

# **Adsorbents for Noxious Gas Sequestration: State of the Art.**

## **ABSTRACT**

Adsorbents such as metal organic frameworks (MOFs), polymers, activated carbon (AC) and membranes are becoming prominent for CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S and NH<sub>3</sub> capture and in some cases, storage. Using the standard adsorbent properties (SAPs) such as adsorption capacity, selectivity, permeability/permeance, regenerability and reusability, ease of functionability and tunability, thermal and chemical stability etc., suitable candidates for noxious gas sequestration can be determined. In order to foster the development and selection of a more efficient adsorbent, a proper documentation of adsorbent performance in terms of SAPs, is crucial. In this study, a critical review of metal organic framework (MOF), polymer, activated carbon (AC) and membrane adsorbents was performed. Using the SAPs, an up to date comparative analysis was done to select the best performing adsorbents. The results of the comparative analysis were then used to categorize the adsorbents suitability for pre – combustion and post - combustion applications. A perspective of future study on adsorbents for noxious gases sequestration, was also presented.

*Keywords: sequestration; adsorbent; metal organic framework; polymer; activated carbon; membrane; noxious gases.*

## **1. INTRODUCTION**

The world's energy demand is continuously increasing with its population growth. A significant part of this energy would be provided by fossil fuels (coal, crude oil and natural). 73.25% of world energy consumption would be provided by fossil fuels by 2040 [1]. Figs. 1 to 3 show global natural gas, crude oil and coal reserves respectively from the years 2016 to 2018, and a projection for production and consumption into the future [2–5]. It is evident from the charts that production and consumption of these fossil fuels would continuously increase into the future (except for coal with a slight reduction). These trends would cumulatively result in the increase in noxious gases released into the atmosphere. These harmful gases such as CO<sub>x</sub>, [6], CH<sub>4</sub>[7], NH<sub>3</sub>, SO<sub>x</sub>, NO<sub>x</sub>, H<sub>2</sub>S [8], Volatile Organic Compounds (VOCs) and volatile organic gases [9] pose a high environmental risk [10]. This therefore necessitates the management of air quality in order to ensure a sustainable environment.

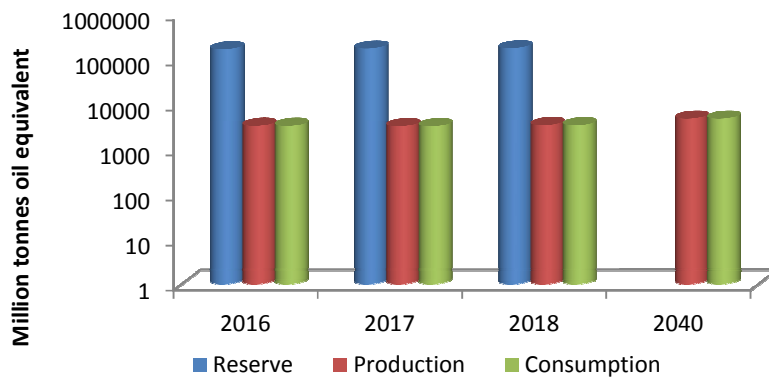


Fig. 1. Natural gas outlook (Source: [2–5])

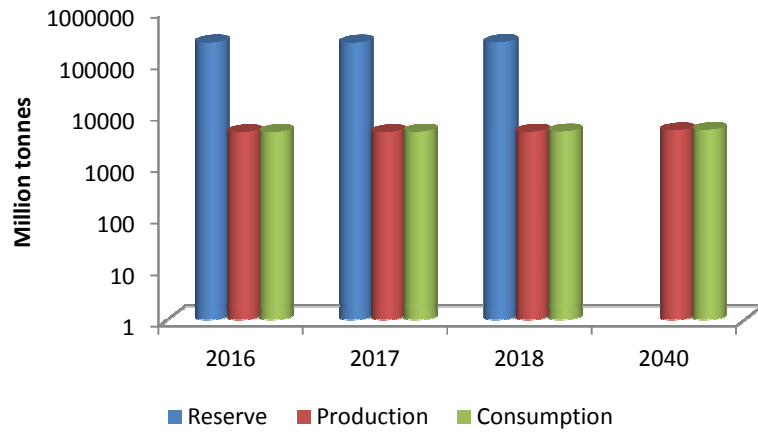


Fig. 2. Crude oil outlook (Source: [2–5])

