO_2 emission. In this study, silica xerogel derived from cheap precursor was used as a CO_2 adsorbent after polyethyleneimine (PEI) functionalization. Fourier transform infrared (FTIR) analyses indicated that PEI functionalized silica xerogels were successfully prepared. N_2 adsorption-desorption isotherms revealed that PEI loading decreased specific surface area and pore volume of the neat silica xerogel in contrast to pore size. An increase in particle size of the neat silica xerogel was observed in the case of PEI loading. Positively surface charged silica xerogels were obtained with PEI loading of the neat silica xerogel which had negatively charged surface. CO_2 adsorption measurements showed that CO_2 adsorption capacity of the neat silica xerogel (0.98 mmol g^{-1}) significantly increased with increasing PEI loading (30 – 70 wt%). At optimum PEI loading (50 wt%), CO_2 adsorption capacity of silica xerogel was determined as 1.94 mmol g^{-1}. After 5 adsorption-desorption cycles, PEI functionalized silica xerogels still exhibited high CO_2 adsorption capacity. The hopeful results showed that PEI functionalized silica xerogels can be used as an adsorbent with a good CO_2 adsorption performance and stability.

Key Words: *CO_2 adsorption, Silica xerogel, PEI functionalization, Amine impregnation, Regenerability*

Polietilenimin ile Modifiye Edilmiş Silika Kserojellerin Kullanımı ile CO_2 Tutumu

ÖZ: CO_2 emisyonundan kaynaklı çevre kirliliğinin azaltılmasında katı adsorbentlerin kullanıldığı CO_2 tutma teknolojileri umut vadeden bir yaklaşımdır. Bu çalışmada ucuz başlangıç malzemesinden elde edilen silika kserojel, polietilenimin (PEI) modifikasyonunun ardından CO_2 adsorbent olarak kullanılmıştır. Fourier dönüşümlü kızılötesi spektrometresi analizleri PEI ile modifiye edilmiş silika kserojellerin başarılı bir şekilde hazırlandığını göstermiştir. N_2 adsorpsiyon-desorpsiyon izotermleri PEI yüklemesinin silika kserojelin gözenek boyutunun aksine spesifik yüzey alanı ve gözenek hacmini azalttığını açığa çıkarmıştır. PEI yüklemesi sırasında silika kserojelin partikül boyutunun arttığı gözlenmiştir. Negatif yüzey yüküne sahip silika kserojele PEI yüklenmesiyle pozitif yüzey yüklü PEI ile modifiye edilmiş silika kserojeller elde edilmiştir. CO_2 adsorpsiyon ölçümleri artan PEI yüklemesiyle (ağırlıkça %30 - 70) silika kserojelin CO_2 adsorpsiyon kapasitesinin (0.98 mmol g^{-1}) önemli ölçüde arttığını göstermiştir. Optimum PEI yüklemesinde (ağırlıkça %50), silika kserojelin CO_2 adsorpsiyon kapasitesi 1.94 mmol g^{-1} olarak belirlenmiştir. 5 kez yapılan adsorpsiyon-desorpsiyon döngüsünün ardından PEI ile modifiye edilmiş silika kserojeller hala yüksek CO_2 adsorpsiyon kapasitesi göstermiştir. Bu ümit vadeden sonuçlar PEI ile modifiye edilmiş silika kserojellerin iyi bir CO_2 adsorpsiyon performansı ve kararlılığı ile adsorbent olarak kullanılabileceğini göstermiştir.

Anahtar Kelimeler: *CO_2 adsorpsiyonu, Silika kserojel, PEI modifikasyonu, Amin emdirme, Yenilenebilirlik*

1. INTRODUCTION

Climate change is a serious problem that affects environment and human health adversely. Greenhouse gases, especially CO_2 which absorbs infrared radiation leading an increase in temperature, are primary factors for global warming (Mondal *et al.,* 2012). It is known that CO_2 emission annually increases by more than 30 billion tons (Li *et al.,* 2013). So, many legislations and agreements have been applied to decrease or stabilize CO_2 concentration in the atmosphere. For example, the European Commission has made a decision related to a decrease in carbon release by 20-95% until 2050 with respect to 1990s (Sher *et al.,* 2020). And also, different technologies have been developed for CO_2 capture: (1) pre-combustion (chemical adsorption, physical adsorption, chemical/physical absorption, chemical looping and membrane technology), (2) post-combustion (oxygen transport membrane boilers, ceramic auto-thermal recovery process, ion transport and membrane technology, cryogenic oxygen, chemical looping and chemical/physical absorption) and (3) oxy-fuel combustion (chemical adsorption, physical adsorption, chemical absorption, cryogenics separation, membrane technology and ionic liquids) (Sang Sefidi and Luis, 2019).

