

Immobilization of Choline Chloride: Urea onto Mesoporous Silica for Carbon Dioxide Capture

(Pemegunan Kolina Klorida: Urea ke atas Silika Mesoliang untuk Penangkapan Karbon Dioksida)

ZAITUN GHAZALI, NUR HASYAREEDA HASSAN, MOHD AMBAR YARMO, TEH LEE PENG & RIZAFIZAH OTHAMAN*

ABSTRACT

A green composite adsorbent based on mesoporous silica-gel (SG) and deep eutectic solvent (DES) mixture of choline chloride-urea (ChCl:U) was synthesized as an alternative for carbon dioxide (CO₂) adsorption. The composite adsorbent was prepared by wet impregnation technique with various ChCl:U (mole ratio 1:2) content in SG at 5-15% (w/w). Fourier transform infrared attenuated total reflectance (ATR-FTIR) results showed successful impregnation of ChCl:U into SG with the presence of C=O carbonyl amide group stretching, N-H scissoring bending, CH₂ bending and C-N stretching peaks. Thermal degradation of the adsorbent started with urea at 130°C followed by ChCl at 300°C. Meanwhile, nitrogen physisorption demonstrated a decrease in specific surface areas of the sorbents with increasing ChCl:U weight percentage due to the blockage of micropores by ChCl:U. The optimum CO₂ adsorption capacity of 22.3 mg/g was achieved by 10%ChCl:U/SG200, which was higher than the immobilised SG200, hence making it relevant to become a green and economical adsorbent for CO₂ capture.

Keywords: Adsorption; carbon capture; choline chloride; deep eutectic solvent; silica gel; urea

ABSTRAK

Penjerap komposit hijau berasaskan gel silika mesoliang (SG) dan pelarut eutektik dalam (DES) kolina klorida-urea (ChCl:U) disintesis untuk penjerapan karbon dioksida (CO₂). Penjerap komposit telah disediakan dengan teknik penjejalan basah dengan muatan 5-15% (b/b) ChCl:U (nisbah mol 1:2). Spektrum inframerah transformasi Fourier-pantulan penuh kecil (ATR-FTIR) membuktikan bahawa ChCl:U telah berjaya dijejalkan ke atas SG dengan kehadiran puncak regangan kumpulan karbonil amida C=O, bengkokan N-H, bengkokan CH₂ dan regangan C-N. Suhu degradasi penjerap bermula dengan urea pada 130°C diikuti oleh ChCl pada 300°C. Analisis penjerapan fizikal nitrogen menunjukkan penurunan luas permukaan dengan peningkatan peratus berat ChCl:U disebabkan mikroliang yang dilitupi oleh ChCl:U. Kapasiti penjerapan CO₂ yang optimum (22.3 mg/g) tercapai dengan menggunakan 10%ChCl:U/SG200 dengan kapasiti penjerapannya lebih tinggi berbanding SG200 tanpa pemegunan. Ini menjadikannya penjerap hijau yang ekonomi untuk penangkapan CO₂.

Kata kunci: Gel silika; kolina klorida; pelarut eutektik dalam; penangkapan karbon; penjerapan; urea

INTRODUCTION

In this millennium era, global warming and climate change have become of the main environmental concerns. Based on the facts and data gathered from the atmosphere, seawater, rock, ice on poles and plants, it is clear that the earth is experiencing global warming (Creamer & Gao 2015). Kyoto Protocol (1998) has listed carbon dioxide (CO₂) with other gases such as nitrous oxide (N₂O), methane (CH₄) and sulfur hexafluoride (SF₆) as greenhouse gases (Rao & Riahi 2006) with the significant increase in the concentration of CO₂ as a major cause of global warming (Vilarrasa-García et al. 201; Zhu et al. 2014). The Paris Climate Change Conference 2015 set the limit of global warming at below 2°C with only 1.5°C temperature rise. This agreement requires every country to reduce CO₂ concentration in the atmosphere. Therefore, researchers are now exploring ways of reducing CO₂ which include carbon capture study.

The most mature way for CO₂ capture is by using aqueous alkanol amines. This technique has several drawbacks such high energy consumption in desorption process, equipment corrosion and high volatility (Marcus 2018; Zhu et al. 2018). Ionic liquid (IL) has also been studied as liquid absorbent with special properties such as low vapour pressure, good thermal stability, tunability and high CO₂ solubility (Ramdin et al. 2012; Yusuf et al. 2018). However, its cost, toxicity, and poor biodegradability limit the application of IL as CO₂ absorbent (Zhang et al. 2015). Recently, increasing attention has been paid to new green solvent, deep eutectic solvents (DES) as a promising alternative to replace amine-based technologies. DES provide interesting advantages such as easy to prepare, biodegradable, low volatility, wide liquid range, water compatibility, low vapour pressure and biocompatible that are favourable in many possible green technologies including CO₂ capture (Zhang et al. 2015).