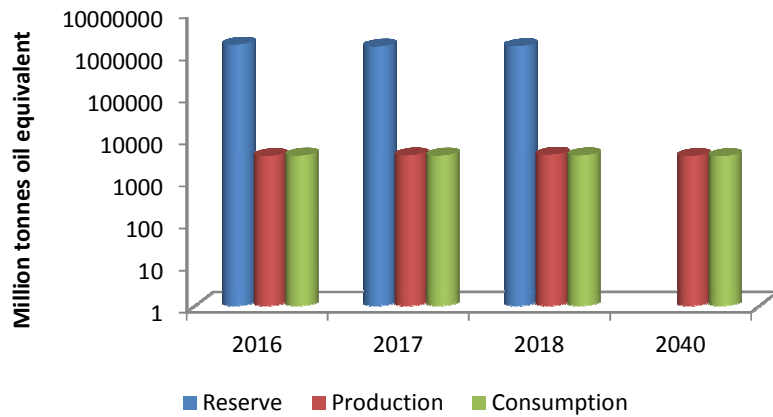


Fig. 3. Coal outlook (Source: [2–5])

Different materials and methods [11–18] have been reported for the separation and capture of hazardous gases either from process systems or the environment. Amongst these compounds, adsorbents such as metal organic frameworks (MOFs), polymers, activated carbon (AC) and membranes, have been considered as promising candidates for gas separation and storage, due to their large surface area and pore volume, good thermal and chemical stability, ease of functionality and tunability, low regeneration cost and high selectivity. These adsorbents can be easily modified for specific applications through pre- and post-functionalization of the structure [19–21]. Adsorbent utilization becomes more feasible when its CO<sub>2</sub> adsorption capacity is above 3 mmol/g [22].

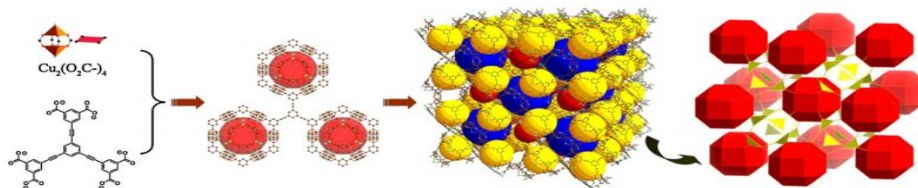
For the purpose of this study, an up to date review of the performance of MOFs, polymers, AC and membrane adsorbents are considered. The major focus of this study therefore, was to identify the best performing adsorbents for noxious gas sequestration and then proffer suitable areas for their application.

## 2. ADSORBENTS FOR CAPTURE OF HARMFUL GASES

Among the numerous types of adsorbents for the capture of harmful gases, MOFs, polymers, membranes and AC are in the forefront of research for harmful gas sequestration as a result of their promising structural properties. *Adsorption, permeability, selectivity, flux rate, reusability and regeneration* are key parameters that determine the deployment of MOFs [21], membranes [23] polymers [24] and AC [25,26] for sequestration of harmful gases in various process systems and conditions. These conditions are imperative for the industrial deployment of these adsorbents for gas capture and storage.

### 2.1 Metal Organic Frameworks (MOFs)

Metal Organic Frameworks (MOFs) are an emerging class of porous materials constructed from metal-containing nodes and organic linkers [27]. Due to the strong bonds that exist between the metal-containing nodes [also known as secondary building units (SBUs)] and organic linkers, MOFs usually boast of a structure with permanent porosity and open crystalline frameworks as shown in Fig. 4. The organic spacers or the metallic SBUs can be altered to control the pore environment of the MOF [28]. Their inherent characteristics/advantages such as large surface area, ease of functionalization, kinetic diameter, electric properties, Open Metal Sites (OMS), high porosity and tuneable size of pores [29] have made them very attractive compounds in applications such as gas storage and separation, catalysis and sensing [30,31]. The ease with which SBUs and organic linkers are changed and altered has led to the synthesis of thousands of various MOF structures. As a result, the structures and properties of MOFs can be designed and systematically tuned by the choice of building blocks used for the synthesis of the framework [32]. Various strategies have also been reported for improving the performance of MOFs [33].



**Fig. 4.** Crystalline structure of Metal Organic Frameworks [32]

MOFs have been investigated for optimization of structure functionality. In this regard, MOFs have been reported to exhibit promising potential for sequestration of gases such as CO<sub>2</sub>, H<sub>2</sub>S, CH<sub>4</sub>, NH<sub>3</sub>, NO<sub>x</sub>, SO<sub>x</sub> etc.[8,14,34–39]. The works of [13,14,40–66] highlight MOFs for CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S and NH<sub>3</sub> sequestration at pre- and post-combustion conditions.

