A brief on tetraethylenepentamine (TEPA) functionalized-adsorbents in CO_2 capture application

K. W. Tan, A. H. Ruhaimi*, C.N.C. Hitam, M.R. Taib

School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia (UTM), 81310 UTM Johor Bahru, Johor, Malaysia

E-mail: hafiiz.ruhaimi@gmail.com

Abstract. Among numerous carbon capture technologies, adsorption is considered one of the most effective approaches to reduce carbon dioxide (CO_2) emissions in the atmosphere. Various modification approaches of adsorbents have been introduced to enhance the CO_2 adsorption ability. Recently, an amine such as tetraethylenepentamine (TEPA) has been extensively used as an adsorbent's promoter because of its high amine density, low viscosity, low cost, and low toxicity properties. This has added an advantage to the adsorbent in terms of economical and environmentally benign. Therefore, it is important to provide the latest review on TEPA-functionalized adsorbents, specifically on the effects of TEPA functionalization, different TEPA loading, diverse adsorption conditions, as well as the structure of adsorbents towards the CO_2 adsorption capacity. Different adsorption conditions over a wide range of adsorption temperatures were thoroughly discussed and several recommendations for future studies were also been proposed.

1. Introduction

Nowadays, as the technology in the century is getting more advanced, more energies are needed for the operation of various sectors, especially in the industrial sectors such as factories and chemical plants. According to the statistics, approximately 70 percent of total global greenhouse gas emissions are from the combustion of fossil fuels, cement production, and other industrial processes (1). These processes are accompanied by high emissions of CO_2, which is a primary greenhouse gas responsible for climate change and global warming (2). Kamran and Park have stated that the amount of CO_2 in the atmosphere has increased from 280 to 410 ppm as the world temperature has risen from 273.6 to 274 K (3). A study conducted by Alkadhem and co-workers has demonstrated that the average Earth temperature will rise by about 274.5 K in this century (4). It is anticipated that the environment and the lives of many species will be adversely impacted if the global warming problem remains severe for the next few decades. Besides, the increment of worldwide global warming also inevitably could result in oxygen depletion and subsequent plankton extinction (5).

In this regard, researchers and concerned industries have been desperately seeking ways to reduce CO_2 emissions to the atmosphere. One of the ways is Carbon Capture and Storage (CCS), a simple approach where it involves the capturing, transporting, and storing of the CO_2 (6). The CCS technologies that are currently available include absorption, adsorption, cryogenic, membrane processes, etc (7). Different from the adsorption process that occurs on the surface, the absorption includes the whole material or liquid volume (6). However, the adsorption technique possesses some advantages such as the high loading capacity at ambient conditions, lower energy demand, and economic regeneration (8).

To date, several adsorbents have been extensively studied such as zeolites, carbon, silica, metal oxide, and metal-organic-frameworks (MOFs) (7). Numerous modification techniques were also reported that could further enhance the CO_2 adsorption performance of these adsorbents.
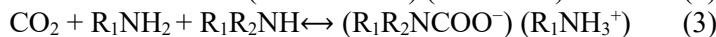
Among these approaches, amine-functionalized solid sorbents have attracted more attention for CO_2 capture applications (2). This is because the combination of high CO_2 affinity of amines and porous materials will exhibit beneficial properties such as high CO_2 adsorption rate and high thermal stability (9). Different from aqueous amine absorbent, the resultant amine-functionalized solid adsorbents did not require a large amount of energy for the regeneration process. These types of adsorbents also have high CO_2 adsorption capacity and could prevent the corrosion problem of equipment which is caused by the use of highly concentrated aqueous amine absorbent (9). In the previous studies, a few types of amines were employed and their effects toward improving the CO_2 uptake capacity of solid adsorbent were thoroughly investigated. These include several types of organic amines such as diethylenetriamine, triethylenetetramine, and TEPA. TEPA is a low cost, low toxicity, and high molecular weight amine with multiple amine groups per molecule (two primary amines (RNH_2) and three secondary amines (R_2NH) groups) (10, 11). Besides, TEPA as a branched polyamine has abundant amino functional groups and could potentially enhance the CO_2 adsorption of solid porous inorganic substrates such as nanosepiolite and mesocellular silica sponge (12). Furthermore, TEPA has a higher density of amine groups and a relatively lower viscosity compared to other amine compounds (13).