DES are generally obtained by mixing quaternary ammonium halide salts as hydrogen-bond acceptor (HBA) with hydrogen-bond donor (HBD) molecules at certain ratio. They are bonded through hydrogen bonds or metal halide bonds that result in lower melting point of the mixture compared to the individual components (Dai et al. 2013). Many types of DESs have been synthesized with various HBA:HBD molar ratio for CO₂ capture purpose. Mixtures of choline chloride (ChCl) or 2-hydroxy-N,N,N-trimethylethanaminium chloride and urea(U) are the most widespread chemicals used upon the design of DESs. Choline chloride:Urea (ChCl:U) are non-toxic, biocompatible, biodegradable, easy to prepare and inexpensive (Sarmad et al. 2017). Li et al. (2008) found that CO₂ showed the highest solubility, 0.309 mol_{CO₂}/mol_{DES} in choline chloride:urea (ChCl:U)(mole ratio 1: 2) at 313 K and 12.5 MPa. Su et al. (2009) in their study, using ChCl:U:H₂O (mole ratio 1:2:1) found that the solubility of CO₂ was 0.2694 mol_{CO₂}/kg_{DES} at 313.15 K and 350 KPa pressure. Meanwhile, Leron et al. (2013) reported that the CO₂ solubility in ChCl:Urea was higher than ChCl:glycerol and ChCl:ethylene glycol (Leron & Li 2013). Sarmad et al. (2017) investigated the CO₂ solubility of various type of DES based on ammonium and phosphonium salt as HBA. They reported that the synthesized DESs had higher CO₂ solubility and lower viscosity than conventional IL. Those findings have given promising insights on the potential of DESs as solvent for CO₂ capture.

However, high viscosity of liquid ChCl:U requires high pressure environment for maximum CO₂ absorption that can lead to increasing operational cost. In addition, DES and other solvents in liquid form at room temperature are difficult to manage. Liquid adsorption material integrated with porous solid materials as supporter can overcome this problem (Gray et al. 2012; Hu et al. 2017). This integration has promising remarks that may increase CO₂ adsorption capacity. An example of effective adsorbent is silica gel (SG). Silica are materials having high surface area that can be applied in various applications (Abdullah et al. 2017; Jon et al. 2013). The existence of micro and meso pores, high thermal stability and excellent in regeneration process of SG are beneficial for CO₂ adsorbent. However, past studies showed that the CO₂ adsorption capacity on SG surface is still low especially at atmospheric temperature and pressure (Yu et al. 2011). Thus, modification of SG through immobilization liquid absorbent, specifically in this study with ChCl:U would be recommended to enhance the CO₂ adsorption capacity.

In this work, solid adsorbents from impregnated choline chloride:urea (ChCl:U) onto silica were synthesized using simple wet impregnation method. The effect of ChCl:U percentage loading on the surface functional group, thermal stability, the surface properties and pore structure of adsorbents were investigated. The adsorbents were screened in terms of their CO₂ adsorption capacity at 25°C and 1 atm.

MATERIALS AND METHODS

MATERIALS

Choline chloride, ChCl (≥98%, Sigma Aldrich) and urea, U (≥99%, Merck) were obtained from Aldrich Chemistry. The support materials used in this work were microporous and mesoporous commercial Silica Gel 60 purchased from Merck with particle size in the range of 0.200-0.063 mm. All materials used as received without further purification. Pure nitrogen and carbon dioxide gases (purity> 99.0%) were obtained from Ply Gas Company, Malaysia.

PREPARATION METHOD

Synthesis of Adsorbents DES was prepared by mixing ChCl and U in the molar ratio of 1:2. Both compounds were pre-dried in the oven at 100°C. The mixture was heated up to 80°C and continuously stirred for 2 h until homogeneous colourless liquid was obtained. The liquid formed was then transferred into a well-sealed bottle and kept in desiccator. Composite materials ChCl:U/SG were prepared using wet impregnation method. Prior to impregnation, SG was calcined at 200°C for 4 h to remove moisture. Twenty mL of ethanol was added to the specified amount of 0.1-0.3 g ChCl:U and the solution was gently stirred until dissolved. Afterwards, 1.7-1.9 g of SG was added to the initial mixture followed by stirring for 4 h at room temperature in a closed system. Then, the mixture was sonicated for 5 min at 5 amplitudes, 3 W and 1600 J by S 4000-010 Sonicator 4000. After that, the mixture was dried at 80°C for 6 h to eliminate volatile compound. SG200, 5%ChCl:U/SG200, 10%ChCl:U/SG200 and 15%ChCl:U/SG200 were the final adsorbent products. Dried adsorbents were kept in sealed bottle in a desiccator before further characterization.

Characterization The presence of surface functional groups was determined using Perkin Elmer Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectrometer in the range of 600-4000 cm⁻¹. Thermogravimetric analysis (TGA) and Differential Thermogravimetric analysis (DTG) were performed for all samples using Mettler Toledo TGA/SDTA 851. Surface area and porosity properties of the samples were characterized using N₂ physisorption at 77 K over Micromeritics ASAP 2020 instrument. Prior to analysis, the samples were degassed at 100°C for 5 h to remove the moisture and adsorbed gas. In this work, Brunauer, Emmet and Teller (BET) method was used to obtain the surface area. Pore volume and pore size distribution were determined by Barret-Joyner-Halenda (BJH) method. Pore size distribution for sorbents was computed using Barret-Joyner-Halenda (BJH) to determine the mesopores filling mechanism.