Many studies have focused on CO_2 capture by post-combustion method including adsorption process (Dutcher *et al.,* 2015). Compared to other methods, adsorption using solid adsorbents is one of the promising methods with the advantages of minimized equipment corrosion, easy handling, low energy and money consumption, and easy regeneration of adsorbents (Li *et al.,* 2015). Nowadays, carbon or silica based adsorbents have been derived from low-cost industrial by-products (fly ash, steel slag, *etc.*), biomass by-products (almond shell, coconut shell, bagasse, rice husk, soybean, *etc.*), water treatment wastes (sewage sludge, *etc.*), and household wastes (plastic waste, carpet waste, *etc.*). For instance, low-cost silica based materials such as MCM-41, MCM-48, SBA-15, and silica aerogel have been used as a CO_2 adsorbent resulting in favorable CO_2 adsorption capacity (Olivares-Marín and Maroto-Valer, 2012; Sher *et al.,* 2020).

Silica xerogels are one of the newly designed materials for CO_2 capture. Through atmospheric pressure drying, silica xerogels are synthesized from silica gels by sol-gel method. Silica xerogels have many unique properties including low-density, high surface area, controllable pore size and volume, and high thermal stability (Dos Santos *et al.,* 2020; S. Aquino *et al.,* 2019; Witoon *et al.,* 2011). Surface property of silica xerogels is an important factor that influences interactions with CO_2 molecules. Depending on various surface functionalization/modification methods, surface properties of silica xerogels show an alteration. Generally, to increase CO_2 adsorption capacity and selectivity, active sites on the surface of silica based materials are increased by surface functionalization using amine based materials (tetraethylenepentamine, polyethyleneimine, N-(3-trimethoxysilylpropyl) diethylenetriamine, (3-aminopropyl) trimethoxysilane, *etc.*) (Panek *et al.,* 2017; Zhang *et al.,* 2019). Amine loading are conducted with three common methods: (1) physically impregnation, (2) chemical grafting and (3) direct single step (Linneen *et al.,* 2013). Physical impregnation is the simplest method in which amine groups physically attached to silica scaffold. Firstly, amine is dissolved in a suitable solvent. After mixing amine solution with silica scaffold, amine functionalized silica based materials are prepared by evaporation of the solvent (Chen *et al.,* 2017).

The present work aimed to investigate the CO_2 adsorption performance of amine functionalized silica xerogel. Polyethyleneimine (PEI) functionalized silica xerogel was synthesized with physically impregnation method. Structural, textural and surface properties of functionalized silica xerogel were studied with different analyses. The CO_2 adsorption capacity of functionalized silica xerogel was specified by thermogravimetric analyses (TGA). The effects of different PEI loading on the CO_2 adsorption capacity of functionalized silica xerogel were examined. CO_2 adsorption-desorption cycles were carried out to determine regenerability and stability of the functionalized silica xerogel. Finally, the CO_2 adsorption capacity of functionalized silica xerogel was compared to that of the silica based materials in literature.

2. MATERIALS AND METHOD

2.1. Materials

Volcanic tuff, which consists of highly SiO_2 ~ 71.5%, was used as a silica precursor. Isopropanol (Merck, ≥ 99.8%), NaOH (Sigma-Aldrich, ≥ 97%), HCl (Sigma-Aldrich, 37%), *n*-hexane (Merck, 98.5%) and PEI (Sigma-Aldrich, average molecular weight: 800) were supplied. The materials were used as received.

2.2. Preparation of PEI functionalized silica xerogels

Firstly, synthesis of silica xerogel was conducted according to our previous study (Guzel Kaya *et al.,* 2019). PEI functionalization of silica xerogel was carried out by physical impregnation method. Different amount of PEI (30, 50 and 70 wt%) was used to functionalize silica xerogel. PEI was mixed with 15 mL isopropanol for 30 min. After adding silica xerogel into PEI solution, the slurry was stirred at 500 rpm for 24 h at room temperature. The final material was dried at 50 °C under vacuum. Silica xerogels were denoted as silica xerogel-PEI-30, silica xerogel-PEI-50 and silica xerogel-PEI-70, respectively, depending on PEI loading.

2.3. Characterization of PEI functionalized silica xerogels

Fourier transform infrared (FTIR) spectra were recorded to investigate chemical bonding of the samples using Bruker Vertex 70 FTIR spectrometer (4000 - 400 cm^{-1}). Based on N_2 adsorption-desorption isotherms obtained by Micromeritics Tristar II 3020 analyzer, BET method was used to determine specific surface area of the samples. And also, pore properties of the samples such as pore volume and pore size were examined utilizing BJH method. Mass of the samples was divided to their volume to specify bulk density of the samples. Particle size of the samples was obtained by Malvern Zetasizer analyzer after dispersing the samples in water (w/v: 1/1). And also, zeta potential of the samples was specified with dispersing the samples in water (w/v: 1/1) by the Malvern equipment.

2.4. CO_2 adsorption measurements

CO_2 adsorption measurements were conducted by thermogravimetric analyses (TGA) using METTLER STAR SW equipment. 10 mg of sample was put in a pan and heated to 100 °C with heating rate of 10 °C min^{-1} under Argon gas (100 mL min^{-1}) for 30 min to remove residual solvents and water molecules. The temperature was decreased to 25 °C with cooling rate of 10 °C min^{-1}, and subsequently pure CO_2 was inserted into the pan with the flow rate of 100 mL min^{-1} for 1 h at 1 bar. CO_2 equilibrium adsorption capacity of the samples was calculated with gained mass throughout the adsorption process.