In this review article, an attempt has been carried out focusing on TEPA-functionalized adsorbents used for CO_2 capture applications. The effects of TEPA functionalization, different TEPA loading, and diverse adsorption conditions over a wide range of adsorption temperatures, as well as the impact of adsorbent's structure towards CO_2 uptake capacity, are also covered in this review. The future opportunities for the study of TEPA-functionalized adsorbents are finally presented to stimulate interest in this interesting area of CO_2 capture application.

2. Discussion

2.1. TEPA-functionalized adsorbents in CO_2 capture application

Recently, TEPA has been investigated as one of the amine alternatives for the functionalization of adsorbents toward effective CO_2 capture. TEPA are a linear molecules with five amine moieties that consists of two kinds of amine groups that are primary (R_1-NH_2) and secondary (R_1-NH-R_2) amines (9, 14). This properties of TEPA have proved the enhancement in the TEPA-functionalized adsorbents during CO_2 adsorption. Many researchers have subsequently concentrated on TEPA- functionalized sorbents as this type of amine offers promising advantages, such as higher density of amine groups and a relatively lower viscosity compared to other amine compounds. For example, based on the paper by Kasikamphaiboon and co-workers, during the adsorption of CO_2 into the MgO adsorbents, carbamates have been formed between two amine groups based on the chemical equations (1)-(3) below (9):

$$CO_2 + 2R_1NH_2 \leftrightarrow (R_1NHCOO^-)(R_1NH_3^+) \qquad (1)$$
$$CO_2 + 2R_1R_2NH \leftrightarrow (R_1R_2NCOO^-)(R_1R_2NH_2^+) \qquad (2)$$
$$CO_2 + R_1NH_2 + R_1R_2NH \leftrightarrow (R_1R_2NCOO^-)(R_1NH_3^+) \qquad (3)$$

In the raw MgO adsorbent, less CO_2 molecule can be adsorbed on to the solid surface, due to the lack of active sites. However, in the TEPA-functionalized MgO adsorbent, the amine groups available in TEPA molecule has provided more active sites for CO_2 adsorption and more alternative pathways for the MgO/CO_2 reaction (7).

Table 1 shows a summary of raw adsorbents and TEPA-functionalized adsorbents prepared using different synthesis methods used for CO_2 capture application.

Table 1. A summary of raw adsorbents and TEPA-functionalized adsorbents prepared using different synthesis methods used for CO_2 capture application.

Synthesis Method	Adsorbent	BET Surface area (m^2/g)	BJH Pore volume (cm^3/g)	Temperature (K)	Pressure (atm)	Adsorption flow condition (CO_2%:inert gas%)/%H_2O	CO_2 uptake (mmol/g)	Stability (mmol/g)	Ref.
Gel-casting method	MM-550	1088.3	1.00	348	1	(100:-)/-	0.65	-	(15)
Gel-casting + Impregnation method	MM-550-TEPA-	10.5	0.02	348	1	(100:-)/-	3.43	3.33 (5th cycle)	
						(12:88 N_2) /-	3.18	2.95 (5th cycle)	
Rapid Synthesis method	AlFu	828.4	0.436	348	1	(15:85 N_2)/-	0.19	-	(1)
						(100:-)/-	0.74	-	
Rapid Synthesis + Wet Impregnation method	AlFu-TEPA-	20.2	0.060	348	1	(15:85 N_2)/-	3.59	-	
						(100:-)/-	4.1	3.87 (10th cycle)	
Improved Hummers' method	GO	289.028	0.046	338	0.09	(10:90 He)/-	0	-	(16)
Improved Hummers' + Ultrasound Activation + Chemical Grafting method	GO-TEPA	194.484	0.042	338	0.09	(10:90 He)/-	1.2	1.08 (10th cycle)	
Pre-oxidation method	HMC	480.88	0.74	333	-	(15:85 N_2)/-	-	-	(13)
Pre-oxidation + Wet Impregnation method	HMC-TEPA-	38.33	0.16	333	-	(15:85 N_2)/-	1.42	-	
						(15:85 N_2)/5	1.46	-	
						(15:85 N_2)/10	1.54	-	
						(15:85 N_2)/15	1.67	1.51 (10th cycle)	
						(15:85 N_2)/19	1.60	-	
Zinc Nitrate Hexahydrate method	MOF-177 powder	2784	1.34	298	1 bar	(100:-)/-	0.86	-	(14)
	MOF-177 pellet	2784	1.34	298	1 bar	(100:-)/-	0.57	-	
Zinc Nitrate Hexahydrate + Wet Impregnation method	MOF-177-TEPA-powder	585	0.330	298	1 bar	(100:-)/-	3.82	-	
	MOF-177-TEPA-pellet			298	1 bar	(100:-)/-	3.31	108.2 wt% (12th cycle)	
Pluronic P123 + Tetraethyl Orthosilicate method	SBA-15(p)	189.46	0.44	348	-	(20:80 N_2)/-	0.61	-	(17)
Pluronic P123 + Tetraethyl Orthosilicate + Wet Impregnation method	SBA-15(p)-TEPA-	2.16	0.007	348	-	(20:80 N_2)/-	5.39	5.0 (9th cycle)	
Sol-gel method	MgO	207	0.81	303	-	(40:60 N_2)/-	0.95	-	(9)

