

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

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

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### 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 (CO<sub>2</sub>) 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, CH<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 (CO<sub>2</sub>). 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 CH<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>.*

*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 (CO<sub>2</sub>) with other gases such as nitrous oxide (N<sub>2</sub>O), methane (CH<sub>4</sub>) and sulfur hexafluoride (SF<sub>6</sub>) as greenhouse gases (Rao & Riahi 2006) with the significant increase in the concentration of CO<sub>2</sub> 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 CO<sub>2</sub> concentration in the atmosphere. Therefore, researchers are now exploring ways of reducing CO<sub>2</sub> which include carbon capture study.

The most mature way for CO<sub>2</sub> 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 CO<sub>2</sub> solubility (Ramdin et al. 2012; Yusuf et al. 2018). However, its cost, toxicity, and poor biodegradability limit the application of IL as CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> showed the highest solubility, 0.309 mol<sub>CO<sub>2</sub></sub>/mol<sub>DES</sub> 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:H<sub>2</sub>O (mole ratio 1:2:1) found that the solubility of CO<sub>2</sub> was 0.2694 mol<sub>CO<sub>2</sub></sub>/kg<sub>DES</sub> at 313.15 K and 350 KPa pressure. Meanwhile, Leron et al. (2013) reported that the CO<sub>2</sub> solubility in ChCl:Urea was higher than ChCl:glycerol and ChCl:ethylene glycol (Leron & Li 2013). Sarmad et al. (2017) investigated the CO<sub>2</sub> solubility of various type of DES based on ammonium and phosphonium salt as HBA. They reported that the synthesized DESs had higher CO<sub>2</sub> solubility and lower viscosity than conventional IL. Those findings have given promising insights on the potential of DESs as solvent for CO<sub>2</sub> capture.

However, high viscosity of liquid ChCl:U requires high pressure environment for maximum CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> adsorbent. However, past studies showed that the CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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<sup>-1</sup>. 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 N<sub>2</sub> 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.

### CO<sub>2</sub> ADSORPTION EVALUATION

The adsorption and desorption isotherms of CO<sub>2</sub> were carried out using Micromeritics ASAP 2020 instrument by replacing N<sub>2</sub> gas with CO<sub>2</sub> gas at room temperature

and atmospheric pressure. Pure 99% CO<sub>2</sub> was used and equipped with circulating water to control the temperature. The interaction between 10%ChCl:U/SG and CO<sub>2</sub> was studied using fluidized-bed reactor with glass column. Approximately 1.0 g of the adsorbent was purged with nitrogen (N<sub>2</sub>) and heated at 100°C for 1 h to remove moisture content and humidity followed by exposure to 99.9% of CO<sub>2</sub> for 24 h with 30 mL/min gas flow rate. The samples were analysed for morphology and elemental composition using FESEM-EDX model ZEISS Supram™ 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<sup>-1</sup>), N-H scissoring bending (1632 cm<sup>-1</sup>), CH<sub>2</sub> bending (1478 cm<sup>-1</sup>) and C-N stretching (1429 cm<sup>-1</sup>) (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<sup>-</sup> 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: BF<sub>4</sub><sup>-</sup>, (CN)<sub>2</sub>N<sup>-</sup>, (CF<sub>3</sub>SO<sub>2</sub>)N<sup>-</sup> and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> 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