CO₂ ADSORPTION EVALUATION

The adsorption and desorption isotherms of CO₂ were carried out using Micromeritics ASAP 2020 instrument by replacing N₂ gas with CO₂ gas at room temperature

and atmospheric pressure. Pure 99% CO₂ was used and equipped with circulating water to control the temperature. The interaction between 10%ChCl:U/SG and CO₂ was studied using fluidized-bed reactor with glass column. Approximately 1.0 g of the adsorbent was purged with nitrogen (N₂) and heated at 100°C for 1 h to remove moisture content and humidity followed by exposure to 99.9% of CO₂ for 24 h with 30 mL/min gas flow rate. The samples were analysed for morphology and elemental composition using FESEM-EDX model ZEISS SupramTM 55.

RESULTS AND DISCUSSION

CHARACTERIZATION OF ADSORBENTS SURFACE FUNCTIONAL GROUP: FTIR SPECTROSCOPY

Figure 1 shows the FTIR spectra of ChCl:U, SG200 and 5-15%ChCl:U/SG200. The assignments of functional groups for each sample are provided in Table 1. The confinement of ChCl:U into SG200 was confirmed by the presence of bands marked in shaded box in Figure 1 that belongs to peaks of C=O carbonyl amide group stretching (1669 cm⁻¹), N-H scissoring bending (1632 cm⁻¹), CH₂ bending (1478 cm⁻¹) and C-N stretching (1429 cm⁻¹) (Hayyan et al. 2015). As compared to IR spectrum of ChCl:U, these bands shifted to higher wavenumber

upon impregnation, possibly due to the formation of hydrogen bond between ChCl:U and SG200 (Guo et al. 2017). It is expected that Cl⁻ anion in ChCl:U would form hydrogen bond with silanol group in silica. Shi et al. (2005) and Zhang et al. (2009) explained that anions of IL: BF₄⁻, (CN)₂N⁻, (CF₃SO₂)N⁻ and CF₃SO₃⁻ may formed hydrogen bonds with silanol group in SG. At the same time, the presence of large number of oxygen and nitrogen containing functional groups in ChCl:U permitted the possible hydrogen bonding formation with SG. Proposed schematic illustration of interaction between SG200 and ChCl:U is shown in Figure 2(a). The interaction is depicted from the mechanism proposed between IL and mesoporous silica (Marwani & Alsafrani 2013).

TERMAL STABILITY: TGA AND DTG THERMOGRAMS

Figure 3 shows the TGA and DTG thermogram of SG200, 5-15%ChCl:U/SG200. DTG curve clearly shows that the decomposition of impregnated ChCl:U depicted the same pattern of curve with three peaks of weight loss. The first (130°C) and second onset decomposition temperature (210°C) belonged to the decomposition of urea. First maximum rate of decomposition occurred at 180°C and secondly at 240°C. Schaber et al. (2014) investigated the decomposition of urea and reported that

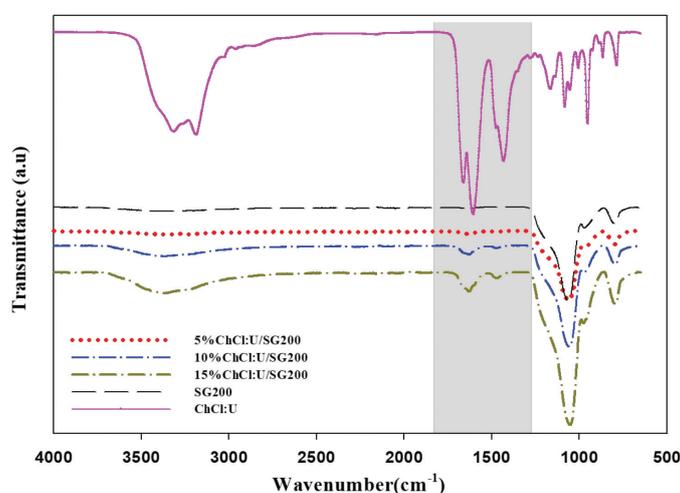


FIGURE 1. ATR-FTIR spectra for ChCl:U, SG200 and 5-15%ChCl:U/SG200

TABLE 1. Detected FTIR peaks for ChCl:U/NS spectrum with matching functional groups and the origin

Wavenumber (cm ⁻¹)	Functional group	Origin
1669	C=O stretch amide	Urea
1632	N-H scissoring band	Urea
1478	CH ₂ bending	ChCl
1429	C-N bending	Urea
1100	Si-O stretching	SG200
951	Si-OH bending	SG200
793	Si-O-Si	SG200