Method	Adsorbent								Ref
Sol-gel + Wet Impregnation method	MgO-TEPA	19	0.22	303	-	(40:60 N_2)/-	4.98	4.71 (10th cycle)	
Acid Leaching method	FSA	541	0.543	298	1 bar	(5:95 inert gas)/-	0.52	-	(18)
Acid Leaching + Physical Impregnation method	FSA-TEPA	185	0.25	298	1 bar	(5:95 inert gas)/-	1.32	1.18 (10th cycle)	
Organic Template method	ZSM-5	398.660	0.442	373	1	(100:-)/-	0.22	-	(19)
Organic Template + Wet Impregnation method	ZSM-5-TEPA	19.045	0.049	373	1	(100:-)/-	1.80	1.53 (5th cycle)	
						(10:90 N_2)/-	1.49	-	
Polyethyleneglycol method	HPS	978.7	2.19	348	1	(15:85 N_2)/-	0.56	-	(20)
Polyethyleneglycol + Typical Impregnation method	HPS-TEPA-	20.32	0.15	348	1	(15:85 N_2)/-	5.01	4.7 (10th cycle)	
Polystyrene Templates method	MHSS	1139	0.284	-	1	(30:70 N_2)/-	0	-	(21)
Polystyrene Templates + Wet Impregnation method	MHSS-TEPA	33	0.082	-	1	(30:70 N_2)/-	10.37	-	
Microemulsion Templating method	MCF-0.8	703.36	1.59	348	-	(15:85 N_2)/-	0	-	(22)
Microemulsion Templating + Wet Impregnation method	MCF-0.8-TEPA	6.68	0.04	348	-	(15:85 N_2)/-	4.75	4.46 (10th cycle)	
						(15:85 N_2)/5	5.26	4.91 (10th cycle)	
Potassium Hydroxide method	MCNT	169.8	1.97	333	-	(10:90 N_2)/1	-	-	(23)
Potassium Hydroxide + Wet Impregnation method	MCNT-TEPA	2.2	0.03	333	-	(10:90 N_2)/1	5.00	4.00 (10th cycle)	
Hydrothermal method	PE-KIT-6	207.61	0.72	333	-	(15:85 N_2)/-	0.94	-	(24)
Hydrothermal + Post-synthetic Impregnation method	PE-KIT-6-TEPA	20.48	0.08	333	-	(15:85 N_2)/-	2.9	-	
Hydrothermal method	TiO_2/NRs	235	1.16	313	1 bar	(100:-)/-	0.76	-	(25)
Hydrothermal + Wet Impregnation method	TiO_2/NRs-TEPA	50	0.43	313	1 bar	(100:-)/-	2.29	2.16 (12th cycle)	

MM-550: Monolithic MCM-41 (Mesoporous silica) at 550°C calcination temperature
AlFu: Aluminium fumarate metal-organic framework
GO-TEPA: Graphene oxide-TEPA under ultrasound irradiation
HMC: Hierarchical mesoporous carbon
MOF-177: Metal organic framework-177
SBA-15(p): Mesoporous silica with pluronic P123
MgO-TEPA: Magnesium oxide-TEPA under biogas (38.4% CO_2 and 61.5% CH_4)
FSA: Fine Slag Adsorbent
ZSM-5: Zeolite Socony Mobil–5
HPS: Hierarchically porous silica
MHSS: Mesoporous hollow silica spheres
MCF-0.8: Mesocellular silica foams with 0.8 molar ratio of 1,3,5-trimethylbenzene (TMB) to P123
MCNT: Modified carbon nanotubes
PE-KIT-6: Mesoporous silica pore-expanded KIT-6
TiO_2/NRs: TiO_2/titanate composite nanorod