CO_2 adsorption-desorption cycles were carried out to show regenerability and stability of PEI functionalized silica xerogels. The samples were heated to 100 °C under Argon gas for 30 min, and then cooled to 25 °C in which CO_2 gas was switched for 1 h at 1 bar. The temperature was again increased to 100 °C under Argon gas for 30 min. The process was repeated for 5 times.

3. RESULTS AND DISCUSSION

Effective PEI functionalization of the silica xerogel was confirmed by FTIR spectra (Figure 1). After PEI loading, new peaks belonging to PEI were observed. The peaks at 1464 cm^{-1} and 1558 cm^{-1} were contributed to $–NH_2$ symmetric and asymmetric bending vibrations, respectively (Taheri *et al.,* 2019). The stretching vibrations of $–CH_2$ attributed to formation of the peak at 2829 cm^{-1} and 2942 cm^{-1} (Niu *et al.,* 2016). While the amount of PEI was increasing, intensity of many peaks showed an increase. Especially an increase in intensity of the broad band at around 3370 cm^{-1} in the FTIR spectrum of silica xerogel loaded with 70 wt% PEI was assigned to –NH stretching vibrations (Lou *et al.,* 2020).

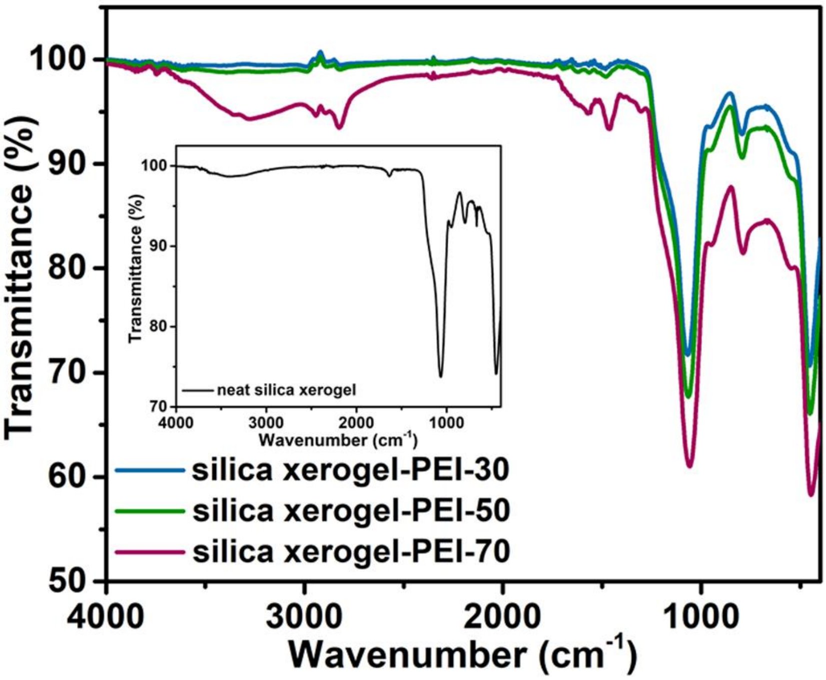

Figure 1. FTIR spectra of PEI functionalized silica xerogels (inset: FTIR spectrum of neat silica xerogel)

Figure 2 shows N_2 adsorption-desorption isotherms of PEI functionalized silica xerogels. It was clear that the amount of adsorbed N_2 significantly decreased in the case of increasing PEI loading. As shown in Table 1, specific surface area (S_{BET}) and pore volume (V_P) of the neat silica xerogel decreased after PEI functionalization. Silica xerogel loaded with 70 wt% PEI had the surface area and pore volume as low as 8 $m^2\ g^{-1}$ and 0.04 $cm^3\ g^{-1}$, respectively. It was resulted from filling pores of functionalized silica xerogels with PEI through PEI diffusion into the pores by pressure and concentration difference force in addition to PEI adsorption on the pore walls (Kong *et al.*, 2016). A slight increase in pore size of the neat silica xerogel was observed in the presence of PEI molecules. In the case of functionalization, smaller pores were generally blocked by functionalization agents; however, larger pores are preserved (Zhao *et al.*, 2019). So, pore size of the materials can show an increase in spite of a decrease in pore volume.

Table 1. Pore structure properties and bulk density of PEI functionalized silica xerogels

Samples	S_{BET} ($m^2\ g^{-1}$)	V_P ($cm^3\ g^{-1}$)	Pore size (nm)	Bulk density ($g\ cm^{-3}$)
Neat silica xerogel	195	0.50	10	0.037
Silica xerogel-PEI-30	40	0.22	18	0.165
Silica xerogel-PEI-50	18	0.11	18	0.176
Silica xerogel-PEI-70	8	0.04	17	0.190

The neat silica xerogel exhibited ultra-low bulk density which is very significant for gas capture processes. However, PEI functionalization caused a sharp increase in bulk density of the neat silica xerogel due to the presence of organic moieties belonging to PEI. Impregnation of PEI molecules into the neat silica xerogel increased the solid part of the silica network resulting in higher bulk density (Guzel Kaya *et al.*, 2020). Bulk density of the neat silica xerogel increased up to 0.190 g cm^{-3} with the loading of 70 wt% PEI (Table 1).