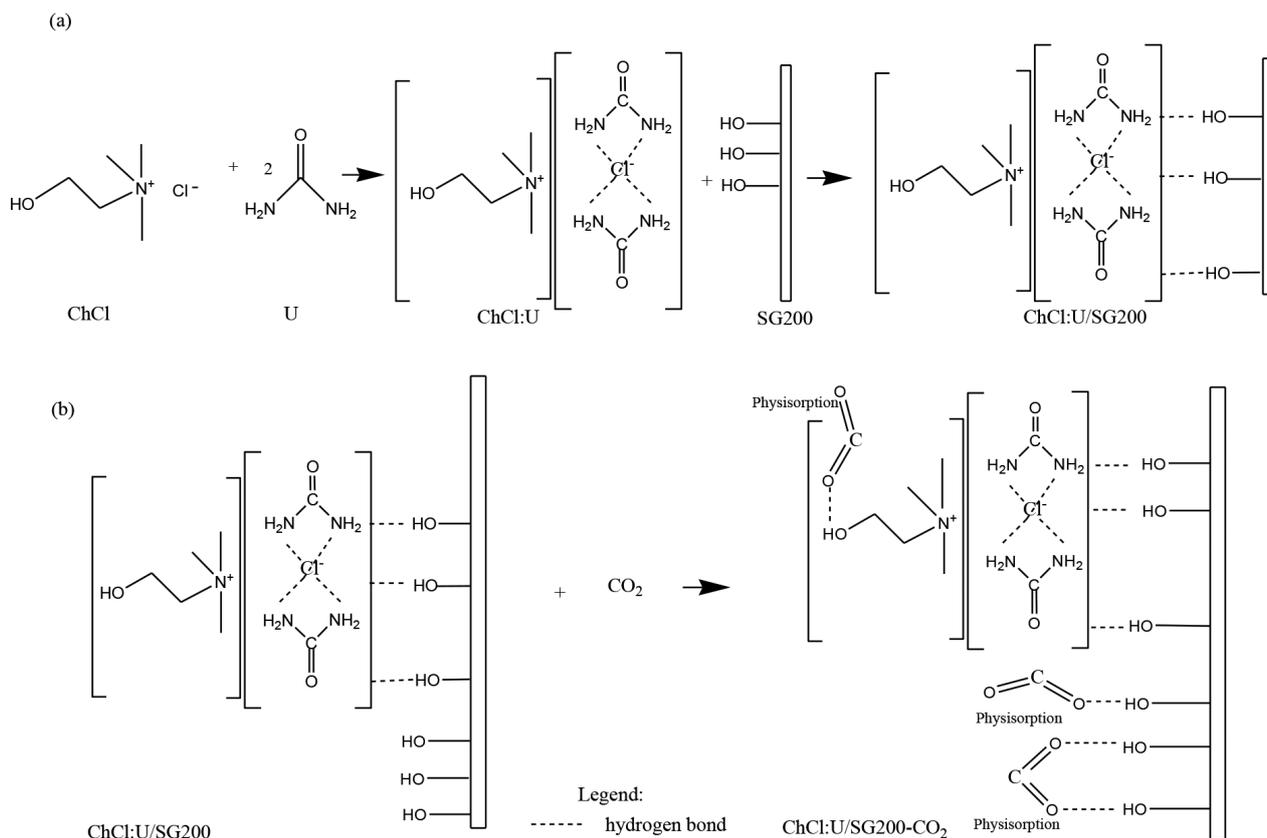


FIGURE 2. Propose schematic illustration mechanism of (a) impregnation of ChCl:U onto SG200 and (b) interaction of ChCl:U/SG200 and CO₂

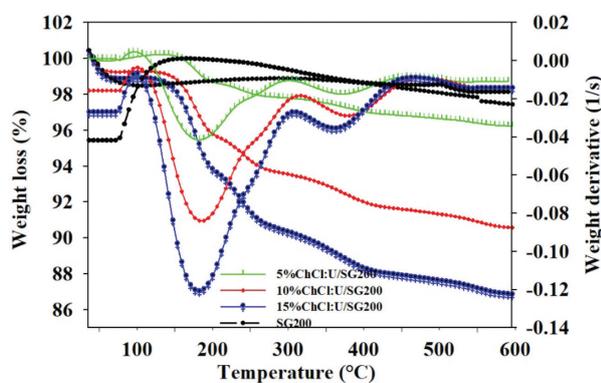


FIGURE 3. TGA and DTG thermograms for SG200 and 5-15%ChCl:U/SG200

at first stage, $\approx 140^\circ\text{C}$, it involved the urea vaporization. The rate of decomposition increased rapidly above 152°C to produce cyanic acid, ammonia and biuret. The second stage estimated $\approx 210^\circ\text{C}$ due to the decomposition of biuret. The third onset decomposition temperature, estimated at 310°C belonged to decomposition of choline chloride. Urea with relatively poor thermal stability would decompose first, followed by ChCl. However, the onset decomposition of ChCl was a little bit higher than pure ChCl which is 300°C (Zhang et al. 2015) due to the formation of hydrogen bond within the -OH from silanol

group and the Cl⁻ from ChCl. Therefore, 5-15%ChCl:U/SG200 sorbents were found to be stable up to 100°C and heated and regenerated at 100°C without decomposing ChCl:U.

POROSITY AND SURFACE AREA

N₂ adsorption-desorption isotherms at 77 K of all samples exhibited Type IV in IUPAC classification as shown in Figure 4(a), which is a common characteristic of mesoporous material with mesopores (Sing et al. 1985). These isotherms with H2 hysteresis were associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high relative pressure that exhibited a narrow neck and wide bodies pore of mesopores (Sing et al. 1985). The porous structures of the adsorbents were tuned by changing the weight percentage loading of ChCl:U onto SG200. This led in reducing the specific surface areas within the range of 268-333 m²/g (Table 2). Meanwhile, the average pore size of 5-15%ChCl:U/SG200 (6.60-6.50 nm) were larger compared to the average pore size of the support SG200 (6.20 nm). This may suggest the ChCl:U loaded on the SG200 with uneven distribution creating its own structure with larger neck widths (Wang et al. 2012).

Smaller average pore diameter for 15%ChCl:U loading compared to 5% and 10% results from more pore filling

and thickening of ChCl:U layer on SG200. These results indicated that mesopores of the support were blocked or covered at higher ChCl:U loading that led to decrease in surface area. It is suggested that during impregnation process, the ChCl:U was first distributed in the micropores and mesopores channels in the SG200 skeleton until it was filled. Further loading, ChCl:U coated the external surface of the supporter frameworks (Abu Tahari et al. 2015; Guo et al. 2017).

