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

V. J. Aimikhe<sup>1\*</sup> and O. E. Eyankware<sup>1</sup>

Department of Petroleum and Gas Engineering, University of Port Harcourt, Nigeria.

#### Authors' contributions

This work was carried out in collaboration between both authors. Author VJA designed the study. managed the analyses of the study, wrote the protocol and the final draft of the manuscript. Author OEE managed the literature searches, the analyses of the study and wrote the first draft of the manuscript. Both authors read and approved the final manuscript.

#### Article Information

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(1) Dr. Ahmed Mohammed Abu-Dief Mohammed, Assistant Professor, Department of Chemistry, Faculty of Science, Sohag University, Sohag, Egypt.

(1) Roberto Flores, Universidad Autonoma del Estado de Morelos, Mexico. (2) Abdu Muhammad Bello, Kano University of Science and Technology, Nigeria. (3) Dara, Jude Ezechi, Nnamdi Azikiwe University, Nigeria. (4) Norhayati Hashim, Universiti Pendidikan Sultan Idris, Malaysia. Complete Peer review History: <a href="https://sdiarticle4.com/review-history/51792">https://sdiarticle4.com/review-history/51792</a>

Review Article

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#### **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, suitable candidates for noxious gas sequestration can be determined. To foster the development and selection of a more efficient adsorbent, 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 gas 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 the production 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],  $CH_4[7]$ ,  $NH_3$ ,  $SO_x$ ,  $NO_x$ ,  $H_2S$  [8], Volatile Organic Compounds (VOCs) and volatile organic gases [9] pose a high environmental risk [10]. This, therefore, necessitates the management of air quality to ensure a sustainable environment.

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, excellent thermal and chemical stability, ease of functionability 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 CO2 adsorption capacity is above 3 mmol/g [22].

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

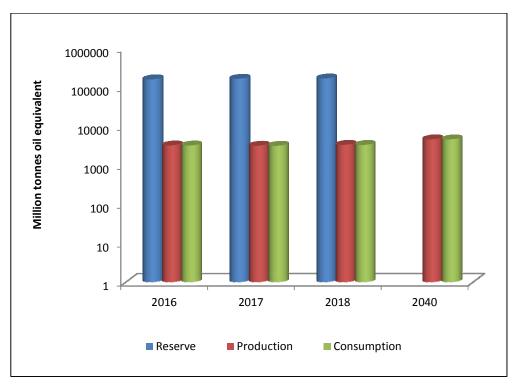


Fig. 1. Natural gas outlook (Source: [2–5])

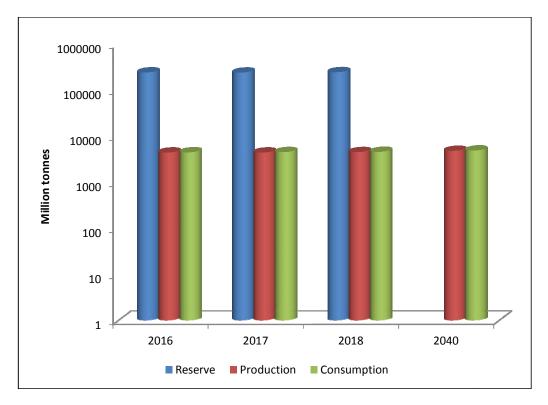


Fig. 2. Crude oil outlook (Source: [2–5])

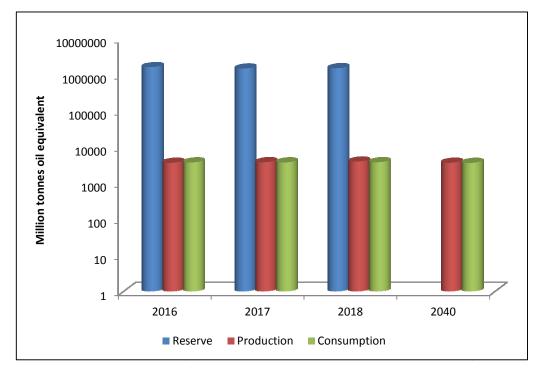


Fig. 3. Coal outlook (Source: [2–5])

# 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 at 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 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 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].

