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To cite this article: M S R M Nasir *et al* 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **476** 012084

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Enhanced carbon dioxide adsorption by amine-modified KCC-1

M S R M Nasir¹, M P Khairunnisa¹, N W C Jusoh^{1,2} and A A Jalil³

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

E-mail: nurfatehah@utm.my

Abstract. The increase of carbon dioxide (CO₂) emission due to anthropogenic activities has become a threat to our environment. Hence there is an urgent need to control its emission via carbon capture and storage (CCS) strategy. However, the readily available method, which is liquid amine absorption, possesses some drawbacks including being energy intensive and may cause material corrosion. Dry CO₂ adsorption using amine-functionalized silica has been studied to provide a simple and cost-effective alternative for CO₂ capture. Recently emerged dendritic fibrous silica possesses excellent morphology and characteristics to be developed as an effective CO₂ adsorbent. Herein, the CO₂ adsorption performance using amine-modified fibrous silica nanoparticle, KCC-1 was studied. As-synthesized KCC-1 was modified with tetraethylenepentamine (TEPA) via impregnation method. Its characteristics were studied before it was subjected to the CO₂ adsorption experiment. The Fourier Transform Infra-red (FTIR) results indicates that TEPA was successfully impregnated with peaks at 3383 cm⁻¹, 2935 cm⁻¹, 2837 cm⁻¹, 1558 cm⁻¹, 1479 cm⁻¹ and 1309 cm⁻¹, while X-ray diffraction (XRD) analysis showed that KCC-1 structure was preserved. KCC-1/TEPA recorded higher adsorption capacity of CO₂ compared to the unmodified KCC-1, with maximum adsorption capacity of 189.86 mg/g. Equilibrium isotherm model fitting of the CO₂ adsorption was also carried out, and the adsorption data of KCC-1/TEPA fitted well to Toth isotherm. Overall, it has been demonstrated that KCC-1/TEPA has excellent potential to be used for CO₂ adsorption, and more studies need to be conducted for its development.

1. Introduction

Anthropogenic activities have been linked with the increase of carbon dioxide (CO₂) emission to the atmosphere since the Industrial Revolution [1]. This is mainly due to the consumption of fossil fuel to meet the energy demand for our economic and social activities [2]. As our demand continues to increase, this means that more fossil fuel will be consumed, and as a result the CO₂ emission, alongside other greenhouse gases (GHG) will increase even further. The direct consequence of this is the global warming effect, which cause many environmental problems such as climate change, polar ice cap melting and rising of sea level.

One way to mitigate this problem is via carbon capture and sequestration (CCS). One of the techniques commonly studied is the post-combustion capture via dry adsorption. This method is highly



attractive as 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 the dry adsorption using amine-impregnated porous silica. Porous silica such as MCM-41 and SBA-15 which impregnated with polyethylenimine (PEI) and tetraethylenepentamine (TEPA) has reported encouraging CO₂ adsorption values. Despite this, the impregnation process has cause massive loss of sorbents surface area, thus inhibiting its adsorption performance [4].

KCC-1 is a dendritic fibrous nanosilica (DFNS) particle that was discovered in 2010 by Polshettiwar and his colleagues [5]. A unique feature of this material is its open fibrous morphology, which increases the amount of surface area available for adsorption [6]. The use of amine-impregnated KCC-1 for CO₂ adsorption has been studied previously by Singh's group, where it was reported that TEPA-impregnated KCC-1 has better adsorption compared to TEPA-impregnated MCM-41[4].

The objective of this study is to study the CO₂ adsorption process using amine-impregnated KCC-1. The KCC-1 particles will be impregnated with TEPA, where its characteristics after impregnation will be compared with KCC-1. Afterwards, it will be subjected to CO₂ adsorption test, from which the data will be used for isotherm fitting analysis.

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 material was synthesized using the microwave-assisted hydrothermal method, as reported in [7]. 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.

Tetraethylenepentamine (TEPA) used for the impregnation method is acquired from Acros Organics of Thermo Fischer Scientific, Germany. TEPA molecular weight is 189.3, with density 0.99 g/cm³ and boiling point of 340°C.

2.2. Amine-impregnation of KCC-1

The steps for the amine impregnation of KCC-1 are modified from [4]. The synthesis begins with 0.5 g of KCC-1 sonicated in 25 mL of ethanol for 30 minutes to fully disperse the particles. Separately, 0.5 g of TEPA is dissolved in 30 mL of ethanol. The two mixture is then mixed together and stirred at 25°C for around three hours to ensure all the components mixed well. Finally, the mixture is then subjected to oven-drying at 85°C until it was fully dried.