All sorbents showed large pore size distribution that covered mesoporous (20–200Å) (Figure 4(b)). The bell shape of the distribution is smaller for 15%ChCl:U/SG200 with several small sharp peaks on SG200 at two pores, 86 Å and 100 Å in diameter, were diminished. This result supported the aforementioned statement that part of the mesopores were blocked. It also suggested that ChCl:U can easily enter narrow pore structure leading to pore filling completely.

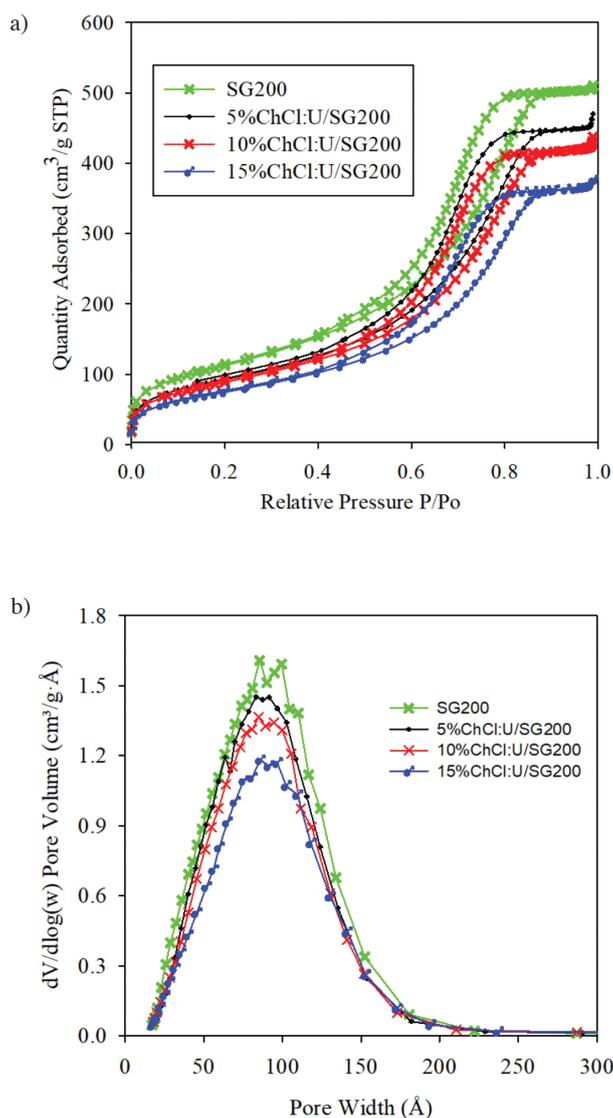


FIGURE 4. a) N₂ adsorption and desorption isotherm
b) pore size distribution for SG200 and 5-15%ChCl:U/SG200

TABLE 2. Physical properties for SG200 and 5-15%ChCl:U/SG200

Adsorbents	S _{BET} (m ² /g)	S _{t-plot external} (m ² /g)	V _{total} (cm ³ /g)	Average pore size (nm)
SG200	397.8	399.3	0.78	6.20
5%ChCl:U/SG200	333.0	353.4	0.73	6.60
10%ChCl:U/SG200	317.5	338.8	0.65	6.54
15%ChCl:U/SG200	268.0	286.8	0.56	6.50

CO₂ ADSORPTION STUDY

Figure 5(a) and 5(b) shows the CO₂ adsorption isotherm and CO₂ maximum adsorption capacity for all samples at 25°C, 1 atm pressure and 99% CO₂. The adsorption capacity of SG200 is improved after ChCl:U impregnation. SG200 managed to adsorb more CO₂ (20.3 mg/g) as a result of physical adsorption between CO₂ and SG200. The CO₂ uptake was being governed by the accessible mesopores in which the CO₂ was trapped in mesopores and might form hydrogen bond with silanol group (Zhang et al. 2009). With 5% and 10%ChCl:U loading, the CO₂ adsorption capacity increased up to 21.3 and 22.3 mg/g, respectively, indicating that the impregnated ChCl:U onto SG200 can capture CO₂ effectively. It suggested that increment of ChCl:U loading up to 10% covered the external and internal pore surface area hence leading to the occurrence of more interaction between ChCl:U and CO₂. Higher loading of ChCl:U up to 15% did not show significant impact to the overall CO₂ uptake but negatively causing extreme decreased in CO₂ adsorption capacity to 19.7 mg/g. Excess ChCl:U to 15% loading has blocked the SG200 mesopores, hence the CO₂ could not diffuse inside the pore (Lee et al. 2014). It can be seen from the steep reduction of the surface area and

pore volume for 15%ChCl:U/SG200. As a result, we can conclude that 10%ChCl:U/SG200 gave the highest CO₂ adsorption capacity.

Figure 6 shows the 10%ChCl:U/SG200 morphology before and after adsorption of CO₂ using FESEM with expansion of 10 000 K and elemental analysis using EDX. The SG200 surface was covered with ChCl:U, therefore, the presence of the pore on the surface of SG200 could not be clearly seen. There were unclear changes in the sample structure before and after the adsorption of CO₂. EDX analysis showed that the CO₂ adsorption occurred when the percentage of atom C and O percentages were increased after CO₂ exposure.

