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

**M S R M Nasir[1], M P Khairunnisa[1], N W C Jusoh[1, 2*] and A A Jalil[3]**

[1]Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia Kuala Lumpur, Jalan Sultan Yahya Petra, Kuala Lumpur, 54100, Malaysia
[2]Center of Hydrogen Energy, Universiti Teknologi Malaysia Kuala Lumpur, Jalan Sultan Yahya Petra, Kuala Lumpur, 54100, Malaysia
[3]School of Chemical and Energy Engineering, Universiti Teknologi Malaysia, UTM Johor Bahru, Johor, 81310, Malaysia

*nurfatehah@utm.my

**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 ($CO_2$) to the atmosphere via $CO_2$ capture. Among all the material used for $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ to attached, hence lead to increase $CO_2$ capture. Overall, it was shown that amount of $CO_2$ adsorbed is related to the amount of TEPA loaded to the sorbent.

## 1. Introduction

The increase of carbon dioxide ($CO_2$) 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 $CO_2$ 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 $CO_2$

adsorption values has been reported using porous silicas such as MCM-41 and SBA-15 which impregnated with polyethehylenimine (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 $CO_2$ adsorption in 2016 [4]. In that paper, it was reported that KCC-1 with higher nitrogen loading recorded higher surface area reduction and $CO_2$ 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 $CO_2$ adsorption of TEPA impregnated KCC-1. The characteristics of each sample was studied and compared, before their $CO_2$ 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 tetraorthosilicate (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 will be 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 2θ 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 ($N_2$) 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 CO$_2$ adsorption test*

The sorbent performance for $CO_2$ 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 $CO_2$ adsorption performances, the test was conducted at 150 mL min$^{-1}$ of 100 % $CO_2$ gas flow, at 40°C temperature until maximum pressure of 30 bar was reached. The amount of $CO_2$ 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 indicates the presence of both primary and secondary amine, was observed. 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 CH$_2$, 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.
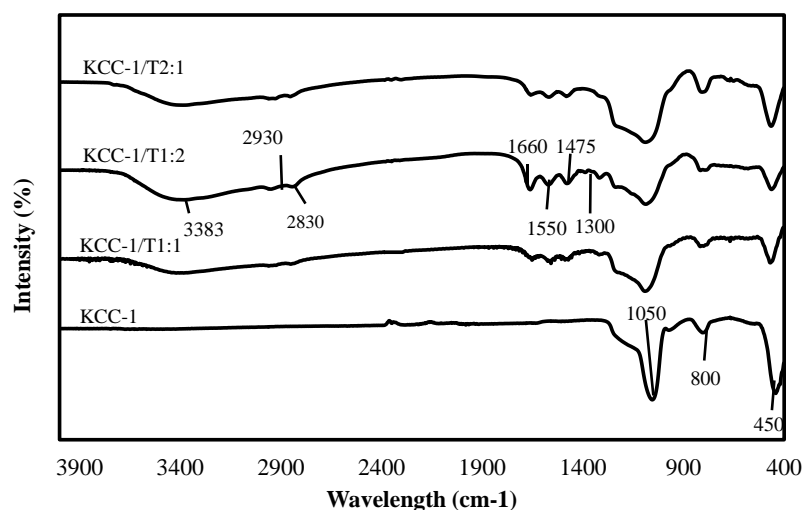