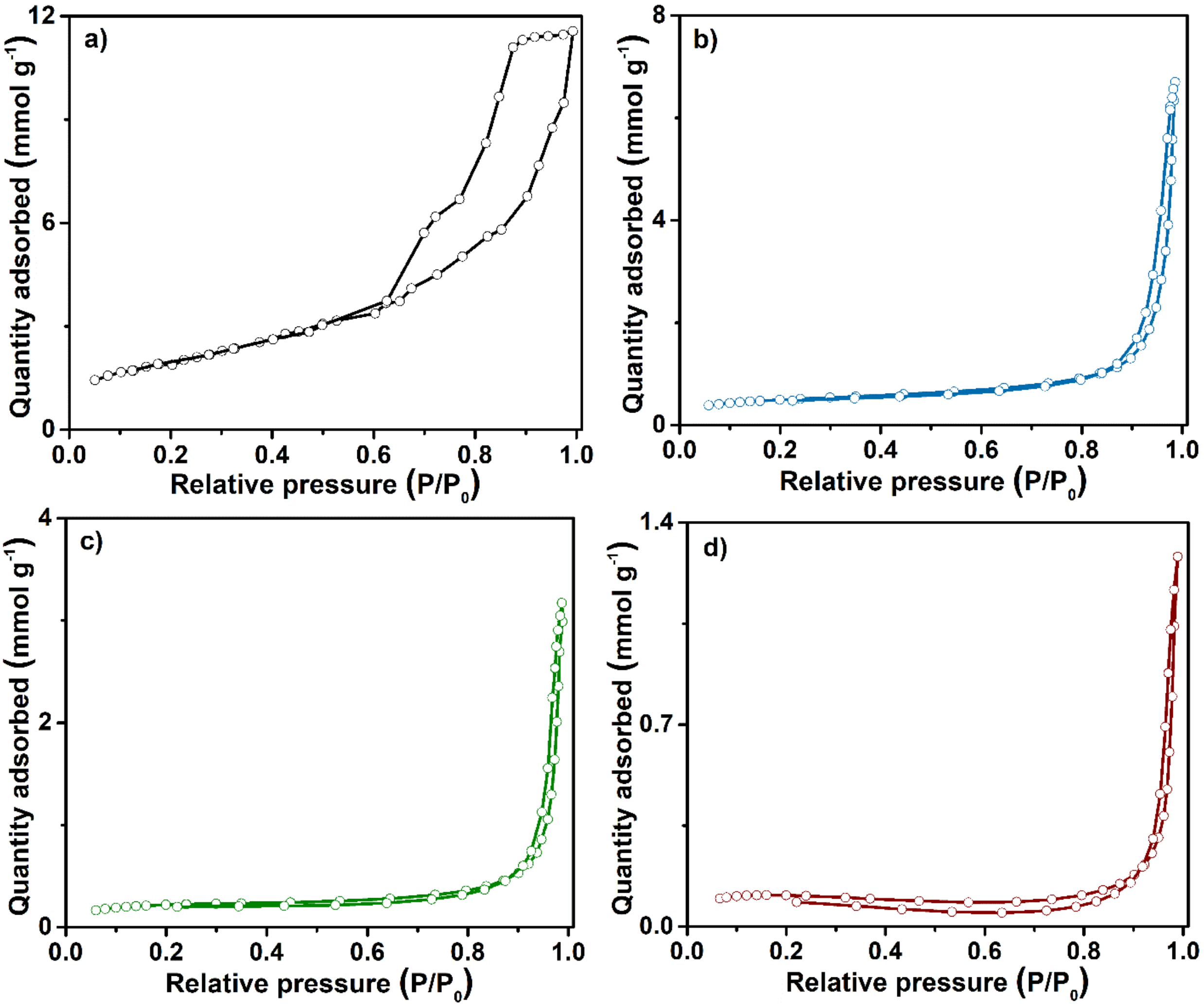

Figure 2. N_2 adsorption-desorption isotherm of **a)** neat silica xerogel, **b)** silica xerogel-PEI-30, **c)** silica xerogel-PEI-50 and **d)** silica xerogel-PEI-70

The particle size of the adsorbents is one of the important factors that affects CO_2 capture process in fixed-bed columns, especially CO_2 adsorption rate (Balsamo *et al.*, 2013; Santiago *et al.*, 2019). Figure 3 shows average particle size of PEI functionalized silica xerogels as a function of PEI loading. The average particle size of the neat silica xerogel was 86 nm. With PEI loading, particle size of PEI functionalized silica xerogels changed between 120 nm and 250 nm. PEI molecules on the silica xerogel surface behaved like a coating which leaded to increase particle size of the samples.