It was suggested that the main adsorption is physisorption in which the trapped CO₂ formed hydrogen bond with the -OH from SG200 silanol group. Figure 2(b) shows the suggested reaction mechanism of the CO₂ sorption on ChCl:U/SG200. There is also a slight possibility of chemical reaction occurrence due to a long period exposure with CO₂ (24 h) which need more supported evidence from analysis result. The information about mechanism involved is still limited and need to be explored.

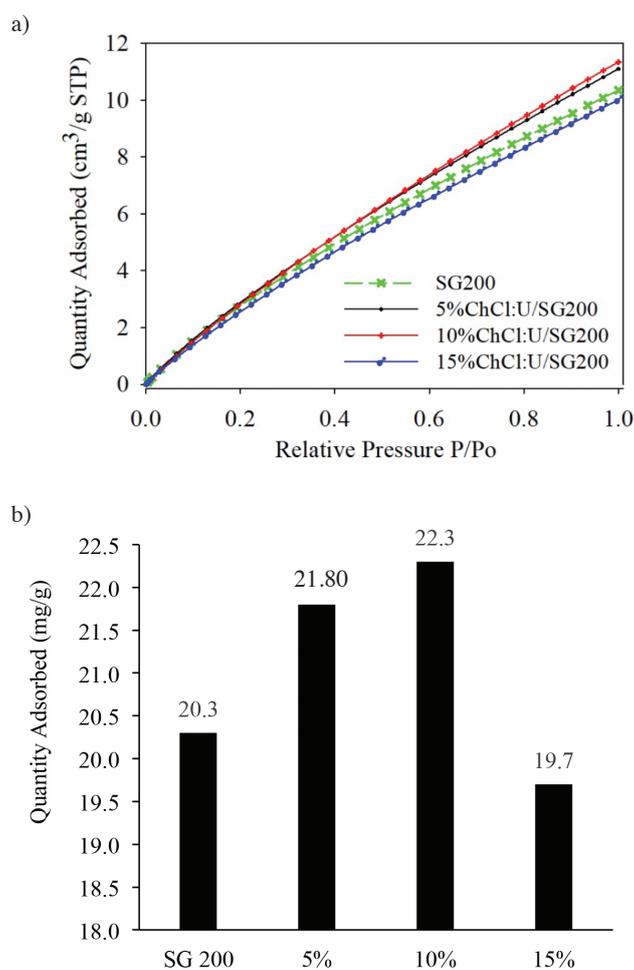


FIGURE 5. (a) CO₂ adsorption isotherm and (b) CO₂ maximum adsorption capacity for SG200, 5-15%ChCl:U/SG200

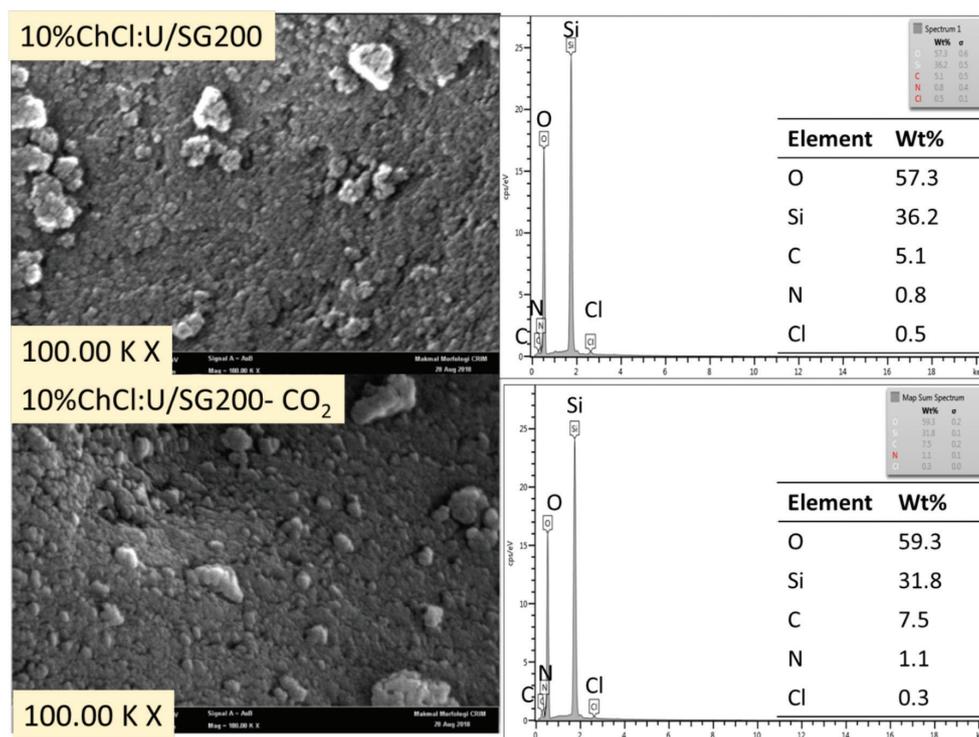


FIGURE 6. FESEM micrograph and EDX analysis for 10%ChCl:U/SG200 a) before exposure with CO₂ and b) after exposure with CO₂ at magnifying scale 10 000K