MOFs have been investigated for the 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>, and SO<sub>x</sub>, [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;

- Amorphouspolymerswhichcompriseconjug ated microporous polymers (CMP) [68], covalent triazine framework [18], porous aromatic framework [18], hyper-cross linked polymers (HCP) [69] and polymers of intrinsic [70].
- Crystalline polymers(covalent organic polymers) [71].

Different polymers have been synthesized for harmful gases sequestration at different process conditions [72] and modification through presynthetic 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.

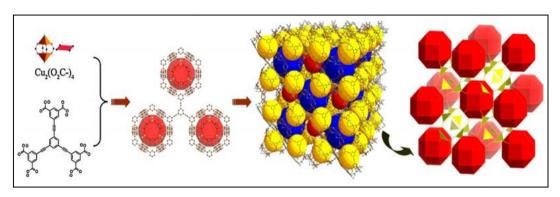


Fig. 4. The crystalline structure of metal-organic frameworks [32]

For instance, for  $CO_2$  adsorption, aminofunctional 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  $CO_2$ ,  $SO_2$ ,  $NH_3$ , and  $H_2S$  sequestration.

## 2.3 Activated Carbon (AC)

AC has been investigated for the 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 of 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 a high amount of fixed carbon that can be processed to AC with high microporosity [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 to produce AC with micropores on the surface of the structure for adsorption abilities.

AC has been investigated for  $SO_x$  and  $NO_x$  [99, 100],  $H_2S$  [101], and  $CO_2$  [100] sequestration at different process conditions. 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  $CO_2$ ,  $SO_2$ ,  $NH_3$ , and  $NO_x$  sequestration have also been reported [90,91,93,98,108,109].

#### 2.4 Membranes

Membranes function as filters, as shown in Fig. 5. They are used for separation [110]. Different researchers have reported membrane used for the capture of harmful gases in literature [17, 111,112] as they are environmentally benign and efficient in energy consumption [113] and exhibit technical and cost-related merits [114].

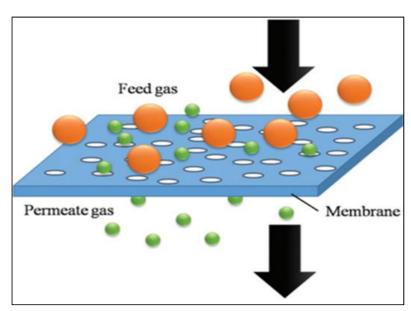


Fig. 5. Separation of different molecules using membrane [118]

Key parameters that determine the 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, excellent chemical and thermal stability, and ability to resist plasticization [116,117], for it to be feasible. Progress in this regard has 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 persist [118]. This structure optimization has resulted in the synthesis of different classes of membranes [110,119–122].

Various studies on the use of membrane for the capture of  $CO_2$  and  $H_2S$ , have also been reported [110,112,122–126].

# 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 as adsorption capacity, selectivity, permeability/permeance (for membranes). regeneration/reusability, thermal and chemical stability, were used to rank these adsorbents to determine the most efficient adsorbent and suitable points for their application. adsorption capacity was used as the highestranking property. Only the best performing adsorbent is reported for each SAP category. The industrial applications considered in this study include pre-combustion and postcombustion 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 and biogas sweetening. 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 precombustion separation of  $CO_2$ as highlighted in Table 2. They have been shown to function within the 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 applications. 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 Postcombustion Conditions

Post-combustion applications occur basically at approximately atmospheric pressure of 1 bar and high or low temperatures [132]. At practical postcombustion 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 could not 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 postcombustion conditions at high temperatures. MOFs 1-een 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  $CO_2$  in a binary mixture of  $CO_2/N_2$ . 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 functional adsorption capacities for post-combustion CO2 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 the 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 CO2, Considering the working temperatures and pressures of the adsorbents, they are most suited for pre- and post-combustion capture at ambient temperatures.