Zeta potential of the adsorbents is another important factor that reveals surface charge of the materials. The neat silica xerogel exhibited negative zeta potential value which was indication of negative surface charge as shown in Figure 3. In the case of PEI loading, PEI functionalized silica xerogels with positively charge were obtained. It is known that zeta potential of CO_2 molecules without surfactants changes from ~ -14 mV to ~ 32 mV depending on pH (2 - 12) (Kim and Kwak, 2017). So, it can be said that good interactions between PEI functionalized silica xerogels and CO_2 molecules are expected.

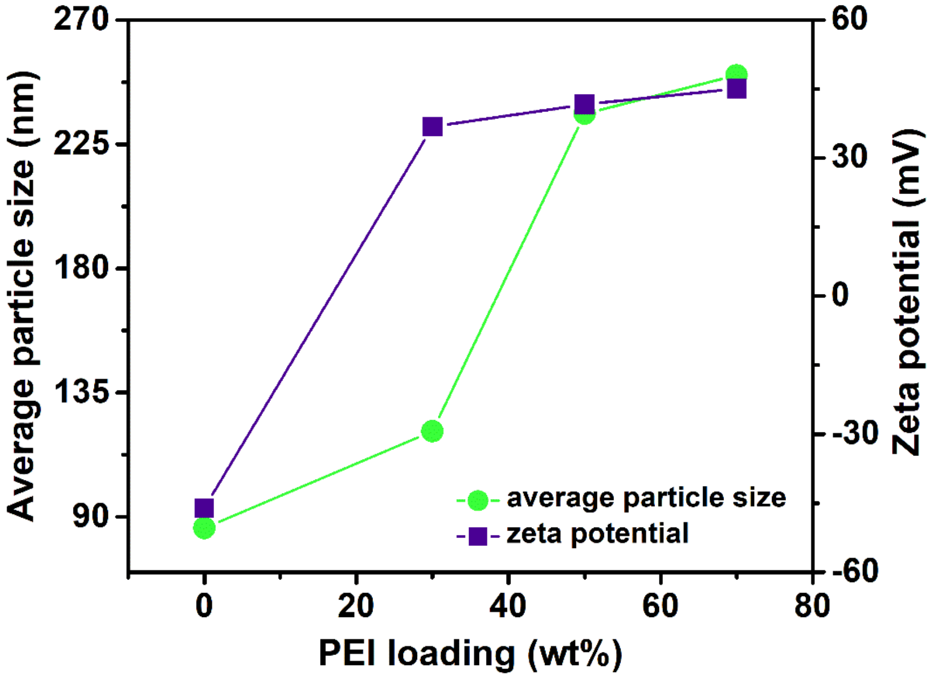

Figure 3. Average particle size and zeta potential of PEI functionalized silica xerogels as a function of PEI loading

Figure 4a shows CO_2 adsorption capacity of the neat silica xerogel and PEI functionalized silica xerogels. It was observed that CO_2 adsorption occurred through two stages including quick initial CO_2 uptake (in ~ 10 min) followed by slower CO_2 uptake. In the first stage, CO_2 adsorption rate was considerably high due to more active sites for CO_2 adsorption. With CO_2 saturation of the samples, CO_2 uptake became slower (Sanz-Pérez *et al.*, 2017).

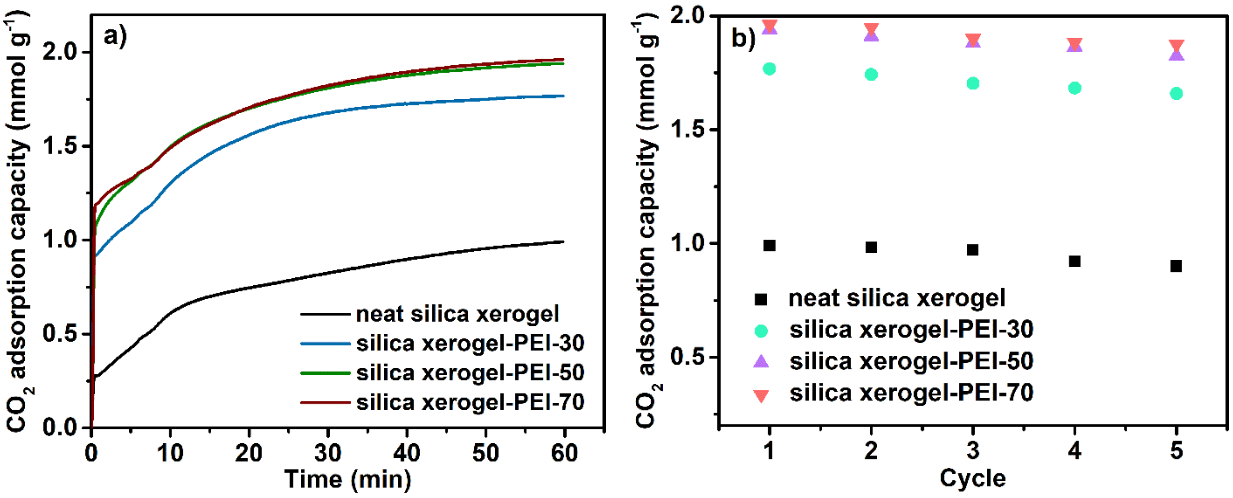

Figure 4. a) CO_2 adsorption capacity and **b)** CO_2 adsorption-desorption cycles of the neat silica xerogel and PEI functionalized silica xerogels