TABLE 3. Adsorption capacity of ChCl:U and ILs as comparison

Solvent/supporter	T (K)	P (MPa)	CO ₂ ACp (mg/g)	References
10%ChCl:U/SG200	303	0.101	22.3	This work
ChCl:Ethylene glycol/AC	303	0.101	9.8	Zulkurnai et al. 2017
10% [Emim][H ₂ SO ₄]/SiO	298	0.101	26.7	Marliza et al. 2017
16% [Emim][Gly]/γ-Al ₂ O ₃	303	0.101	25.0	Balsamo et al. 2018
16% [Emim][Gly]/AC	303	0.101	17.2	Erto et al. 2015

*AC= activated carbon (Filtrisorb 400), T= Temperature, P= Pressure, ACp= Adsorption Capacity

The adsorption capacity of 10%ChCl:U/SG200 from this study was compared with the adsorption of supported ChCl:U and ILs obtained from literatures as shown in Table 3. The adsorption capacity of 10%ChCl:U/SG200 was comparable to IL [Emim][H₂SO₄]/SiO and [Emim][Gly]/γ-Al₂O₃ although the supporters used (SiO and γ-Al₂O₃) had larger surface area. Furthermore, adsorption capacity of 10%ChCl:U/SG200 was better than ChCl:U and [Emim][Gly] supported activated carbon. These results showed 10%ChCl:U/SG200 adsorbent as a potential candidate for CO₂ capture alternative as its adsorption capacities were higher than the non-functionalised SG200. The ability and effectiveness of this adsorbent in capturing CO₂ at room temperature 25°C and atmospheric pressure 1 atm making it a practical material for CO₂ capture.

CONCLUSION

In this work, choline chloride:urea (ChCl:U) impregnated onto silica gel (SG) was synthesized as a new green solid adsorbent for CO₂ capture. The 10% addition of ChCl:U onto SG was the optimum ratio with the highest CO₂ adsorption capacity of 22.3 mg/g. The adsorption of CO₂ in impregnated ChCl:U was found to be comparable with other impregnated liquid adsorbents. Therefore, 10%ChCl:U/SG200 could be regarded as a promising adsorbent for CO₂ capture at room temperature and atmospheric pressure.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Universiti Kebangsaan Malaysia (UKM) for funding this project under

research grants of ST-2017-008 and FRGS/1/2017/STG01/UKM/02/5, Polymer Research Centre (PORCE) for technical support and Centre for Research and Instrumentation Management (CRIM) for the instrument facilities.

