Characteristics and carbon dioxide adsorption performance of amine-impregnated KCC-1 with different loading ratio

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Abstract. With our climate condition worsening day by day, the effort to mitigate this effect has been intensified. One of the ways to curb this issue is by reducing the release of carbon dioxide (CO₂) to the atmosphere via CO₂ capture. Among all the material used for CO₂ capture, amine-impregnated porous silica was observed to be a promising adsorbent. Research has shown its potential, but the accessibility issues caused by its narrow pore opening limits its capabilities. KCC-1, the latest member of the porous silica family, possesses unique fibrous morphology that can solve this problem. In this paper, a series of Tetraethylenepentamine (TEPA)-impregnated KCC-1 (KCC-1/TEPA) synthesized at three different loading ratios (KCC-1 to TEPA 2:1, 1:1 and 1:2) is reported. Characteristics study was conducted to determine the effect of loading ratio on its properties, and its CO₂ adsorption capacity was evaluated. FTIR peaks at 3430 cm⁻¹, 3300 cm⁻¹, 2950 cm⁻¹, 2841 cm⁻¹, 1658 cm⁻¹, 1565 cm⁻¹ and 1465 cm⁻¹ revealed that the impregnation was successful, while XRD diffractogram indicated that KCC-1 structure remained preserved in all impregnated samples. Increased surface area and pore volume reduction was observed with the increase of TEPA-loading ratio. KCC-1/T1:2 reported the highest CO₂ adsorption value among all three impregnated sample with 141 mg/g, while KCC-1/T2:1 recorded the lowest (82 mg/g). Results indicated that increasing TEPA loading ratio increases the number of active sites for CO₂ to attached, hence lead to increase CO₂ capture. Overall, it was shown that amount of CO₂ adsorbed is related to the amount of TEPA loaded to the sorbent.

1. Introduction
The increase of carbon dioxide (CO₂) emission to the atmosphere has been attributed to anthropogenic activities [1]. The main cause is our fossil fuel consumption as sources of energy for our economic and social activities [2]. With the increasing energy demand, more fossil fuel will be consumed, increasing the CO₂ and other greenhouse gases (GHG) emission even further. This in turn creates environmental problem such as global warming, climate change, polar ice cap melting and rising of sea level.

Carbon capture and sequestration (CCS) has been identified as a potential solution for this problem. One of the explored method is the post-combustion capture via dry adsorption. The advantage of this method is it is easy to use, energy efficient and do not cause corrosion to equipment [2, 3]. Among the sorbent that has been studied over the years is amine-impregnated porous silica. Encouraging CO₂
adsorption values has been reported using porous silicas such as MCM-41 and SBA-15 which impregnated with polyethylenimine (PEI) and tetraethylenepentamine (TEPA). However, massive loss of sorbents surface area was also reported, which was caused by the impregnation process. This, plus its narrow pore opening, causes accessibility issues that limits its adsorption performance [4].

In 2010, Polshettiwar et al. first reported the successful synthesis of dendritic fibrous nanosilica (DFNS) named as KCC-1 [5]. Unlike other porous silica, KCC-1 has a unique open fibrous morphology that increases the amount of surface area available for adsorption [6]. Singh et al. explored the use of KCC-1 for CO₂ adsorption in 2016 [4]. In that paper, it was reported that KCC-1 with higher nitrogen loading recorded higher surface area reduction and CO₂ adsorption. However, investigation into the effect of higher amine loading to the sorbent’s characteristics and adsorption behaviour was not carried out.

The objective of this paper is to study the effect of different TEPA loading ratio to the characteristics and CO₂ adsorption of TEPA impregnated KCC-1. The characteristics of each sample was studied and compared, before their CO₂ adsorption performance was evaluated. Finally, the adsorption behaviour of the adsorption process will also be studied by fitting the adsorption data with several existing isotherm models.

2. Methodology

2.1 Materials

The KCC-1 used in this research was produced by School of Chemical and Energy Engineering, from Universiti Teknologi Malaysia (UTM) Johor Bahru. The materials was synthesized using the microwave-assisted hydrothermal method, as reported in [5]. Typically the synthesis procedure begins with 2.5 g of tetraethoxysilicate (TEOS) being dissolved in cyclohexane and pentanol (23 g and 1.144 g) mixture. Afterwards, 1 g of cetylpyridinium bromide (CPB), 0.6 g of urea and 30 mL water will be added into the solution. After 30 minutes of stirring the solution will be treated with microwave radiation for 4 hours. Afterwards, the product was cooled to room temperature (25 °C), before centrifugation to separate the solid product. The product will be washed with distilled water and acetone before it was air dried at 110 °C. Finally, it will be calcined at 550 °C for 6 hours.