2.2. The effect of TEPA functionalization towards CO_2 uptake capacity

Numerous studies have verified that the impregnation of TEPA has contributed to a better CO_2 uptake capacity of the solid adsorbents. A simple proposed mechanism is shown in Figure 1.
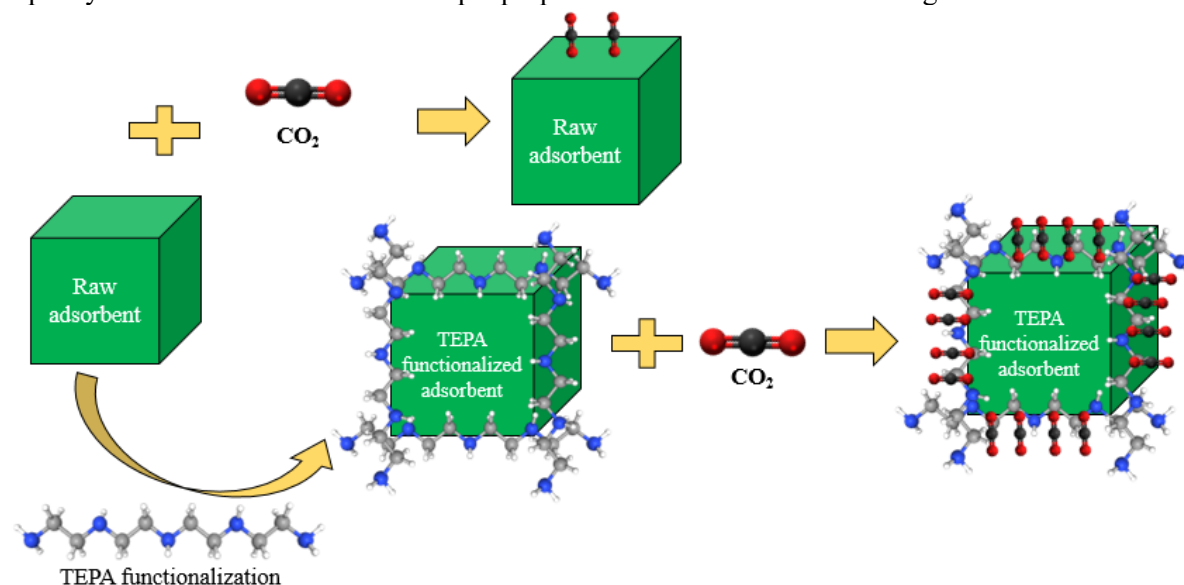

Figure 1. Proposed mechanism of CO_2 adsorption over a raw adsorbent and a TEPA-functionalized adsorbent.

According to previous studies, the decrease in BET surface areas and pore sizes of the modified sorbents (Table 1) could be observed, suggesting that the TEPA molecules have been successfully loaded onto the sorbents' surface and pore volume. It could also be perceived that the CO_2 uptake capacity of TEPA-functionalized adsorbents is much higher than that of raw adsorbents. For instance, the CO_2 adsorption capacity of MM-550-TEPA-70% was significantly increased to 3.43 mmol/g after the impregnation of TEPA, as compared to the raw MM-550 (0.65 mmol/g) (15). As a matter of fact, the adsorption process of raw MM-550 adsorbent is the physical adsorption type. After impregnating with 70% TEPA, the participation of the chemical reaction between the amine-functional groups and the CO_2 molecular has provided more active sites for eased CO_2 molecule capture. Moreover, upon TEPA-functionalization, the resultant modified graphene oxide (GO) has demonstrated a high CO_2 adsorption capacity (1.2 mmol/g) than pure GO (0 mmol/g) at 338K and 0.09 atm (16). In this study, ultrasound irradiation is used to exfoliate the graphene layers and produce more available active sites to attach the amine functional groups to the graphene matrix.

On the other hand, aside from N_2 adsorption-desorption isotherm investigated on the after effect of the amine functionalization, other characterisation analysis also able to demonstrate the differences result from the success of the TEPA-functionalization approach onto the solid support. As the evidence of the XRD analysis in the study from Kasikamphaiboon and co-workers, by comparing the diffraction pattern of MgO with those of MgO-TEPA-x with different TEPA loadings, it can be observed that the diffraction intensity of MgO decreases with increasing TEPA loadings (9). It has been known that diffraction intensities are relative to the degrees of pore filling. Therefore, the loss of intensity is possibly caused by the incorporation of amine into the pore channels of the support. This indicates that TEPA is succesfully loaded into the pore of the raw MgO adsorbent, which found in-line with other amine-functionalization related studies. The study have also proved that the functionalization of TEPA into MgO adsorbent has significantly improved the CO_2 uptake capacity (9). In fact, the CO_2 adsorption of the pristine MgO reaches the saturation point within only 12 min, resulting in a low adsorption capacity