**Figure 1.** FTIR spectra of TEPA-impregnated KCC-1 at different loading ratio

Figure 2 shows the XRD diffractogram for 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.
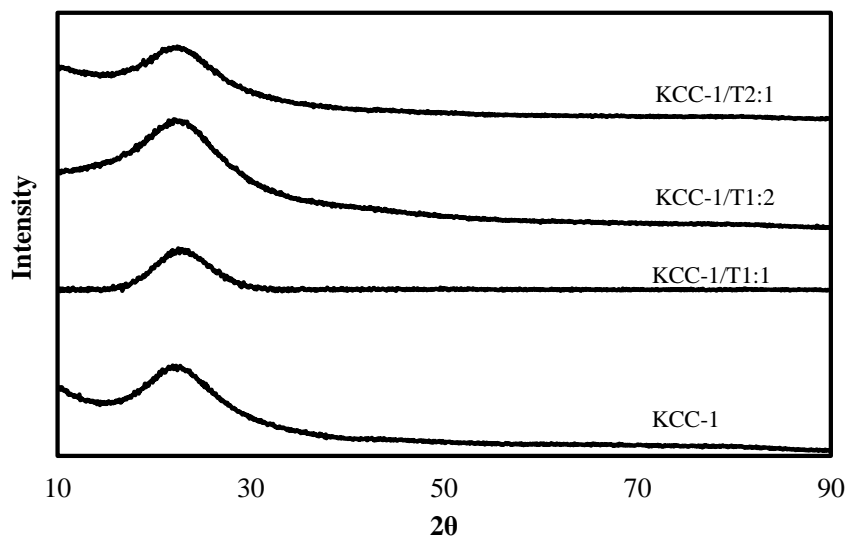


**Figure 2**. XRD diffractogram of TEPA-impregnated KCC-1 at different weight ratio

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/T1:2, 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 ($m^2/g$) | Total Pore Volume ($cm^3/g$) |
|---|---|---|
| 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 $CO_2$ 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.
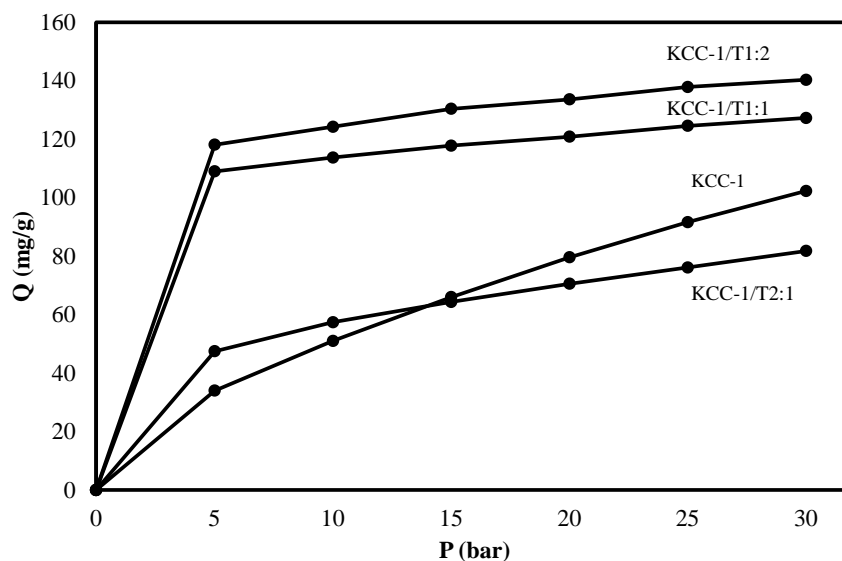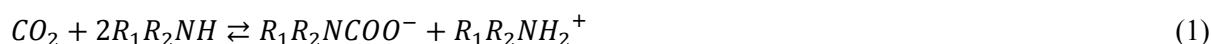
**Figure 3.** $CO_2$ adsorption of TEPA-impregnated KCC-1 at different weight ratio

The adsorption of $CO_2$ with TEPA impregnated KCC-1 involves a specific chemical reaction between primary and secondary amine with CO to formed carbamate ions. It was first proposed by Caplow in 1968 [11] and can be represented by the equation below:

$$CO_2 + 2R_1R_2NH \rightleftarrows R_1R_2NCOO^- + R_1R_2NH_2{}^+ \tag{1}$$

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 $CO_2$.

**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/SiO$_2$ | 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ adsorption capacity. This result gives a better understanding on one of the factors influencing the $CO_2$ adsorption performance of KCC-1/TEPA and can be utilized for further study in this field.

**Acknowledgment**

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