## 2.2. Polymers

Porous Organic Polymers (POP) are composed of organic building blocks connected through covalent bonds, exhibiting thermal and chemical stabilities, large surface area, ease of synthesis and low density [67]. There are two classes of POP. They include;

- i. Amorphous polymers which comprise conjugated microporous polymers (CMP) [68], covalent triazine framework [18], porous aromatic framework [18], hyper-cross linked polymers (HCP) [69] and polymers of intrinsic microporosity [70]
- ii. Crystalline polymers (covalent organic polymers) [71].

Different polymers have been synthesized for harmful gases sequestration at different process conditions [72] and modification through pre-synthetic and post synthetic functionalization [73] have been reported for improved performance for specific applications [15]. The agents used for functionalization are compounds that increase the affinity of porous polymers for a specific noxious gas. For instance, for CO<sub>2</sub> adsorption, amino functional groups [74], –N heterocycles [75], phenolic motifs [15] are utilized. The method of synthesis plays a key role in the structure of a polymer which invariably affects the adsorption capacity. The different monomers (building blocks) and methods of synthesis are explained by [76]. Polymers have also shown excellent reusability [75] and low heat of adsorption [77]. The works of [11,15,18,69,73,78–85] highlight the use of polymers for CO<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>S sequestration.

## 2.3. Activated Carbon (AC)

AC has been investigated for capture of noxious gases [86,87]. This is due to reduced cost of production, large surface area, ease of modification of pores, good thermal and chemical stability, hydrophobic nature, stability in the presence of heat and chemical resistance [88]. AC shows promising potential for practical applications in terms of balance of performance [89] considering cost of production, benign effect on the environment, availability of precursor materials [90,91] and sustainability [92], and have been reported to exhibit reusability, promising adsorption kinetics [26] and stability after several sorption cycles [63], requiring low regeneration energy [93]. A key determinant to the adsorption performance of AC is the type of precursor used in its synthesis. Different precursors have been reported in the literature for the production of AC.

They include bamboo [94], petroleum coke [95], rice husk char [26] wood [96], coconut shell [97], sugarcane bagasse [91], argan fruit shells [98], pinewood shavings char, biochar [89] etc. Amongst these precursors, biochar stands out as it exhibits high porosity and high amount of fixed carbon that can be processed to AC with high micro porosity [89]. Therefore, biochar precursors should receive further investigation in its use for the production of AC for gas sequestration. It is imperative to state that these precursors should have low ash and volatile matter content so as to produce AC with micropores on the surface of the structure for adsorption abilities.

AC have been investigated for SO<sub>x</sub> and NO<sub>x</sub> [99,100], H<sub>2</sub>S [101] and CO<sub>2</sub> [100] sequestration at different process conditions. In order to optimize capture and selectivity of AC for specific

gases, modification of the structure to increase its affinity for specific gases have been reported [102–108]. Various studies on the use of AC for CO<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub> and NO<sub>x</sub> sequestration, have also been reported [90,91,93,98,108,109].

## 2.4. Membranes

Membranes basically function as filters as shown in Fig. 5. They are used for separation [110]. Different researchers have reported membrane use for capture of harmful gases in literature [17,111,112] as they are environmental benign and efficient in energy consumption [113] and exhibit technical and cost-related merits [114]. Key parameters that determine feasibility of membranes for industrial applications are *permeability and selectivity* [115]. Membranes should therefore possess high permeability, permeance, high selectivity, low cost of production and regeneration, good chemical and thermal stability, and ability to resist plasticization [116,117], in order for it to be feasible. Progress in this regard have been recorded in literature where properties of membranes have been optimized even though challenges such as high cost, low physical and chemical stability, low selectivity and low hydrothermal stability still persist [118]. This structure optimization has resulted in the synthesis of different class of membranes [110,119–122].

Various studies on the use of membrane for the capture of CO<sub>2</sub> and H<sub>2</sub>S, have also been reported [110,112,122–126].