of 0.95 mmol/g. As expected, after impregnating with TEPA, the adsorption capacity expressively increases to a promising value (4.98 mmol/g). Similarly, the TEPA-modified pore-expanded KIT-6 has shown a higher CO_2 capture capacity (2.9 mmol/g) than that of raw PE-KIT-6 (0.94 mmol/g). (24). The addition of TEPA on titanate-TiO_2 composite has also enhanced the CO_2 uptake capacity to 2.29 mmol/g (25). From the abovementioned studies, it is believed that the enhanced adsorption performance of the TEPA-functionalized adsorbents is due to the presence of beneficial interaction between $-NH_2$ groups of the loaded amines and CO_2 that significantly aided the CO_2 uptake.

It is noted that there are 2 different functionalization methods of TEPA into the raw adsorbents, namely impregnation method and grafting method. In the former, amine is immobilized in the channel of solid adsorbents by van der Waals forces (26). Wet impregnation method is widely used as it is the easiest way of placing amines on solid surfaces (27). By using this method, amines are mixed with the support material by the help of a solvent. Then, by evaporation of the diluted solution, the excess solvent is removed. On the other hand, for grafting method, CO_2-philic sites are immobilized by chemical bonds through the condensation of alkanolamine and silanol groups (26). During the grafting of amine into solid adsorbents, a covalent bond is formed between the amine chains and the surfaces formed by the reaction of the silanol groups with the silanes on the chain (27). In this method, the amount of amine that can be doped into the support material is dependent on the density of the appropriate silanol groups. In terms of advantages, wet impregnation method can be prepared practically, has high amine capacity and decreased corrosion behaviour (27). In the case of grafting method, the strong chemical bond of the amines is advantageous because high temperature is required to break the bonds, thus increasing the amine-grafted adsorbents' thermal stability (27).

2.3. The effect of different TEPA loading towards CO_2 uptake capacity

It is well-recognized that the diverse amine loadings including TEPA could suggestively affect the CO_2 capture performance. It was previously reported that the increase in TEPA loading within a suitable range has increased the breakthrough time and adsorption capacity of the adsorbents, as more amine active sites for CO_2 adsorption, are provided (9). However, the excess TEPA loading has led to the blockage of the pore of adsorbents by the aggregated TEPA, which hinders the diffusion of CO_2 to react with the active sites in the pores. As the optimum TEPA loading, 40% MM-550-TEPA has shown the maximum breakthrough time and adsorption capacity of 34 min and 4.98 mmol/g, respectively. In a similar study, it was verified that the increasing of TEPA loading has increased the CO_2 adsorption capacity of MM-550 adsorbent (15). Herein, the optimum TEPA loading is 70% with the highest adsorption capacity of 3.43 mmol/g at pure CO_2 gas, and a further increase of TEPA to 75% has led to a decrease in the CO_2 adsorption capacity.

In a study by Zhang et. al., an increasing trend in CO_2 uptake capacity was observed upon increasing the TEPA loading from 10% to 20%, and as expected, a further increase of TEPA amount to 30% and above have caused the decreasing trend (18). As the optimum TEPA amount, 20% FSA-TEPA has demonstrated an adsorption capacity of 1.32 mmol/g. In order to investigate the effect of TEPA loadings on the CO_2 capture of mesoporous hollow silica spheres (MHSS), 9-52wt% of TEPA were impregnated onto MHSS adsorbents. It was perceived that the CO_2 adsorption capacity was increased from 3.01 to 10.37 mmol/g when the loading amount of TEPA was increased from 9 to 47 wt% (21). Nonetheless, a further increase of TEPA loading to 52wt% could not auxiliary increase the CO_2 adsorption capacity, most probably due to the aggregation of excessive TEPA amine on the MHSS support. This inevitably leads to a reduction in the accessibility of CO_2 inside the adsorbent porosity, thus decreased the performance.

2.4. The effect of different adsorption conditions towards CO_2 uptake capacity

It is widely known that the different adsorption conditions have diversely impacted the CO_2 adsorption capacity. Similar to other amine groups, the TEPA-functionalized adsorbents have shown variation in CO_2 capture performance upon changing the adsorption reaction conditions. In this respect, the next

sections were provided to present the effect of those reaction conditions on the CO_2 uptake of numerous TEPA-functionalized adsorbents.