2.2 Sample preparation

The steps for the amine impregnation of KCC-1 was modified from [4]. To synthesize KCC-1 with TEPA at 1:1 loading ratio, 0.5 g of KCC-1 was sonicated in 25 mL of ethanol for 30 minutes to disperse the particles. Separately, 0.5 g of TEPA was dissolved in 30 mL of ethanol. The two mixture then was mixed together and stirred at 25 °C for around three hours. Finally, the mixture was oven-dried at 85 °C until it was fully dried. These steps then were repeated using different weight of KCC-1 and TEPA to achieve 1:2 and 2:1 loading ratio. The samples was denoted as KCC-1/Tx:y, where x:y refers to the ratio of KCC-1 to TEPA for that sample.

2.3 Characteristics Analysis

2.3.1 Fourier Transfer Infra-red (FTIR) analysis. FTIR spectroscopy analysis was carried out to determine the functional groups present in the particles before and after impregnation. The instrument used was the IRT Tracer-100 from Shimadzu of Japan at wavelength scan of 400-4000 cm⁻¹. The sample was prepared by mixing it with potassium bromide (KBr) at ratio 1:100 before being pressed to form a pellet. Prior to sample analysis, a background scan with blank KBr pellet was carried out first to eliminate peaks that might occur from KBr.

2.3.2 X-ray diffraction (XRD) analysis. X-ray diffraction (XRD) analysis was carried out to determine the crystallinity of the particles before and after impregnation. This was done using Advance D8 X-ray
Powder Diffractometer from Bruker of United States. All samples was subjected to the analysis at 20 angle from 2° to 90° with 0.053 step size value.

2.3.3 Surface area analysis. The surface area analysis was carried out using nitrogen (N₂) adsorption-desorption analysis using the NOVAtouch surface area and pore size analyser by Quantachrome, Anton Paar of United States. About 0.1 g of sample initially degassed for 60 minutes at 100°C for the impregnated samples and 300°C for pristine KCC-1 before subjected to N2 gas adsorption-desorption cycle. Data obtained from the adsorption-desorption isotherm was used to find the Brunauer-Emmett-Teller (BET) surface area and total pore volume.

2.4 CO₂ adsorption test

The sorbent performance for CO₂ adsorption was measured using Sorption Measuring Instrument with Magnetic Suspension Balance system by Rubotherm from Germany. First 0.5 g sample was loaded into the magnetic suspension balance, before pre-treated at 85°C in vacuum conditions until it weight stabilized to remove adsorbed ambient moisture. Buoyancy measurement of the sample was then carried out at 40°C and 30 bar to determine the weight and volume of the sample. For the CO₂ adsorption performances, the test was conducted at 150 mL min⁻¹ of 100 % CO₂ gas flow, at 40°C temperature until maximum pressure of 30 bar was reached. The amount of CO₂ adsorbed was measured at every 5 bar interval.

3. Results and Discussion

Figure 1 shows the FTIR spectrometer of KCC-1 and all three TEPA-impregnated KCC-1. In all the samples, peaks corresponding to KCC-1 was spotted, which was at wavelength of 1250 cm⁻¹, 1050 cm⁻¹, 800 cm⁻¹, and 450 cm⁻¹. For all the TEPA-impregnated samples, broad overlapping peaks at around 3400 cm⁻¹ and 3300 cm⁻¹, which belongs to the stretching of CH₂, and at 1660 cm⁻¹ which can be attributed to N-H bending of amine. The same corresponding to presence of amine group were also observed, with peaks at 2935 cm⁻¹ and 2831 cm⁻¹, which belongs to the stretching of CH₃, and at 1660 cm⁻¹ which can be attributed to N-H bending of amine. Meanwhile peaks at 1566 cm⁻¹, 1477 cm⁻¹ and 1300 cm⁻¹ are other characteristics peak of TEPA [7], which indicated the presence of TEPA in the surface of KCC-1 after impregnation, meaning that the impregnation process was successful. Increasing intensity of these peaks was also observed when the loading ratio was increased, indicating the higher amount of TEPA present in the sample.

![Figure 1. FTIR spectra of TEPA-impregnated KCC-1 at different loading ratio](image-url)
Figure 2 shows the XRD diffractogram for KCC-1 with different TEPA loading ratio. All three samples recorded the same broad peak at 2θ value around 23°. The results were very similar with other previously reported XRD analysis of KCC-1 [8, 9]. The broad peak shows that all the samples had an amorphous structure. There were no additional peaks observed with all three TEPA-impregnated samples, therefore it is safe to assume that the structure of KCC-1 is preserved after impregnation. The intensity of the peak was also found to be increasing with the increase of TEPA loading ratio. TEPA has been reported to have a XRD peak at around 19° [10], hence the overlapping peaks of KCC-1 and TEPA contributed to this added peak intensity.

Table 1 shows the surface area analysis of KCC-1 impregnated with TEPA at different loading ratio. Massive loss of surface area and pore volume was recorded with all three TEPA-impregnated KCC-1 samples, as compared with KCC-1. The highest loss of surface area and pore volume was recorded with KCC-1/T2:1, with 95% reduction of surface area and 80.7% reduction of pore volume, while KCC-1/T2:1 has the lowest reduction in both surface area and pore volume with 85.38% and 64% loss respectively. As TEPA-loading ratio increased, more TEPA molecules are attached to the surface and pores of KCC-1, causing the surface area and pore volume to decrease even further.