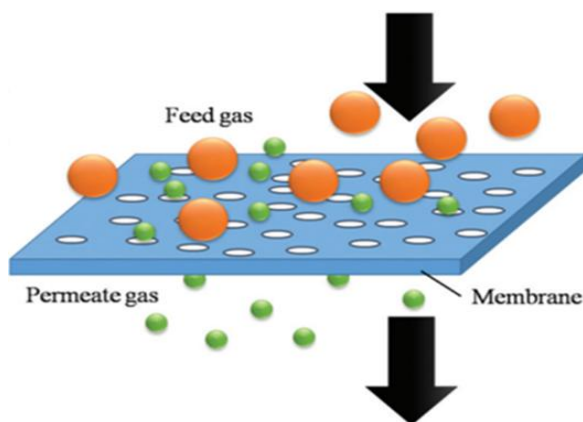


Fig. 5. Separation of different molecules using membrane [118]

## 3. PERFORMANCE EVALUATION OF ADSORBENTS USING SELECTED SAPS

This section considers the performance of adsorbents reviewed in this study for industrial applications. Although adsorbents for carbon sequestration have not attained the stage of commercial applications [127], they are currently in their demonstration phase. Parameters such as *adsorption capacity, selectivity, permeability/permeance (for membranes), regeneration/reusability, thermal and chemical stability*, were used to rank these adsorbents for the purpose of determining the most efficient adsorbent and suitable points for their application. Adsorption capacity was used as the highest-ranking property. Only the best performing adsorbent is reported for each SAP category. The industrial applications considered in this study include pre-combustion and post-combustion conditions.

### 3.1. CO<sub>2</sub> Adsorption capacity at pre-combustion conditions

Pre-combustion conditions typically occur at relatively high pressures and low/high temperatures. Such conditions can include process systems such as natural gas, biogas sweetening, etc. Polymers and AC have shown high adsorption capacities at high pressures amongst adsorbents reviewed in this study as highlighted in Table 1. Polymers PPN-4 [128] and PAF-1 [129] exhibited the highest adsorption capacities of 48.20 mmol/g and 29.55 mmol/g at pressures of 50 bar and 40 bar respectively at ambient temperatures. ACs LSB3-800 [86] and SBL-PNP-1-4-750 [130] also showed high adsorption capacities of 20.9 mmol/g and 19.65 mmol/g at pressures of 20 bar each at 298K.

Membranes showed suitability for pre-combustion separation of CO<sub>2</sub> as highlighted in Table 2. They have been shown to function within pressure range of pre-combustion carbon capture. Membranes COF 300/6FDA-DAM MMM and COF 300/Pebax MMM [131] can be applied in pre-combustion conditions if their thermal stability at high temperatures is improved.

MOFs did not show high adsorption capacities as much as polymers and AC for pre-combustion application. The highest performing MOFs for pre-combustion conditions were HKUST-1 and MIL-101 (Cr) [130] with adsorption capacities of 8.07 mmol/g and 7.19 mmol/g at pressures of 10 bar and temperatures of 303K.

### 3.2. CO<sub>2</sub> Adsorption capacity at post-combustion conditions.

Post combustion applications occur basically at approximately atmospheric pressure of 1 bar and high or low temperatures [132]. At practical post combustion conditions of flue gases from systems such as automobiles, petrol generators, motorcycles, gas turbine power plants, oil turbine plants, coal fired plants, water pyrolysis and cement production, only a few adsorbents were found to be applicable as reported in Table 1. Most of the adsorbents showed a decrease in working capacity as temperature increased and ultimately resulted in the decomposition of the structure which implied that the adsorbents cannot be used at relatively high temperature conditions. This can be attributed to the fact that as temperature increases, adsorption capacity of adsorbents such as AC decreases [133]. The low adsorption capacities of AC with values between 0.2 mmol/g to 1.80 mmol/g at 1 bar and 373K [104] and that of NORF700 [134] and NCLK3 [135] with adsorption capacities of 2.10 mmol/g and 2.00 mmol/g at 1 bar and 323K, support this claim. Polymers, AC and MOFs do not exhibit high adsorption capacities for CO<sub>2</sub> in post-combustion conditions at high temperatures. MOFs 1-ene and 1-dmen [136], TAEA modified MIL-101 (Cr) [45] and 1-nmen [136] had the highest adsorption capacities of 5.05 mmol/g, 4.34 mmol/g, 4.05 mmol/g and 2.92 mmol/g respectively, at ~1 bar and 313K. Amongst these MOFs, 1-dmen [52] has shown promising potential for practical applications due to its high selectivity of 554 for CO<sub>2</sub> in a binary mixture of CO<sub>2</sub>/N<sub>2</sub>. It is therefore evident that these values for adsorption capacity are not as high as those recorded in pre-combustion conditions as pressure increase results in increase in adsorption capacities [137].