CO_2 adsorption capacity of the neat silica xerogel (0.98 mmol g^{-1}) was significantly increased in the case of PEI loading. An increase in amount of PEI had synergistic effects on CO_2 adsorption capacity of the samples that was contributed to more amine content promoting higher CO_2 adsorption. CO_2 adsorption capacity of silica xerogel loaded with 50 wt% PEI was determined as 1.94 mmol g^{-1}. Compared to CO_2 adsorption capacity of silica xerogel loaded with 50 wt% PEI, 70 wt% PEI loading provided a slight increase in CO_2 adsorption capacity of the silica xerogel (1.96 mmol g^{-1}). It is known that excessive PEI loading generally decreases or slightly increases CO_2 adsorption capacity of the materials. It is originated from PEI agglomerations on the surface of materials as well as increasing pore size making mass transfer difficult (Thi Le *et al.*, 2014). And also, the time required to achieve 90% of the equilibrium CO_2 adsorption capacity showed an increase from 21.9 min to 24.6 min with increasing PEI loading from 30 wt% to 70%, respectively. An increase in the time can be explained with PEI coating on the material surface in addition to PEI filled pores decelerates CO_2 diffusion (Panek *et al.*, 2017).

Under dry conditions, CO_2 adsorption mechanism is explained with reactions between amine groups and CO_2 molecules resulting in carbamate formation as expressed by the following equation. Firstly, zwitterion intermediate is formed by nucleophilic attack of amine group to CO_2. And then, the zwitterion is deprotonated by another amine group in which formation of carbamate, consists of two nitrogen, is observed (Wang *et al.*, 2015; Zeleňák *et al.*, 2008).

$$CO_2 + 2RNH_2 \rightarrow RNHCOO^- + RNH_3^+$$

Table 2 exhibits CO_2 adsorption capacity of other PEI functionalized silica based materials. Compared to that of the other materials, CO_2 adsorption capacity of PEI functionalized silica xerogel was higher. And also, when considered using cheap silica precursor to synthesize silica xerogel, the material can be regarded as a potential CO_2 adsorbent.

Table 2. Comparison of CO_2 adsorption capacity of other PEI functionalized silica based materials

Material	PEI loading (wt%)	Adsorption capacity (mmol g^{-1})	Reference
MCM-36	16.3	0.27	(Cogswell *et al.*, 2015)
SBA-15	43	0.81	(Gargiulo *et al.*, 2014)
MCM-41	50	1.00	(Xu *et al.*, 2002)
Core-shell 5A/silica	40	1.06	(Liu *et al.*, 2016)
Silica gel bead	15	1.16	(Minju *et al.*, 2015)
Fumed silica	50	1.70	(Goeppert *et al.*, 2011)
Silica xerogel	50	1.94	In this study
HMS	45	2.90	(Chen *et al.*, 2010)
KIT-6	50	3.07	(Son *et al.*, 2008)
Pore expanded MCM-41	55	4.77	(Heydari-Gorji *et al.*, 2011)

In CO_2 adsorption processes, regeneration of adsorbents is substantial for energy and cost saving. Generally, temperature swings (50 – 120 °C) are preferred to regenerate the adsorbent under an inert gas. However, at high temperatures, amine degradation caused a decrease in CO_2 adsorption capacity of amine functionalized adsorbents (Chen *et al.*, 2017). Figure 4b shows CO_2 adsorption capacity of PEI functionalized silica xerogels for each cycle. A slight decrease was observed in CO_2 adsorption capacity of the materials after 5 cycles that was assigned to possibility of amine leaching as well as deactivation of available sites on material surface (Kishor and Ghoshal, 2017). As a result, PEI functionalized silica xerogel with good stability can be used for long-term CO_2 adsorption processes.

4. CONCLUSION

PEI functionalized silica xerogels were successfully prepared by physical impregnation method.

Effective PEI functionalization of the neat silica xerogel was supported by FTIR results. With increasing PEI loading from 30 wt% to 70%, specific surface area of the neat silica xerogel considerably decreased. While pore volume of the neat silica xerogel was decreased in the case of PEI loading, an increase in pore size of the neat silica xerogel was observed. Due to the behaviour of PEI molecules as a coating on the silica xerogel surface, particle size of PEI functionalized silica xerogels was higher than that of the neat silica xerogel. PEI loading provided to increase zeta potential of the neat silica xerogel that improved interactions between CO_2 and amine groups on the silica xerogel. Synergistic effects of PEI functionalization on the CO_2 adsorption capacity of the neat silica xerogel were specified. Up to 50 wt% PEI loading, a significant increase in CO_2 adsorption capacity of the neat silica xerogel was observed. However, 70 wt% PEI loading slightly increased CO_2 adsorption capacity compared to CO_2 adsorption capacity of the silica xerogel loaded with 50 wt% PEI. At the end of CO_2 adsorption-desorption cycles, PEI functionalized silica xerogels showed good regeneration and stability. According to the results, it can be said that PEI functionalized silica xerogels are potential adsorbents for long-term CO_2 capture applications regarding as energy and cost saving.