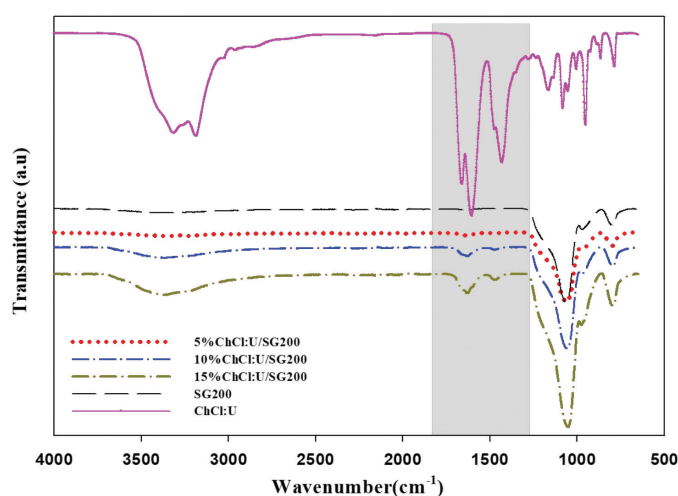


FIGURE 1. ATR-FTIR spectra for ChCl:U, SG200 and 5-15%ChCl:U/SG200

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

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

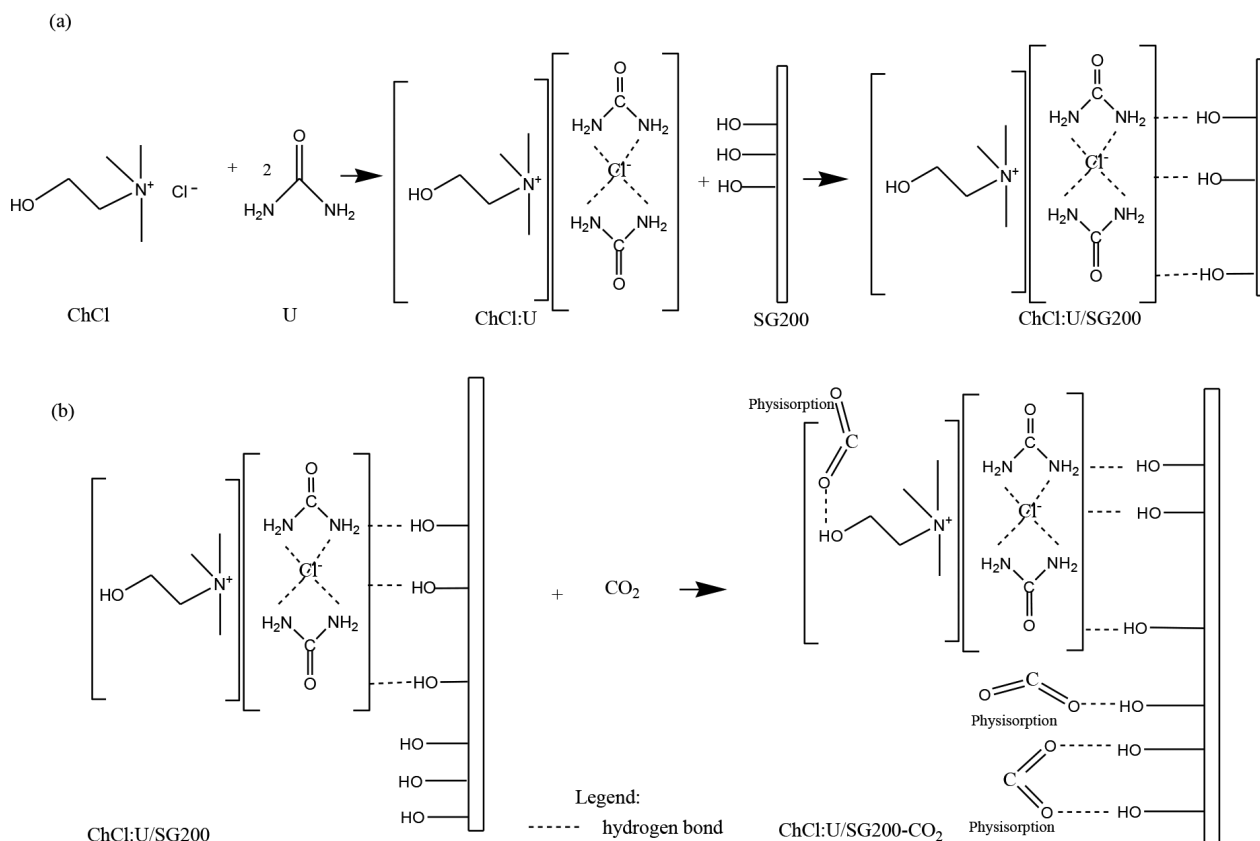


FIGURE 2. Propose schematic illustration mechanism of (a) impregnation of ChCl:U onto SG200 and (b) interaction of ChCl:U/SG200 and CO<sub>2</sub>