Most adsorbents showed good adsorption capacities for post combustion CO<sub>2</sub> capture at ambient temperatures, with polymer and AC exhibiting the highest adsorption capacities. Polymer IHBPA (TEPA) [138] and PI-COF-2 [80] had adsorption capacities of 7.65 mmol/g and 5.8 mmol/g respectively at 1 bar and 298K while AC CuO NP-AC [108], ARG-K-Im [98] and DAC-AC-CO<sub>2</sub>[98] had adsorption capacities of 6.72 mmol/g, 5.63 mmol/g and 5.52 mmol/g respectively at 1 bar and 298K. MOF UTSA-120a [46] was the highest performing MOF in this regard with adsorption capacity of 5.00 mmol/g at 1 bar and 296K, all other MOFs performed below this value in this study. This may be due to the incorporation of functional tetrazine groups into the structure which improved its affinity for CO<sub>2</sub>. Considering

the working temperatures and pressures of the adsorbents, they are mostly suited for pre- and post - combustion capture at *ambient temperatures*.

### **3.3. CO<sub>2</sub> Selectivity of adsorbents at pre- and post-combustion conditions.**

In terms of selectivity for CO<sub>2</sub> in flue gas stream, MOFs have shown exceptional selectivity that outperformed other adsorbents such as polymers, adsorbents and membranes. This can be attributed to their ease of functionalization using CO<sub>2</sub>-philic functional groups. MIL-140 [41] and UTSA-120a [46] showed one of the highest selectivity of 1900 and ~600 for CO<sub>2</sub> in binary mixtures (CO<sub>2</sub>/N<sub>2</sub>). An extremely high selectivity of 7531 for CO<sub>2</sub>/N<sub>2</sub> binary mixture was recorded for MOF MFUM-1(Cu) [139] without information on its adsorption capacity. MOFs 1-dmen [136] and 1-ipen [136] have also been reported to exhibit selectivities of 554 and 273 respectively.

### **3.4. Regenerability and reusability of adsorbents at pre- and post-combustion conditions.**

Some of the adsorbents can be regenerated and re-used for CO<sub>2</sub> capture without losing their adsorption capacities. MOF 1-een [136] has been reported to retain its adsorption capacity after 600 sorption cycles, the highest recorded in this study. Other adsorbents such as AC NSCS-4-700 [63], CNS-AC [90], DAC-AC-CO<sub>2</sub> [109], polymer (IHBPA (TEPA) [138] and MOFs 1-dmen [52] and 1-een [136] have been shown to retain their adsorption capacities between five to eleven sorption cycles.

### **3.5. Thermal stability of adsorbents at pre- and post-combustion conditions.**

Polymer CQN-1g [52] had the highest thermal stability at 773K. Other polymer compounds such as TAP-3 [15] and NHC-CAP-1 [75] had thermal stabilities up to 573K and 373K respectively while AC NSCS-4-700 [75] had thermal stabilities up to temperatures of 473K. Some MOFs such as MFM-305 [13], MIL-140 [41] and Cu-Sp5 [140] have been shown to be thermally stable at temperatures of 723K, 573K and 503K respectively. Some adsorbents in this study therefore exhibit thermal stabilities at high temperatures obtainable in most industrial processes. This shows that the adsorbents have potential for use at high temperature conditions. However, literature in this regard remains scarce.

### **3.6. Permeance and selectivity for CO<sub>2</sub> of membranes at pre- and post-combustion conditions.**

Membranes have also shown promising permeance and selectivity for CO<sub>2</sub> in flue gas mixtures. UiO-66CN@sPIM-1 [120] recorded the highest CO<sub>2</sub> permeance amongst reviewed membranes with a value of 12063 Barrer and selectivity (CO<sub>2</sub>/N<sub>2</sub>) of 53.5 at atmospheric conditions. MoS<sub>2</sub>-SILM membrane [141] has been shown to exhibit the highest selectivity of 462 for CO<sub>2</sub>. Also, membranes such as MOF-801/PEBA MMM [141] and COF-5/Pebax [126] with selectivities of 66 and 49.3, respectively for SCO<sub>2</sub>/N<sub>2</sub>. Most of the membranes recently synthesized exhibit high CO<sub>2</sub> permeance and promising selectivity for CO<sub>2</sub> separation which exceeded the standard values for industrial use of 2250 for CO<sub>2</sub> permeability and >30 for selectivity. The fact that most membranes have good permeance and selectivity for CO<sub>2</sub>, makes them well suited for industrial gas separation process applications.