REFERENCES

- Abu Tahari, M.N., Hakim, A., Wan Isahak, W.N.R., Samad, W.Z. & Yarmo, M.A. 2015. Adsorption of CO₂ on Octadecylamine-Impregnated on SiO₂: Physical and chemical interaction studies. *Advanced Materials Research* 1087: 137-141.
- Balsamo, M., Erto, A., Lancia, A., Totarella, G., Montagnaro, F. & Turco, R. 2018. Post-combustion CO₂ capture: On the potentiality of amino acid ionic liquid as modifying agent of mesoporous solids. *Fuel* 218(April 2017): 155-161.
- Creamer, A.E. & Gao, B. 2015. *Carbon Dioxide Capture: An Affective Way to Combat Global Warming*. New York: Springer Berlin Heidelberg.
- Dai, Y., Van Spronsen, J., Witkamp, G., Verpoorte, R. & Choi, Y.H. 2013. Ionic liquids and deep eutectic solvents in natural products research: Mixtures of solids as extraction solvents. *Journal of Natural Product* 76: 2162-2173.
- Erto, A., Silvestre-albero, A., Silvestre-albero, J., Rodríguez-reinoso, F., Balsamo, M., Lancia, A. & Montagnaro, F. 2015. Carbon-supported ionic liquids as innovative adsorbents for CO₂ separation from synthetic flue-gas. *Journal of Colloid and Interface Science* 448: 41-50.
- Gray, M.L., Champagne, K.J., Fauth, D., Baltrus, J.P. & Pennline, H. 2012. Performance of immobilized tertiary amine solid sorbents for the capture of carbon dioxide. *International Journal of Greenhouse Gas Control* 2(2008): 3-8.
- Guo, X., Ding, L., Kanamori, K., Nakanishi, K. & Yang, H. 2017. Functionalization of hierarchically porous silica monoliths with polyethyleneimine (PEI) for CO₂ adsorption. *Microporous and Mesoporous Materials* 245: 51-57.
- Hayyan, M., Abo-Hamad, A., AlSaadi, M.A. & Hashim, M.A. 2015. Functionalization of graphene using deep eutectic solvents. *Nanoscale Research Letters* 10(1): 2-26.
- Hu, J., Yang, X., Yu, J. & Dai, G. 2017. Carbon dioxide (CO₂) absorption and interfacial mass transfer across vertically confined free liquid film-a numerical investigation. *Chemical Engineering & Processing: Process Intensification* 111: 46-56.
- Jon, N., Abdullah, I. & Othaman, R. 2013. Effects of silica on the formation of epoxidised natural rubber/polyvinyl chloride membrane. *Sains Malaysiana* 42(4): 469-473.
- Lee, C.H., Hyeon, D.H., Jung, H., Chung, W., Jo, D.H., Shin, D.K. & Kim, S.H. 2014. Effects of pore structure and PEI impregnation on carbon dioxide adsorption by ZSM-5 zeolites. *Journal of Industrial and Engineering Chemistry* 23: 251-256.
- Leron, R.B. & Li, M.H. 2013. Solubility of carbon dioxide in a choline chloride-ethylene glycol based deep eutectic solvent. *Thermochimica Acta* 551: 14-19.
- Leron, R.B., Caparanga, A. & Li, M.H. 2013. Carbon dioxide solubility in a deep eutectic solvent based on choline chloride and urea at T = 303.15-343.15K and moderate pressures. *Journal of the Taiwan Institute of Chemical Engineers* 44(6): 879-885.
- Marcus, Y. 2018. Gas solubilities in deep eutectic solvents. *Monatshefte Fur Chemie* 149(2): 211-217.
- Marliza, T.S., Yarmo, M.A., Hakim, A., Tahari, M.N.A., Hisham, M.W.M. & Taufiq-Yap, Y.H. 2017. CO₂ capture on NiO supported imidazolium-based ionic liquid. *American Institute of Physics* 20008: 1-8.
- Marwani, H.M. & Alsafrani, A.E. 2013. New solid phase extractor based on ionic liquid functionalized silica gel surface for selective separation and determination of lanthanum. *Journal of Analytical Science and Technology* 4(1): 13.
- Ramdin, M., De Loos, T.W. & Vlucht, T.J.H. 2012. State-of-the-art of CO₂ capture with ionic liquids. *Industrial and Engineering Chemistry Research* 51: 8149-8177.
- Rao, S. & Riahi, K. 2006. The role of non-CO₂ greenhouse gases in climate change mitigation: Long-term scenarios for the 21st century. *Energy Journal* 27: 177-200.
- Sarmad, S., Mikkola, J.P. & Ji, X. 2017. Carbon dioxide capture with ionic liquids and deep eutectic solvents: A new generation of sorbents. *ChemSusChem* 10(2): 324-352.
- Schaber, P.M., Colson, J., Higgins, S., Thielen, D., Anspach, B. & Brauer, J. 2004. Thermal decomposition (pyrolysis) of urea in an open reaction vessel. *Thermochimica Acta* 424(1-2): 131-142.
- Shi, F., Zhang, Q., Li, D. & Deng, Y. 2005. Silica-gel-confined ionic liquids: A new attempt for the development of supported nanoliquid catalysis. *Chemistry - A European Journal* 11(18): 5279-5288.
- Sing, S.W.K., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J. & Siemieniowska, T. 1985. Reporting physisorption data for gas/solid systems. *Pure Applied Chemistry* 57: 603-619.
- Vilarrasa-García, E., Cecilia, J.A., Santos, S.M.L., Cavalcante, C.L., Jiménez-Jiménez, J., Azevedo, D.C.S. & Rodríguez-Castellón, E. 2014. CO₂ adsorption on APTES functionalized mesocellular foams obtained from mesoporous silicas. *Microporous and Mesoporous Materials* 187: 125-134.
- Wang, K., Shang, H., Li, L., Yan, X., Yan, Z., Liu, C. & Zha, Q. 2012. Efficient CO₂ capture on low-cost silica gel modified by polyethyleneimine. *Journal of Natural Gas Chemistry* 21(3): 319-323.
- Yu, B., Cong, H., Zhao, X.S. & Chen, Z. 2011. Carbon dioxide capture by Dendrimer-modified silica nanoparticles. *Adsorpt. Sci. Technol.* 29(8): 781-788.
- Yusuf, N.Y.M., Masdar, M.S., Isahak, W.N.R.W. & Nordin, D. 2018. Impregnated carbon- ionic liquid as innovative adsorbent for H₂/CO₂ separation from biohydrogen. *International Journal of Hydrogen Energy* 44(6): 3414-3424.
- Zhang, J., Ma, Y., Shi, F., Liu, L. & Deng, Y. 2009. Room temperature ionic liquids as templates in the synthesis of mesoporous silica via a sol-gel method. *Microporous and Mesoporous Materials* 119(1-3): 97-103.
- Zhang, Y., Ji, X. & Lu, X. 2015. Choline-based deep eutectic solvents for mitigating carbon dioxide emissions. *Novel Materials for Carbon Dioxide Mitigation Technology*, edited by Shi, F. & Morreale, B. New York: Elsevier B.V. pp. 87-116.
- Zhu, J., He, B., Huang, J., Li, C. & Ren, T. 2018. Effect of immobilization methods and the pore structure on CO₂ separation performance in silica-supported ionic liquids. *Microporous and Mesoporous Materials* 260(October 2017): 190-200.
- Zhu, J., Xin, F., Huang, J., Dong, X. & Liu, H. 2014. Adsorption and diffusivity of CO₂ in phosphonium ionic liquid modified silica. *Chemical Engineering Journal* 246: 79-87.

Zaitun Ghazali, Nur Hasyareeda Hassan, Mohd Ambar Yarmo,
Teh Lee Peng & Rizafizah Othaman*
School of Chemical Sciences and Food Technology
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor Darul Ehsan
Malaysia

Zaitun Ghazali, Nur Hasyareeda Hassan & Rizafizah Othaman*
Polymer Research Center
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor Darul Ehsan
Malaysia

Mohd Ambar Yarmo & Teh Lee Peng
Catalyst Research Group
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor Darul Ehsan
Malaysia

*Corresponding author; email: rizafizah@ukm.edu.my

Received: 7 February 2019

Accepted: 28 March 2019