2.3 Characteristics of TEPA-impregnated KCC-1

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

2.3.2. FTIR analysis. FTIR spectroscopy analysis will be carried out to determine the functional groups present in the particles before and after impregnation. The instrument that will be used is the IRT Tracer-100 from Shimadzu of Japan at wavelength scan of 400-4000 cm⁻¹. The sample is 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 will be carried out first to eliminate peaks that might occur from KBr.

2.3.3. Surface area analysis. The surface area analysis was carried out using N₂ adsorption-desorption analysis. The instrument used is the NOVAtouch surface area and pore size analyser by Quantachrome, Anton Paar of United States. About 0.1 g of sample was initially degassed at 300°C for 60 minutes before subjected to N₂ gas adsorption-desorption cycle. For the TEPA-impregnated sample the degassing will take place at 75°C for 4 hours. Data obtained from the adsorption-desorption isotherm will be used to find the Brunauer-Emmett-Teller (BET) surface area, average pore size and total pore volume.

2.4. CO₂ adsorption test

The sorbent performance for CO₂ adsorption will be measured using Sorption Measuring Instrument with Magnetic Suspension Balance system by Rubotherm from Germany. The sample will first be loaded into the magnetic suspension balance at 50°C in vacuum conditions until its weight stabilizes to remove adsorbed ambient moisture. Buoyancy measurement of the sample will be carried out at 40°C and 30 bar to determine the weight and volume of the sample. For the CO₂ adsorption performances, the test will be conducted at 150 mL min⁻¹ of 100% CO₂ gas flow, at 40°C temperature until maximum pressure of 30 bar is reached with 5 bar per step.

3. Results and Discussion

3.1. Characteristics of KCC-1 and KCC-1/TEPA

Figure 1 shows the XRD diffractogram of both KCC-1 and KCC-1/TEPA. From the figure we can see that the KCC-1 and KCC-1/TEPA sample showed a broad peak at 2θ value of 20°. This is consistent with the findings for amorphous material. This observation is consistent with several of the earlier studies on KCC-1 [8-10]. This indicates that the unique KCC-1 structure was preserved after the impregnation process.

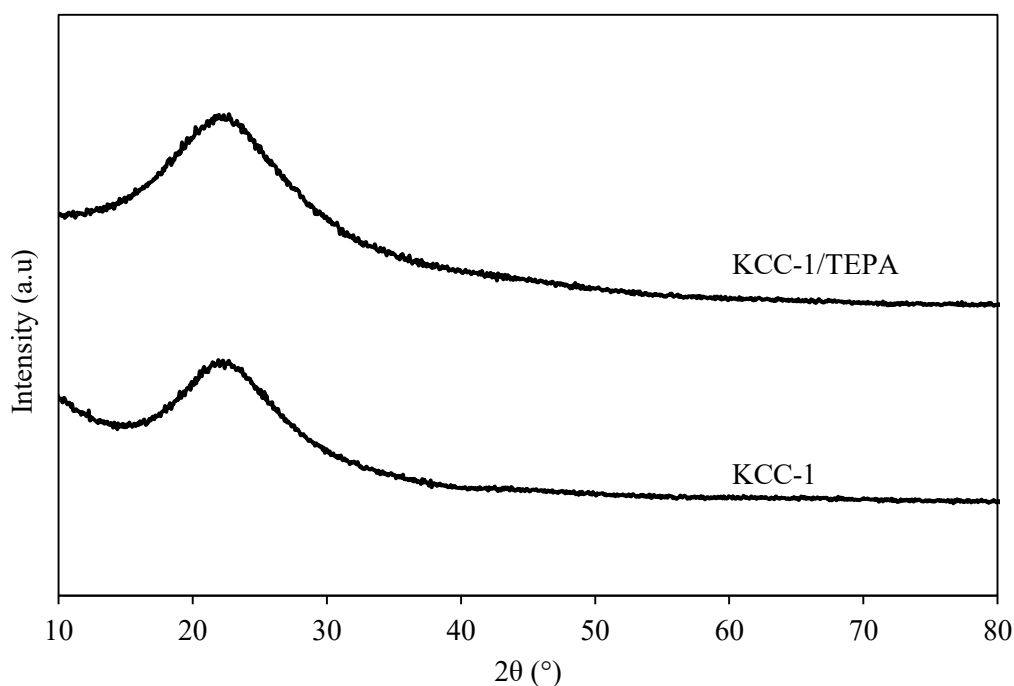


Figure 1. XRD diffractogram of KCC-1 and KCC-1/TEPA.