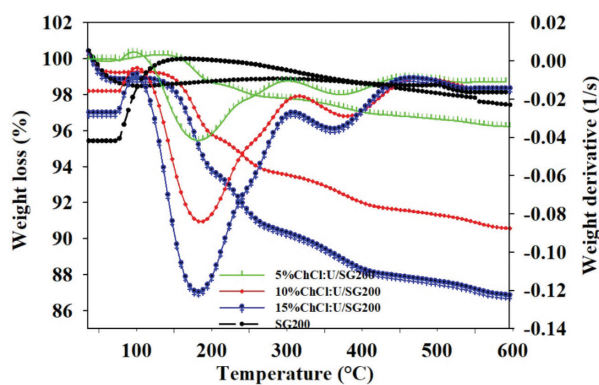


FIGURE 3. TGA and DTG thermograms for SG200 and 5-15%ChCl:U/SG200

at first stage,  $\approx 140^{\circ}\text{C}$ , it involved the urea vaporization. The rate of decomposition increased rapidly above  $152^{\circ}\text{C}$  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  $310^{\circ}\text{C}$  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  $300^{\circ}\text{C}$  (Zhang et al. 2015) due to the formation of hydrogen bond within the -OH from silanol

group and the Cl<sup>-</sup> from ChCl. Therefore, 5-15%ChCl:U/SG200 sorbents were found to be stable up to  $100^{\circ}\text{C}$  and heated and regenerated at  $100^{\circ}\text{C}$  without decomposing ChCl:U.

#### POROSITY AND SURFACE AREA

N<sub>2</sub> 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 m<sup>2</sup>/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.

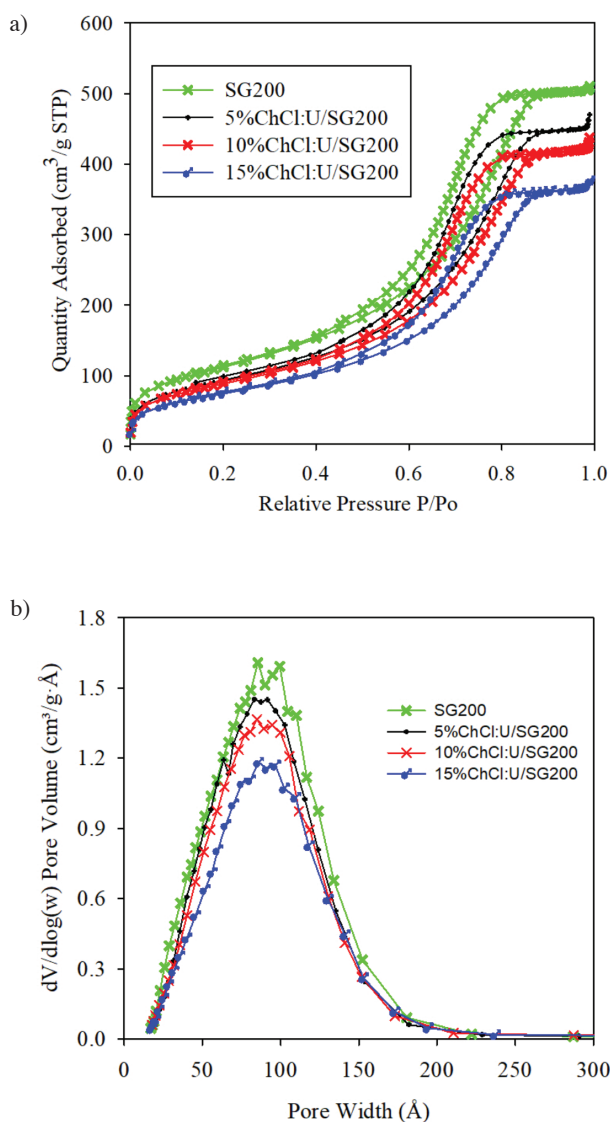


FIGURE 4. a) N<sub>2</sub> adsorption and desorption isotherm  
b) pore size distribution for SG200 and 5-15%ChCl:U/SG200