2.4.1. Adsorption temperature. As one of the important parameters, the temperature undoubtedly has a noteworthy effect on the CO_2 adsorption capacity (1). For instance, the CO_2 adsorption capability of AlFu decreases with the increase in the adsorption temperature. In the absence of TEPA, the CO_2 adsorption capacity of AlFu was only 0.27 mmol/g at 318 K. Upon addition of 50% TEPA, the CO_2 uptake amount is 3.4 mmol/g at 333 K and significantly increases to 3.59 mmol/g for AlFu-TEPA-60% at 348 K. From this observation, it could be concluded that the rising in the adsorption temperature can help the CO_2 molecules to overcome the kinetic barrier and reduce the diffusion resistance. However, as anticipated, the overloading of TEPA amount would negatively impact the overall performance by blocking the pore structures of AlFu and hinders the reaction between CO_2 molecules with the internal TEPA of modified AlFu.

Moreover, in another study, TEPA-functionalized SBA-15(p) has shown increased adsorption capacity from 4.41 to 5.39 mmol/g when the temperature rose from 323 K to 348 K. However, when the temperature reached 363 K, the adsorption capacity drastically dropped to 4.98 mmol/g (17). This is because when the adsorption temperature is higher than the optimal adsorption temperature, CO_2 uptake is controlled by thermodynamics and the CO_2 adsorption decreases with the temperature increase. In contrast, the CO_2 adsorption capacity of pure ZSM-5 was decreased with the increase of adsorption temperature [19]. After incorporation of low amine loading (ZSM-5-TEPA-3g), the CO_2 uptake was increased and then decreased with the increase of adsorption temperature. A different observation was observed when high amine loadings of ZSM-5-TEPA-5g, ZSM-5-TEPA-7g, and ZSM-5-TEPA-9g were used, in which the CO_2 adsorption was increased with the increase of adsorption temperatures. This can be explained by the fact that the ZSM-5 adsorption of CO_2 was a physical adsorption process and an exothermic reaction, a dissimilar condition to that of high TEPA loadings-ZSM-5.

Furthermore, in a study on hierarchically porous silica, HPS-TEPA-60% adsorbent has demonstrated the highest amount of CO_2 capture when the temperature increases to the optimum, and decreased upon a further increase in the temperature (20). This is most possibly due to the expansion of TEPA when a high temperature was used that might block the pore of the HPS support and increase the CO_2 diffusion resistance for retarded performance.

2.4.2. Flow condition. Liu and co-workers have conducted the CO_2 adsorption in pure CO_2 gases and mixture gases of 15% CO_2, 85% N_2, respectively (1). It was perceived that for both raw AlFu and modified adsorbent with different TEPA loadings, the CO_2 adsorption capacity under a pure CO_2 atmosphere is higher than that under a mixture of gases. Therefore, it could be summarized that a higher partial pressure of CO_2 leads to a superior amount of saturated CO_2 adsorption. When the concentration of CO_2 raised from 5 to 40 vol%, the saturated adsorption capacity of MCF-0.8-TEPA60% was increased (22). This is because when the mixed gases with high concentrations of CO_2 pass through the adsorbent, the content of CO_2 molecule per unit volume was raised, and thus more CO_2 molecules could quickly contact the adsorption sites in the pores. Other than the existence of the above-mentioned mixture gases, many impurity gases such as SO_2 and NO_x, water vapor, and some other acid impurities might also be present in the flue gas. It was early reported that the CO_2 adsorption capability reduces from 5.26 to 4.64 mmol/g and the regeneration amount is only 3.85 mmol/g when the MCF-0.8-TEPA60% adsorbent is exposed to acid impurities. This result indicates that the acid impurities in the mixed gas have a negative influence on CO_2 adsorption and adsorbent regeneration properties of adsorbents.

2.4.3. Moisture present. From the study by Wang et. al., it was observed that the saturated adsorption capacity and TEPA efficiency of HMC-TEPA-30% are enhanced obviously in the presence of water vapor (13). When the water vapor content increased from 0 to 15 vol%, the reaction between amine groups with CO_2 and H_2O was facilitated, thus increasing adsorption capacity and TEPA efficiency. However, the CO_2 adsorption capacity decreases as the water vapor content is further increased from 15

to 19 vol%. Similarly, a study by Irani and co-workers also stated that the addition of 1 vol% moisture has increased the CO_2 sorption capacity by 56% (3.2–5 mmol/g) compared to dry gas adsorption (23). In contrast, when the moisture concentration increased more than 1 vol%, the adsorption capacity decreased from 5 mmol/g to 3.5 mmol/g. In both works, the decrease in CO_2 uptake at high water content can be explained due to the presence of excess water molecules that unavoidably occupy the available adsorption sites, thus reducing the exposure to CO_2 molecules.