Figure 2 shows the FTIR spectra of the KCC-1 and KCC-1/TEPA samples. In all the samples, peaks at wavelength of 1215 cm^{-1} , 1050 cm^{-1} , 800 cm^{-1} , and 450 cm^{-1} were observed. These peaks are consistent with peaks corresponding to KCC-1, as reported by several previous studies [4, 10]. For KCC-1/TEPA samples, peaks corresponding to presence of amine group were also observed. Broad peak at 3383 cm^{-1} can be attributed to the stretching NH in the amine group, while peaks at 2935 cm^{-1} and 2837 cm^{-1} can be traced to the stretching of CH_2 . Peaks at 1558 cm^{-1} , 1479 cm^{-1} and 1309 cm^{-1} were also observed, which has been identified as characteristics peak of TEPA [11]. This indicates that the TEPA impregnation process has been successfully carried out.

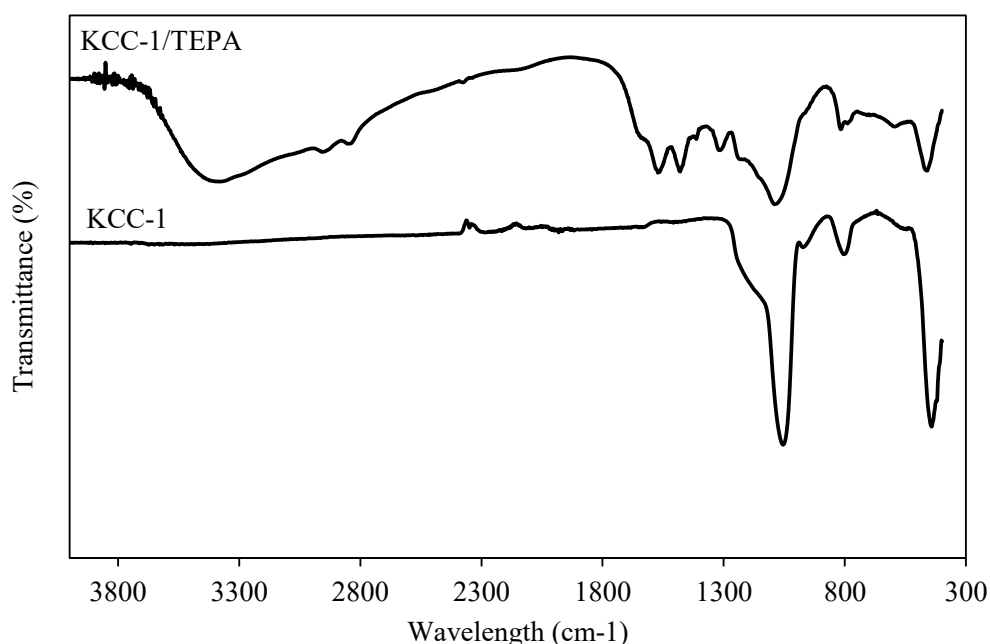


Figure 2. FTIR spectra of KCC-1 and KCC-1/TEPA.

Table 1 shows the summary of surface area analysis of both KCC-1 and KCC-1/TEPA. The table shows that a huge reduction of surface area (88.98%) and pore volume (73.68%) happened after impregnation. This was expected as the TEPA molecules occupied to the KCC-1 surface and pores after the impregnation process. The massive reduction of the surface area lead to the increase of average pore size.

Table 1. Summary of surface area analysis of KCC-1 and KCC-1/TEPA.

Sample	BET Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Size (nm)
KCC-1	560.295	1.269	4.531
KCC-1/TEPA	61.720	0.334	10.837

3.2. CO_2 adsorption performance

Figure 3 below shows the adsorption performance of both KCC-1 and KCC-1/TEPA. KCC-1/TEPA recorded the maximum CO_2 adsorption capacity of 189.856 mg/g , while KCC-1 recorded 153.270 mg/g maximum. It is also can be seen that around 15 bar of pressure, KCC-1/TEPA reached its equilibrium, while for KCC-1 it never reached equilibrium until the maximum pressure of 30 bar.