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

Adsorbents	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>t-plot external</sub> (m <sup>2</sup> /g)	V <sub>total</sub> (cm <sup>3</sup> /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

CO<sub>2</sub> ADSORPTION STUDY

Figure 5(a) and 5(b) shows the CO<sub>2</sub> adsorption isotherm and CO<sub>2</sub> maximum adsorption capacity for all samples at 25°C, 1 atm pressure and 99% CO<sub>2</sub>. The adsorption capacity of SG200 is improved after ChCl:U impregnation. SG200 managed to adsorb more CO<sub>2</sub> (20.3 mg/g) as a result of physical adsorption between CO<sub>2</sub> and SG200. The CO<sub>2</sub> uptake was being governed by the accessible mesopores in which the CO<sub>2</sub> was trapped in mesopores and might form hydrogen bond with silanol group (Zhang et al. 2009). With 5% and 10%ChCl:U loading, the CO<sub>2</sub> adsorption capacity increased up to 21.3 and 22.3 mg/g, respectively, indicating that the impregnated ChCl:U onto SG200 can capture CO<sub>2</sub> 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 CO<sub>2</sub>. Higher loading of ChCl:U up to 15% did not show significant impact to the overall CO<sub>2</sub> uptake but negatively causing extreme decreased in CO<sub>2</sub> adsorption capacity to 19.7 mg/g. Excess ChCl:U to 15% loading has blocked the SG200 mesopores, hence the CO<sub>2</sub> 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 CO<sub>2</sub> adsorption capacity.

Figure 6 shows the 10%ChCl:U/SG200 morphology before and after adsorption of CO<sub>2</sub> 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 CO<sub>2</sub>. EDX analysis showed that the CO<sub>2</sub> adsorption occurred when the percentage of atom C and O percentages were increased after CO<sub>2</sub> exposure.

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

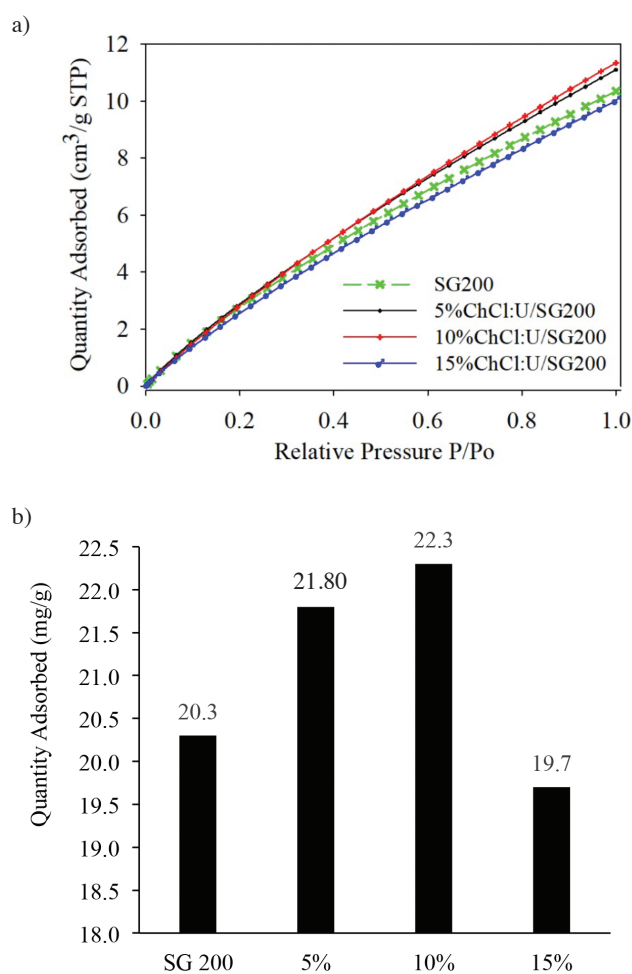


FIGURE 5. (a) CO<sub>2</sub> adsorption isotherm and (b) CO<sub>2</sub> maximum adsorption capacity for SG200, 5-15%ChCl:U/SG200