**Table 1. Selected CO<sub>2</sub> adsorbents with the highest adsorption capacity.**

Material	Adsorbent	CO <sub>2</sub> Uptake (mmol/g)	P (bar)	T (K)	Slcty (CO <sub>2</sub> /N <sub>2</sub> )	Stability	Cycles of Performance	Potential point of application
PPN-4	Polymer	48.20	50	298	-	-	-	Pre-combustion capture of CO <sub>2</sub>
PAF-1	Polymer	29.55	40	298	-	-	-	Pre-combustion capture of CO <sub>2</sub>
LSB3-800	AC	20.9	30	298	-	-	-	Pre-combustion capture of CO <sub>2</sub>
SBL-PNP-1-4-750	AC	19.65	20	298	-	-	-	Pre-combustion capture of CO <sub>2</sub>
SBL-PNP-1-4-750	AC	16.2	20	298	-	-	-	Pre-combustion capture of CO <sub>2</sub>
HCP-1	Polymer	13.1	30	298	-	-	-	Pre-combustion capture of CO <sub>2</sub>
NSCS-4-700	AC	11.68	8	298	-	-	Showed no loss of adsorption capacity after 10 sorption cycles at 473K regeneration temperature	Pre-combustion capture of CO <sub>2</sub>
CNS-AC	AC	8.36	30	303	-	-	Adsorption performance remained unchanged after the 6 <sup>th</sup> sorption cycle	Pre-combustion capture of CO <sub>2</sub>
HKUST-1	MOF	8.07	10	303	-	-	-	Pre-combustion capture of CO <sub>2</sub>

IHBPA (TEPA)	Polymer	7.65	1	298	-	Thermal stable up to 363K	Maintained adsorption capacity after 10 <sup>th</sup> sorption cycle.	Post combustion capture of CO <sub>2</sub> at ambient temperatures
MIL-101 (Cr)	MOF	7.19	10	303	-	-	-	Pre-combustion capture of CO <sub>2</sub>
CuO NP-AC	AC	6.72	1	298	-	-	-	Post combustion capture of CO <sub>2</sub> at ambient temperature
PI-COF-2	Polymer	5.8	1	298	-	-	-	Post combustion capture of CO <sub>2</sub> at ambient temperature
ARG-K-Im	AC	5.63	1	298	-	-	-	Post combustion capture of CO <sub>2</sub> at ambient temperature
DAC-AC-CO <sub>2</sub>	AC	5.52	1	298	28.4	-	Shown stability and maintained its initial adsorption capacity up to 11 <sup>th</sup> sorption cycle	Post combustion capture of CO <sub>2</sub> at ambient temperature; selectivity has to be improved upon for viable applicability
1-eeen	MOF	5.05 4.04	1 0.15	313	293	-	Working capacity dropped from 13.89wt% to 12.36wt% at the 100 <sup>th</sup> sorption cycle	Sequestration of CO <sub>2</sub> flue gases at post combustion conditions from automobiles, motorcycles, generators etc.

UTSA-120a	MOF	5.00	1	296	~600	-	-	Post combustion capture of CO <sub>2</sub> at ambient conditions due to high selectivity
CQN-1g	Polymer	4.57	1	298	-	Thermally stable up to 773K	-	Post combustion capture of CO <sub>2</sub> at ambient temperatures; Possibility of practical use for CO <sub>2</sub> capture.
1-dmen	MOF	4.34	1	313	554	-	Retained its adsorption capacity after 7 <sup>th</sup> sorption cycle	Post combustion capture of CO <sub>2</sub> from exhaust gas of automobiles, petrol generators, motorcycles etc.
NSCS-4-700	AC	4.27	1	298	-	-	Retained adsorption capacity after 10 sorption cycles at 473K regeneration temperature	Post combustion capture of CO <sub>2</sub> at ambient temperature
TAEA modified MIL-101 (Cr)	MOF	4.06	0.15	313	-	-	-	Post combustion capture of CO <sub>2</sub> from exhaust gas of automobiles, petrol generators etc.
1-ipen	MOF	4.05	1	313	273	-	-	Post combustion capture of CO <sub>2</sub> at ambient temperature

1 **Table 2: CO<sub>2</sub> permeance and selectivity capacity of membranes**

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Material	P (bar)	T (K)	CO <sub>2</sub> permeance	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	Potential point of application
UiO-66-CN@sPIM-1	1.4	298	12063 <sup>a</sup>	53.5	-	Separation of CO <sub>2</sub> from binary air mixture (CO <sub>2</sub> /N <sub>2</sub> ) at atmospheric Conditions.
COF 300/6FDA-DAM MMM	8	298	8257 <sup>a</sup>	-	75	Pre-combustion separation of CO <sub>2</sub>
COF 300/Pebax MMM	8	298	8054 <sup>a</sup>	-	110	Pre-combustion separation of CO <sub>2</sub>
TFC#1	3	298	8010 <sup>b</sup>	35.8	-	-
TFC#6	3	298	3010 <sup>b</sup>	55.7	-	-
FIHM-PEGDME-500-180	3.5	303	1566.8 <sup>a</sup>	35.1	-	-
MoS <sub>2</sub> -SILM	1	293	200 <sup>b</sup>	462	-	Post combustion capture of CO <sub>2</sub> at ambient temperatures