REFERENCES

Balsamo, M., Rodríguez-Reinoso, F., Montagnaro, F., Lancia, A., Erto, A., 2013, "Highlighting the Role of Activated Carbon Particle Size on CO_2 Capture from Model Flue Gas", *Industrial & Engineering Chemistry Research*, 52, 12183-12191.

Chen, C., Son, W.-J., You, K.-S., Ahn, J.-W., Ahn, W.-S., 2010, "Carbon dioxide capture using amine-impregnated HMS having textural mesoporosity", *Chemical Engineering Journal*, 161, 46-52.

Chen, C., Zhang, S., Row, K. H., Ahn, W.-S., 2017, "Amine–silica composites for CO_2 capture: A short review", *Journal of Energy Chemistry*, 26, 868-880.

Cogswell, C. F., Jiang, H., Ramberger, J., Accetta, D., Willey, R. J., Choi, S., 2015, "Effect of Pore Structure on CO_2 Adsorption Characteristics of Aminopolymer Impregnated MCM-36", *Langmuir*, 31, 4534-4541.

Dos Santos, L. M., Bernard, F. L., Polesso, B. B., Pinto, I. S., Frankenberg, C. C., Corvo, M. C., ... & Einloft, S., 2020, "Designing silica xerogels containing RTIL for CO_2 capture and CO_2/CH_4 separation: Influence of ILs anion, cation and cation side alkyl chain length and ramification", *Journal of Environmental Management*, 268, 110340.

Dutcher, B., Fan, M., Russell, A. G., 2015, "Amine-based CO_2 capture technology development from the beginning of 2013-a review", *ACS Applied Materials & Interfaces*, 7, 2137-48.

Gargiulo, N., Peluso, A., Aprea, P., Pepe, F., Caputo, D., 2014, "CO_2 Adsorption on Polyethylenimine-Functionalized SBA-15 Mesoporous Silica: Isotherms and Modeling", *Journal of Chemical & Engineering Data*, 59, 896-902.

Goeppert, A., Czaun, M., May, R. B., Prakash, G. K. S., Olah, G. A., Narayanan, S. R., 2011, "Carbon Dioxide Capture from the Air Using a Polyamine Based Regenerable Solid Adsorbent", *Journal of the American Chemical Society*, 133, 20164-20167.

Guzel Kaya, G., Yilmaz, E., Deveci, H., 2019, "A novel silica xerogel synthesized from volcanic tuff as an adsorbent for high-efficient removal of methylene blue: parameter optimization using Taguchi experimental design", *Journal of Chemical Technology & Biotechnology*, 94, 2729-2737.

Guzel Kaya, G., Yilmaz, E., Deveci, H., 2020, "Synthesis of sustainable silica xerogels/aerogels using inexpensive steel slag and bean pod ash: A comparison study", *Advanced Powder Technology*, 31, 926-936.

Heydari-Gorji, A., Belmabkhout, Y., Sayari, A., 2011, "Polyethylenimine-Impregnated Mesoporous Silica: Effect of Amine Loading and Surface Alkyl Chains on CO_2 Adsorption", *Langmuir*, 27, 12411-12416.

Kim, M.-S., Kwak, D.-H., 2017, "Effect of Zeta Potential on Collision-Attachment Coefficient and Removal Efficiency for Dissolved Carbon Dioxide Flotation", *Environmental Engineering Science*, 34, 272-280.

Kishor, R., Ghoshal, A. K., 2017, "Amine-Modified Mesoporous Silica for CO_2 Adsorption: The Role of Structural Parameters", *Industrial & Engineering Chemistry Research*, 56, 6078-6087.

Kong, Y., Jiang, G., Wu, Y., Cui, S., Shen, X., 2016, "Amine hybrid aerogel for high-efficiency CO_2 capture: Effect of amine loading and CO_2 concentration", *Chemical Engineering Journal*, 306, 362-368.

Li, B., Duan, Y., Luebke, D., Morreale, B., 2013, "Advances in CO_2 capture technology: A patent review", *Applied Energy*, 102, 1439-1447.

Li, K., Jiang, J., Tian, S., Yan, F., Chen, X., 2015, "Polyethyleneimine–nano silica composites: a low-cost and promising adsorbent for CO_2 capture", *Journal of Materials Chemistry A*, 3, 2166-2175.

Linneen, N. N., Pfeffer, R., Lin, Y. S., 2013, "Amine Distribution and Carbon Dioxide Sorption Performance of Amine Coated Silica Aerogel Sorbents: Effect of Synthesis Methods", *Industrial & Engineering Chemistry Research*, 52, 14671-14679.

Liu, X., Gao, F., Xu, J., Zhou, L., Liu, H., Hu, J., 2016, "Zeolite@Mesoporous silica-supported-amine hybrids for the capture of CO_2 in the presence of water", *Microporous and Mesoporous Materials*, 222, 113-119.

Lou, F., Zhang, A., Zhang, G., Ren, L., Guo, X., Song, C., 2020, "Enhanced kinetics for CO_2 sorption in amine-functionalized mesoporous silica nanosphere with inverted cone-shaped pore structure", *Applied Energy*, 264, 114637.