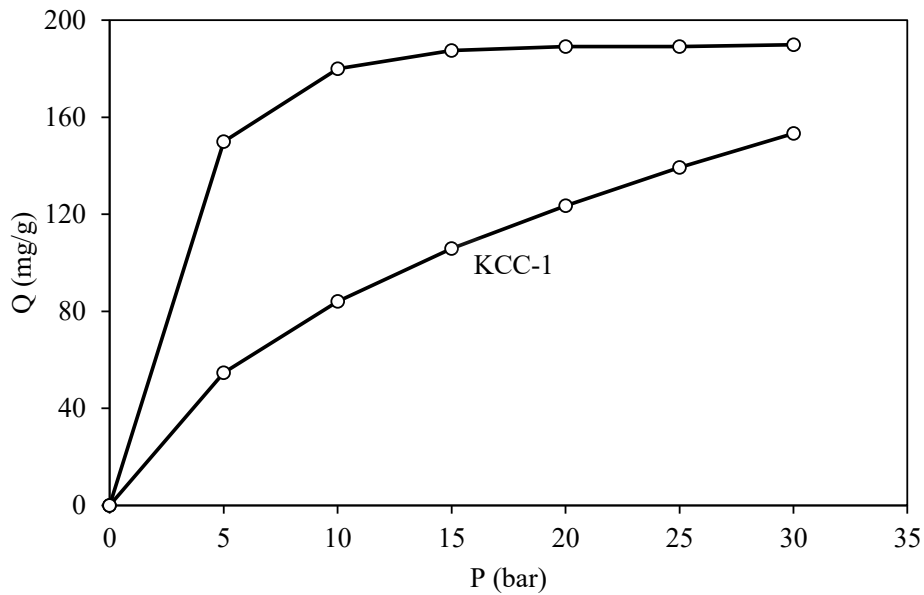


Figure 3. CO₂ adsorption isotherm of both KCC-1 and KCC-1/TEPA.

3.3. Equilibrium isotherm fitting

Table 2 below shows the equilibrium isotherm fitting for the adsorption data with KCC-1/TEPA. For two factor models (Langmuir and Freundlich), simple linear regression method was used, while for three factor models (Toth, Sips and Redlich-Peterson), the model fitting was carried out using MS Excel solver tool. The coefficient of correlation, R^2 values obtained indicates that the data fitted best with Toth isotherm. High fit with Toth isotherm strongly suggests that the surface of KCC-1/TEPA has heterogenous properties [12].

Table 2. Constants and correlation coefficients for adsorption isotherm models.

Isotherm	Constants	R^2
Langmuir	K_L (bar ⁻¹)	0.806
	Q_m (mg/g)	200
Freundlich	K_f (mg/g)	128.144
	$1/n$	0.1261
Toth	K_T (mg/g)	410.1301
	a_T (bar ⁻¹)	4.0968
	$1/t$	0.8450
Sips	B (bar ⁻¹)	0.1004
	q_m	191.0544
	$1/n$	2.2324
Redlich-Peterson	K_R	68.5916
	A_R (bar ⁻¹)	0.2047
	g	1.1401

Table 3 below shows the comparison of the adsorption performance recorded in this study and other TEPA-impregnated porous silica reported. From the table it is clear that our TEPA-impregnated KCC-1 is has higher CO₂ adsorption compared to previously studied KCC-1, pore expanded KIT-6 and Si-

MCM-41. This is due to the fibrous morphology possessed by KCC-1, allowing more surface area available for CO₂ adsorption. This highlighted the potential of KCC-1/TEPA to be developed as a CO₂ adsorbent.

Table 3. Comparison of CO₂ adsorption capacity of TEPA-impregnated porous silica.

Adsorbent	Adsorption Capacity (mg/g)	Source
TEPA-MCM-41	118.8	[13]
SBA-TEPA(50)	113.5	[14]
PE-SBA-15 (17e)-TEPA	164.0	[15]
KCC-1-TEPA _{ads}	177.0	[4]
50 wt. %-TEPA-Si-MCM-41	70.41	[16]
PE-KIT-6(T)-35	127.629	[17]
0.64EB-TEPA/SiO ₂	88.0	[18]
SBA-393-50T	124.548	[19]
KCC-1/TEPA	189.856	This study

4. Conclusions

In this study, DFNS particle of KCC-1 was impregnated with TEPA. Its characteristics and its CO₂ adsorption performance were evaluated. Result from the characteristics study indicates that the impregnation was successful without any significant change to the structure of KCC-1. The TEPA-impregnated KCC-1 was shown to have higher CO₂ adsorption capacity at 40°C and 30 bar of maximum pressure compared to KCC-1. The adsorption process data also fitted the Toth isotherm model very well. Overall, it has been demonstrated here the KCC-1/TEPA has excellent qualities as a CO₂ adsorbent, and worth to be explored further.

Acknowledgement

The authors would like to acknowledge the contribution from University Teknologi Malaysia Transdisciplinary Research Grant TDRG-Q.K130000.3453.06G61 for providing funds for this research, Centre of Hydrogen Energy (CHE), UTM KL for providing input and assistance, and MJIT Postgraduate Incentive for scholarship.

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