2.4.4. Adsorbent structure. A study by Gaikwad et. al. has suggested that the powder form of MOF adsorbent is not suitable for industrial applications even though it possesses a higher CO_2 adsorption capacity (0.86 mmol/g for raw MOF-177 and 3.82 mmol/g for TEPA-modified MOF-177) (14). This is because the MOF powders are easily moving and inevitably block the system under continuous fluid flow in a packed column. As a result, the CO_2 adsorption capacity of MOF-177-TEPA-20% pellet was decreased concerning that of TEPA-20% powder due to reduced crystallinity, condensed geometry, and pore blockage by polymer binder during pelletization under ambient pressure. In short, MOFs are normally isolated as crystalline powders that are not industrially favourable due to their limitations in processing. Shaping MOFs into different forms such as the pellet form while preserving or improving their properties is a better approach as they can be easily processed, handled, and stored (28).

3. Concluding remarks and future opportunities
In this work, the recent research progress of TEPA-modified adsorbents used for CO_2 adsorption has been comprehensively discussed. The impregnation of TEPA into various adsorbents has increased the CO_2 adsorption capacity of the modified adsorbents. Different TEPA loadings have diversely affected the CO_2 uptake capacity, in which the increase in TEPA loading to the optimum amount has also enhanced the adsorption capacity, due to the increased amount of amine functionalities. When the TEPA loading exceeds the optimum amount, the CO_2 adsorption capacities decrease since the surface area and pore volume are dominant factors governing the CO_2 adsorption capacity over the amine functionality of TEPA. Various temperatures also contributed to the CO_2 adsorption capacity of adsorbents. The free volume of TEPA in adsorbents increased when the temperature increased, hence eased the diffusion of CO_2 molecules into the inner layer of TEPA for faster CO_2 adsorption by the amine groups. Over the optimum temperature, the effect of heat became dominant over the increased free volume, thus decreasing the adsorption capacity. In addition, higher partial pressure of CO_2 gases during the adsorption process has increased the CO_2 capture capacity. The moisture present in the flow gas also improved the adsorption capacity, as long as it was within the optimum amount. Besides, the adsorbent structure is considered an important parameter in real-life applications. Nonetheless, there was a lack of studies regarding this matter. As discussed above, adsorbents in pellet forms might be a better option for industrial usage. The adsorption performance should also be evaluated under actual industrial conditions where impurities such as NO_x, SO_x, and air are present.

References
[1] Liu Q, Ding Y, Liao Q, Zhu X, Wang H, Yang J. 2019 Fast synthesis of Al fumarate metal-organic framework as a novel tetraethylenepentamine support for efficient CO2 capture *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **579** 123645.
[2] Dao DS, Yamada H, Yogo K. 2020 Enhancement of CO2 Adsorption/Desorption Properties of Solid Sorbents Using Tetraethylenepentamine/Diethanolamine Blends *ACS Omega* **5**(37) 23533-41.

[3] Kamran U, Park S-J. 2021 Chemically modified carbonaceous adsorbents for enhanced CO2 capture: A review *Journal of Cleaner Production* **290** 125776.

[4] Alkadhem AM, Elgzoly MAA, Onaizi SA. 2020 Novel Amine-Functionalized Magnesium Oxide Adsorbents for CO2 Capture at Ambient Conditions *Journal of Environmental Chemical Engineering* **8**(4) 103968.

[5] Sekerci Y, Ozarslan R. 2020 Oxygen-plankton model under the effect of global warming with nonsingular fractional order *Chaos, Solitons & Fractals* **132** 109532.

[6] Hussin F, Aroua MK. 2020 Recent trends in the development of adsorption technologies for carbon dioxide capture: A brief literature and patent reviews (2014–2018) *Journal of Cleaner Production* **253** 119707.

[7] Ruhaimi AH, Aziz MAA, Jalil AA. 2021 Magnesium oxide-based adsorbents for carbon dioxide capture: Current progress and future opportunities *Journal of CO2 Utilization* **43** 101357.

[8] Wilberforce T, Olabi AG, Sayed ET, Elsaid K, Abdelkareem MA. 2021 Progress in carbon capture technologies *Science of The Total Environment* **761** 143203.

[9] Kasikamphaiboon P, Khunjan U. 2018 CO2 Adsorption from Biogas Using Amine-Functionalized MgO *International Journal of Chemical Engineering* **2018** 1706405.