Minju, N., Abhilash, P., Nair, B. N., Mohamed, A. P., Ananthakumar, S., 2015, "Amine impregnated porous silica gel sorbents synthesized from water–glass precursors for CO_2 capturing", *Chemical Engineering Journal*, 269, 335-342.

Mondal, M. K., Balsora, H. K., Varshney, P., 2012, "Progress and trends in CO_2 capture/separation technologies: A review", *Energy*, 46, 431-441.

Niu, M., Yang, H., Zhang, X., Wang, Y., Tang, A., 2016, "Amine-Impregnated Mesoporous Silica Nanotube as an Emerging Nanocomposite for CO_2 Capture", *ACS Applied Materials & Interfaces*, 8, 17312-17320.

Olivares-Marín, M., Maroto-Valer, M. M., 2012, "Development of adsorbents for CO_2 capture from waste materials: a review", *Greenhouse Gases: Science and Technology*, 2, 20-35.

Panek, R., Wdowin, M., Franus, W., Czarna, D., Stevens, L. A., Deng, H., ... & Snape, C. E., 2017, "Fly ash-derived MCM-41 as a low-cost silica support for polyethyleneimine in post-combustion CO_2 capture", *Journal of CO_2 Utilization*, 22, 81-90.

S. Aquino, A., O. Vieira, M., Ferreira, A. S. D., Cabrita, E. J., Einloft, S., O. de Souza, M., 2019, "Hybrid Ionic Liquid–Silica Xerogels Applied in CO_2 Capture", *Applied Sciences*, 9, 2614.

Sang Sefidi, V., Luis, P., 2019, "Advanced Amino Acid-Based Technologies for CO_2 Capture: A Review", *Industrial & Engineering Chemistry Research*, 58, 20181-20194.

Santiago, R., Lemus, J., Hospital-Benito, D., Moya, C., Bedia, J., Alonso-Morales, N.,... & Palomar, J., 2019, "CO_2 Capture by Supported Ionic Liquid Phase: Highlighting the Role of the Particle Size", *ACS Sustainable Chemistry & Engineering*, 7, 13089-13097.

Sanz-Pérez, E. S., Dantas, T. C. M., Arencibia, A., Calleja, G., Guedes, A. P. M. A., Araujo, A. S., & Sanz, R., 2017, "Reuse and recycling of amine-functionalized silica materials for CO_2 adsorption", *Chemical Engineering Journal*, 308, 1021-1033.

Sher, F., Iqbal, S. Z., Albazzaz, S., Ali, U., Mortari, D. A., Rashid, T., 2020, "Development of biomass derived highly porous fast adsorbents for post-combustion CO_2 capture", *Fuel*, 282, 118506.

Son, W.-J., Choi, J.-S., Ahn, W.-S., 2008, "Adsorptive removal of carbon dioxide using polyethyleneimine-loaded mesoporous silica materials", *Microporous and Mesoporous Materials*, 113, 31-40.

Taheri, F. S., Ghaemi, A., Maleki, A., Shahhosseini, S., 2019, "High CO_2 Adsorption on Amine-Functionalized Improved Mesoporous Silica Nanotube as an Eco-Friendly Nanocomposite", *Energy & Fuels*, 33, 5384-5397.

Thi Le, M. U., Lee, S.-Y., Park, S.-J., 2014, "Preparation and characterization of PEI-loaded MCM-41 for CO_2 capture", *International Journal of Hydrogen Energy*, 39, 12340-12346.

Wang, X., Chen, L., Guo, Q., 2015, "Development of hybrid amine-functionalized MCM-41 sorbents for CO_2 capture", *Chemical Engineering Journal*, 260, 573-581.

Witoon, T., Tatan, N., Rattanavichian, P., Chareonpanich, M., 2011, "Preparation of silica xerogel with high silanol content from sodium silicate and its application as CO_2 adsorbent", *Ceramics International*, 37, 2297-2303.

Xu, X., Song, C., Andresen, J. M., Miller, B. G., Scaroni, A. W., 2002, "Novel Polyethylenimine-Modified Mesoporous Molecular Sieve of MCM-41 Type as High-Capacity Adsorbent for CO_2 Capture", *Energy & Fuels*, 16, 1463-1469.

Zeleňák, V., Badaničová, M., Halamová, D., Čejka, J., Zukal, A., Murafa, N., & Goerigk, G., 2008, "Amine-modified ordered mesoporous silica: Effect of pore size on carbon dioxide capture", *Chemical Engineering Journal*, 144, 336-342.

Zhang, S., Chen, C., Ahn, W.-S., 2019, "Recent progress on CO_2 capture using amine-functionalized silica", *Current Opinion in Green and Sustainable Chemistry*, 16, 26-32.

Zhao, P., Zhang, G., Xu, Y., Lv, Y., 2019, "Amine functionalized hierarchical bimodal mesoporous silicas as a promising nanocomposite for highly efficient CO_2 capture", *Journal of CO_2 Utilization*, 34, 543-557.