3 <sup>a</sup> = Barrer; 1 Barrer = 10<sup>-10</sup> cc (STP)cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-2</sup>

4 <sup>b</sup> = GPU; 1 GPU = 10<sup>-6</sup> cc (STP)cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>

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7 **3.7. Adsorbent performance for other noxious gases sequestration at pre- and**

8 **post-combustion conditions.**

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10 For NH<sub>3</sub> capture at post combustion conditions at ambient temperatures, polymer PCP-1

11 [142] had the highest adsorption capacity of 22.8 mmol/g as shown in Table 3. MOF

12 Cu<sub>2</sub>Cl<sub>2</sub>BBTA [143] and MOF-4 [143] also had good adsorption capacities of 19.79 mmol/g

13 and 17.8 mmol/g respectively. Unfortunately, the thermal and chemical stability of these

14 adsorbents for NH<sub>3</sub> capture were not investigated by the authors. Same applies to their

15 regenerability and reusability except for Polymer PCP-1 [142] which showed very low

16 reusability potential due to the reduced number of pores during successive sorption cycles

17 as a result of structure collapse.

18

19 MOFs, polymers, AC and membrane have been reported to also sequester noxious gases

20 such as SO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>S, considerably at pre-combustion and post combustion conditions,

21 despite the chemical stability challenge posed by compounds such as SO<sub>2</sub> and H<sub>2</sub>S to

22 adsorbents. For SO<sub>2</sub> capture, MOF compounds such as MOF-3 [56], NH<sub>2</sub>-MIL-125 (Ti) [144],

23 MFM-300 (Sc) [55] and MIL-160 [144], MOC-1 and MOC-3 [54] had better adsorption

capacity at post combustion conditions at ambient temperatures, as shown in Table 4. Unfortunately, none of these compounds were investigated at temperatures consistent with Flue Gas Desulfurization (FGD) systems.

MOF MIL-53 (Al) TDC [57] was found to be the highest performing adsorbent for H<sub>2</sub>S capture at post combustion conditions at ambient temperatures, more than Polymers PM<sub>012</sub>@Ui-66@H<sub>2</sub>S-MIPsM [145] and BPP-5 [146] as shown in Table 5. Furthermore, Polymer BPP-5 [146] had a better chemical stability and potential for regenerability and reusability. MOF MIL-101@M-0.5-0.5[147] was found to be the only adsorbent with high potential for H<sub>2</sub>S capture at pre-combustion conditions with adsorption capacity of 36.1 mmol/g at 10 bar and 298K. Membrane NbOFFIVE-1-NI/6FDA-DAMMM [146] showed capacity to simultaneously separate CO<sub>2</sub> and H<sub>2</sub>S from methane (CH<sub>4</sub>), with a selectivity of 48 for CO<sub>2</sub>+H<sub>2</sub>S over CH<sub>4</sub> and a permeance of 950 CO<sub>2</sub>+H<sub>2</sub>S. This compound has potential for natural gas sweetening if the permeance property is improved.

**Table 3. Selected NH<sub>3</sub> adsorbents with the highest adsorption capacity**

Material	Adsorbent	NH <sub>3</sub> Uptake mmol/g	P (bar)	T (K)	Cycles Performance	Potential Point of Applications
PCP-1	Polymer	22.3	1	298	Adsorption capacity reduced at 3 <sup>rd</sup> sorption cycle; Reduction of 5.2 mmol/g between 1 <sup>st</sup> and 2 <sup>nd</sup> sorption cycles was recorded.	NH <sub>3</sub> capture at ambient conditions
Cu <sub>2</sub> Cl <sub>2</sub> BBTA	MOF	19.79	1	298	-	NH <sub>3</sub> capture at ambient conditions.
MOF-4	MOF	17.8	1	298	-	NH <sub>3</sub> capture at ambient conditions.