[10] Wang J, Park YK, Jo YM. 2020 Sequential improvement of activated carbon fiber properties for enhanced removal efficiency of indoor CO2 *Journal of Industrial and Engineering Chemistry* **89** 400-8.

[11] Wang J, Adelodun AA, Oh JM, Jo YM. 2020 TEPA impregnation of electrospun carbon nanofibers for enhanced low-level CO2 adsorption *Nano Convergence* **7**(1) 7.

[12] Mohamad NA, Nasef MM, Nia PM, Zubair NA, Ahmad A, Abdullah TAT, et al. 2021 Tetraethylenepentamine-containing adsorbent with optimized amination efficiency based on grafted polyolefin microfibrous substrate for CO2 adsorption *Arabian Journal of Chemistry* **14**(4) 103067.

[13] Wang Y, Guo T, Hu X, Hao J, Guo Q. 2020 Mechanism and kinetics of CO2 adsorption for TEPA-impregnated hierarchical mesoporous carbon in the presence of water vapor *Powder Technology* **368** 227-36.

[14] Gaikwad S, Kim Y, Gaikwad R, Han S. 2021 Enhanced CO2 capture capacity of amine-functionalized MOF-177 metal organic framework *Journal of Environmental Chemical Engineering* **9**(4) 105523.

[15] Zhou C, Yu S, Ma K, Liang B, Tang S, Liu C, et al. 2021 Amine-functionalized mesoporous monolithic adsorbents for post-combustion carbon dioxide capture *Chemical Engineering Journal* **413** 127675.

[16] Liu Y, Sajjadi B, Chen W-Y, Chatterjee R. 2019 Ultrasound-assisted amine functionalized graphene oxide for enhanced CO2 adsorption *Fuel* **247** 10-8.

[17] Zhang G, Zhao P, Hao L, Xu Y. 2018 Amine-modified SBA-15(P): A promising adsorbent for CO2 capture *Journal of CO2 Utilization* **24** 22-33.

[18] Zhang J, Zuo J, Ai W, Zhang J, Zhu D, Miao S, et al. 2021 Preparation of mesoporous coal-gasification fine slag adsorbent via amine modification and applications in CO2 capture *Applied Surface Science* **537** 147938.

[19] Wang Y, Du T, Song Y, Che S, Fang X, Zhou L. 2017 Amine-functionalized mesoporous ZSM-5 zeolite adsorbents for carbon dioxide capture *Solid State Sciences* **73** 27-35.

[20] Zhang G, Zhao P, Xu Y. 2017 Development of amine-functionalized hierarchically porous silica for CO2 capture *Journal of Industrial and Engineering Chemistry* **54** 59-68.

[21] Bae JY, Jang SG. 2019 Characteristics of CO2 Capture by Tetraethylenepentamine Modified Mesoporous Silica Morphology *J Nanosci Nanotechnol* **19**(10) 6291-6.

[22] Zhao P, Zhang G, Xu Y, Lv Y-K, Yang Z, Cheng H. 2019 Development of Amine-Functionalized Silica Foams with Hierarchical Pore Structure for CO2 Capture *Energy & Fuels* **33**(4) 3357-69.

[23] Irani M, Jacobson AT, Gasem KAM, Fan M. 2017 Modified carbon nanotubes/tetraethylenepentamine for CO2 capture *Fuel* **206** 10-8.

[24] Wei J, Mei D, Lin Z, Geng L, Chen S, Liao L. 2018 Effects of TETA or TEPA Loading on CO2 Adsorption Properties Using Pore-Expanded KIT-6 as Support *Nano* **13**(04) 1850042.

[25] Kapica-Kozar J, Michalkiewicz B, Wrobel RJ, Mozia S, Piróg E, Kusiak-Nejman E, et al. 2017 Adsorption of carbon dioxide on TEPA-modified TiO2/titanate composite nanorods *New Journal of Chemistry* **41**(16) 7870-85.

[26] Rao N, Wang M, Shang Z, Hou Y, Fan G, Li J. 2018 CO2 Adsorption by Amine-Functionalized MCM-41: A Comparison between Impregnation and Grafting Modification Methods *Energy & Fuels* **32**(1) 670-7.

[27] Ünveren EE, Monkul BÖ, Sarıoğlan Ş, Karademir N, Alper E. 2017 Solid amine sorbents for CO2 capture by chemical adsorption: A review *Petroleum* **3**(1) 37-50.

[28] Valizadeh B, Nguyen TN, Stylianou KC. 2018 Shape engineering of metal–organic frameworks *Polyhedron* **145** 1-15.