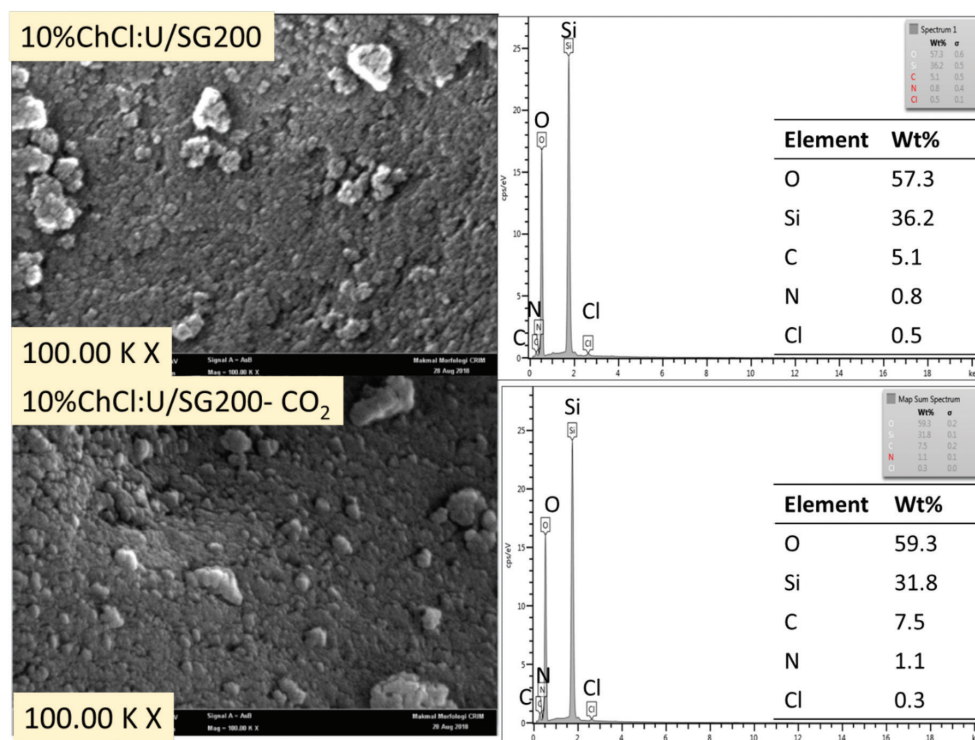


FIGURE 6. FESEM micrograph and EDX analysis for 10%ChCl:U/SG200 a) before exposure with CO<sub>2</sub> and b) after exposure with CO<sub>2</sub> at magnifying scale 10 000K

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

Solvent/supporter	T (K)	P (MPa)	CO <sub>2</sub> 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 <sub>2</sub> SO <sub>4</sub> ]/SiO	298	0.101	26.7	Marliza et al. 2017
16% [Emim][Gly]/γ-Al <sub>2</sub> O <sub>3</sub>	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][H<sub>2</sub>SO<sub>4</sub>]/SiO and [Emim][Gly]/γ-Al<sub>2</sub>O<sub>3</sub> although the supporters used (SiO and γ-Al<sub>2</sub>O<sub>3</sub>) 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 CO<sub>2</sub> capture alternative as its adsorption capacities were higher than the non-functionalised SG200. The ability and effectiveness of this adsorbent in capturing CO<sub>2</sub> at room temperature 25°C and atmospheric pressure 1 atm making it a practical material for CO<sub>2</sub> capture.

## CONCLUSION

In this work, choline chloride:urea (ChCl:U) impregnated onto silica gel (SG) was synthesized as a new green solid adsorbent for CO<sub>2</sub> capture. The 10% addition of ChCl:U onto SG was the optimum ratio with the highest CO<sub>2</sub> adsorption capacity of 22.3 mg/g. The adsorption of CO<sub>2</sub> 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 CO<sub>2</sub> capture at room temperature and atmospheric pressure.

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