44 **Table 4: Selected SO<sub>2</sub> adsorbents with the highest adsorption capacity**

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Material	Adsorbent	SO <sub>2</sub> Uptake (mmol/g)	P (bar)	T (K)	Selectivity	Stability	Cycles of Performance	Potential point of application
MOF-177	MOF	25.7	1	293	-	Chemically unstable	-	Not suitable for practical applications.
MOF-3	MOF	10.9	1	298	-	-	-	SO <sub>2</sub> capture at ambient conditions.
NH <sub>2</sub> -MIL-125(Ti)	MOF	10.8	0.95	293	SO <sub>2</sub> /CO <sub>2</sub> – 47-55	-	Showed irreversible adsorption capacity; working capacity reduced at 2 <sup>nd</sup> cycle of performance.	SO <sub>2</sub> capture at ambient conditions.
MFM-300(Sc)	MOF	9.4	1	298	-	-	Adsorption capacity remained unchanged after 10 sorption cycles; regeneration occurred at room temperature.	SO <sub>2</sub> capture at ambient conditions
MIL-160	MOF	7.2	0.95	293	SO <sub>2</sub> /CO <sub>2</sub> – 124-128	Thermal and chemical stable	Exhibited good adsorption stability with slight reduction in sorption capacity after 5 sorption cycle	SO <sub>2</sub> capture at ambient conditions

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**Table 5. Selected H<sub>2</sub>S adsorbents with the highest adsorption capacity**

Material	Adsorbent	H <sub>2</sub> S Uptake (mmol/g)	P (bar)	T (K)	Stability	Cycles of Performance	Potential point of application
MIL-101@M-0.5-0.5	MOF	36.1 7.63	10 35	298	-	-	Pre-combustion capture of H <sub>2</sub> S from syngas stream.
MIL-53 (Al)-TDC	MOF	18.1	1	303	Chemically stable in the presence of H <sub>2</sub> S	Adsorption capacity was retained after 5 sorption cycles; structure exhibits low temperature of 473K for regeneration; regeneration can be achieved at temp. of 338K.	Integrated Gasification Combined Cycle (IGCC) for H <sub>2</sub> S capture at ambient temperatures
BPP-5	Polymer	17.7	1	298	Superior stability in extremely basic conditions	Author suggested that structure will keep working capacity after various adsorption-desorption cycles	H <sub>2</sub> S capture at ambient conditions

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## 64 4. CONCLUSIONS AND PERSPECTIVES

65 In this review, the performance of selected categories of adsorbents for noxious gas  
66 sequestration have been evaluated. The suitability of the adsorbents with the highest SAPs  
67 such as adsorption capacity, selectivity, permeance, regenerability and reusability, thermal  
68 and chemical stability was determined for pre-combustion and post combustion industrial  
69 applications. Perspectives of future studies was also presented.

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71 In terms of adsorption capacity, Polymers, AC and MOFs are suitable for CO<sub>2</sub> adsorption at  
72 pre- and post – combustion conditions. Some polymers and ACs were found to have very  
73 high adsorption capacities compared to MOFs. MOFs on the other hand, having the highest  
74 adsorption capacities are best suited for SO<sub>2</sub> capture. For H<sub>2</sub>S and NH<sub>3</sub> adsorption, MOFs  
75 and Polymers had the highest adsorption capacity, making them more suitable than ACs.

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77 MOFs have been revealed to show exceptional selectivity for CO<sub>2</sub> and SO<sub>2</sub> in binary  
78 mixtures of CO<sub>2</sub>/N<sub>2</sub> and SO<sub>2</sub>/CO<sub>2</sub> respectively, making it a suitable candidate for CO<sub>2</sub> and  
79 SO<sub>2</sub> capture. Most membranes showed selectivity and permeance capacities suitable for  
80 industrial applications (>30 for selectivity and >2250 for permeance).

### 82 4.1 Perspective for Future Study

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84 Most of the temperature conditions at which these adsorbents were investigated are below  
85 practical temperature conditions obtainable in post – combustion process systems. This  
86 therefore creates a challenge in their industrial deployment. It is therefore needful to  
87 investigate the capture and storage capacities of these adsorbent at higher temperatures, so  
88 as to ensure their industrial applicability for improved environmental sustainability. Also,  
89 information on the selectivity, stability, regenerability and reusability of most of the  
90 adsorbents, were not reported. It becomes imperative for these parameters to be properly  
91 investigated and reported. The adsorption capacities of MOFs for CO<sub>2</sub>, Polymers and ACs  
92 for SO<sub>2</sub>, as well as ACs for H<sub>2</sub>S and NH<sub>3</sub>, should be further investigated and improved upon.

## 95 COMPETING INTERESTS

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97 Authors have declared that no competing interests exist.

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