Table 1: Surface area analysis of KCC-1 and TEPA-impregnated KCC-1 at different loading ratio

| Sample       | BET surface area (m²/g) | Total Pore Volume (cm³/g) |
|--------------|-------------------------|---------------------------|
| KCC-1        | 560.295                 | 1.2692                    |
| KCC-1/T2:1   | 81.917                  | 0.4543                    |
| KCC-1/T1:1   | 61.720                  | 0.3344                    |
| KCC-1/T1:2   | 28.082                  | 0.2446                    |

Figure 3 shows the CO₂ adsorption isotherm of KCC1-1 and all three TEPA impregnated samples at different loading ratio. The highest adsorption capacity was recorded with KCC-1/T1:2 sample with 141 mg/g, followed by KCC-1/T1:1 with 125 mg/g, KCC-1 with 102.3 mg/g and KCC-1/T2:1 with 81.8 mg/g. Initially at lower pressure, the adsorption capacity of KCC-1/T2:1 was higher than KCC-1, but as the pressure increase, the adsorption capacity of KCC-1 also increases. At 20 bar it was higher than KCC-1/T2:1, it continued until maximum pressure of 30 bar.
The adsorption of CO$_2$ with TEPA impregnated KCC-1 involves a specific chemical reaction between primary and secondary amine with CO to form carbamate ions. It was first proposed by Caplow in 1968 [11] and can be represented by the equation below:

$$CO_2 + 2R_1R_2NH \rightleftharpoons R_1R_2NCOO^- + R_1R_2NH_2^+$$ (1)

On this basis, by increasing the amount of TEPA loading into KCC-1’s surface, we also increased the number of amine groups available to react with CO$_2$. Hence, this allows for CO$_2$ adsorption capacity to increase, which is reflected by the KCC-1/T1:2 performance. Similarly, reducing the TEPA loading ratio resulted in smaller number of amine groups present, hence limiting the adsorption performance of KCC-1/T2:1 sample.

Serna-Guerrero et al. [11] argued that the adsorption process with amine-functionalized silica involved contribution from both chemisorption from the previously mentioned mechanism and physisorption process. This was evident in the isotherm shape, where no samples recorded a saturation at higher pressure like common Langmuir isotherm. Instead, here it was observed that the adsorption continues to increase as pressure increases, albeit at slower pace than at lower pressure.

For unimpregnated KCC-1, there are no amine group presence, therefore the adsorption process is purely physisorption. At lower pressure the amount of CO$_2$ uptake was limited, but when the pressure increased the adsorption capacity also increased [12]. As KCC-1 has a significantly larger surface area compared to TEPA-impregnated KCC-1, this allowed KCC-1 to have higher CO$_2$ adsorption capacity at 30 bar pressure.

Table 2 below shows the comparison of the CO$_2$ adsorption performance between this study and other TEPA-impregnated porous silica reported. KCC-1/T1:2 has a much better CO$_2$ adsorption performance than all other TEPA-impregnated porous silica, including MCM-41, SBA-15 and KIT-6. The fibrous morphology of KCC-1 and high TEPA loading allows for high CO$_2$ adsorption to be achieved. This indicates that KCC-1/T1:2 has huge potential as an adsorbent for CO$_2$. **Figure 3.** CO$_2$ adsorption of TEPA-impregnated KCC-1 at different weight ratio
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Table 2. Adsorption capacity of KCC-1/T1:2 and previously reported TEPA-impregnated silica

| Silica                      | Adsorption Capacity (mg/g) | Source |
|-----------------------------|----------------------------|--------|
| TEPA-MCM-41                 | 118.8                      | [13]   |
| SBA-TEPA(50)                | 113.5                      | [14]   |
| 50 wt%-TEPA-Si-MCM-41       | 70.41                      | [15]   |
| PE-KIT-6(T)-35              | 127.6                      | [16]   |
| 0.64EB-TEPA/SiO₂            | 88                         | [17]   |
| SBA-393-50T                 | 124.52                     | [18]   |
| KCC-1/T1:2                  | 141                        | This study |

4. Conclusions
In this paper, KCC-1 particles were impregnated with TEPA in three different loading ratio; 1:1, 1:2 and 2:1, where each characteristics and CO₂ adsorption performance was evaluated afterwards. The characteristics indicated that the loading ratio did not radically alter the characteristics of the adsorbent. KCC-1/T1:2 recorded the highest CO₂ adsorption capacity after 30 bar pressure, while KCC-1/T1:1 recorded the lowest. The results of these experiments showed that increasing the TEPA loading ratio help to increase the CO₂ adsorption capacity. This result gives a better understanding on one of the factors influencing the CO₂ adsorption performance of KCC-1/TEPA and can be utilized for further study in this field.

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