# 3.3 CO<sub>2</sub> Selectivity of Adsorbents at Preand Post-combustion Conditions

In terms of selectivity for  $CO_2$  in flue gas streams, 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  $CO_2$ -philic functional groups. MIL-140 [41] and UTSA-120a [46] showed one of the highest selectivity of 1900 and  $\sim 600$  for  $CO_2$  in binary mixtures  $(CO_2/N_2)$ . Extremely high selectivity of 7531 for  $CO_2/N_2$  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  ${\rm CO_2}$  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-1 q [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] are 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 CO2 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 CO2 makes them well suited 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 points 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	-	Thermally stable up to 363K	Maintained adsorption capacity after the 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	-	Showed 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

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 points of application
1-een	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 the 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

Table 2. CO<sub>2</sub> permeance and selectivity capacity of membranes

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 points 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

 $^{a}$  = Barrer;1 Barrer =  $10^{-10}$ cc (STP)cm cm $^{-2}$  s $^{-1}$  cmHg $^{-2}$ ;  $^{b}$  = GPU;1 GPU =  $10^{-6}$ cc (STP)cm $^{-2}$  s $^{-1}$  cmHg $^{-1}$ 

Table 3. Selected NH₃ adsorbents with the highest adsorption capacity

Material	Adsorbent	NH₃ Uptake mmol/g	P (bar)	T (K)	Cycles of performance	Potential points of application
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

Table 4. Selected SO<sub>2</sub> adsorbents with the highest adsorption capacity

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	Thermally and chemically stable	Exhibited good adsorption stability with a slight reduction in sorption capacity after 5 sorption cycle	SO <sub>2</sub> capture at ambient conditions

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

Material	Adsorbent	H₂S 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 H₂S from syngas stream
MIL-53 (AI)- TDC	MOF	18.1	1	303	Chemically stable in the presence of H <sub>2</sub> S	The 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 fundamental conditions	The author suggested that structure maintained its working capacity after various adsorption-desorption cycles	H <sub>2</sub> S capture at ambient conditions

# 3.7 Adsorbent Performance for Other Noxious Gases Sequestration at Preand Post-combustion Conditions

For NH<sub>3</sub> capture at post-combustion conditions at ambient temperatures, polymer PCP-1 [142] had the highest adsorption capacity of 22.8 mmol/g. as shown in Table 3. MOF Cu<sub>2</sub>Cl<sub>2</sub>BBTA [143] MOF-4 [143] also had aood adsorption capacities of 19.79 mmol/g and 17.8 mmol/g respectively. Unfortunately, the thermal and chemical stability of these adsorbents for NH<sub>3</sub> capture was not investigated by the authors. The same applies to their regenerability and reusability except for Polymer PCP-1 [142] which showed very low reusability potential due to the reduced number of pores during successive sorption cycles as a result of structural collapse.

MOFs, polymers, AC, and membrane have also been reported to sequester noxious gases such as SO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>S, considerably at precombustion and post-combustion conditions, despite the chemical stability challenges posed by compounds such as SO<sub>2</sub> and H<sub>2</sub>S to adsorbents. For SO<sub>2</sub> capture, MOF compounds such as MOF-3 [56], NH<sub>2</sub>-MIL-125 (Ti) [144], 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 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 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 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 adsorption capacity of 36.1 mmol/g at 10 bar and Membrane NbOFFIVE-1-NI/6FDA-DAMMMM [146] showed the capacity to simultaneously separate CO2 and H2S 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 permeance of 950 CO<sub>2</sub>+H<sub>2</sub>S. This compound has the potential for natural gas sweetening if the permeance property is improved.

#### 4. CONCLUSIONS AND PERSPECTIVES

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

In terms of adsorption capacity, Polymers, AC, and MOFs are suitable for  $CO_2$  adsorption at preand post-combustion conditions. Some polymers and ACs were found to have very high adsorption capacities compared to MOFs. MOFs, on the other hand, having the highest adsorption capacities are best suited for  $SO_2$  capture. For  $H_2S$  and  $NH_3$  adsorption, MOFs and Polymers had the highest adsorption capacity, making them more suitable than ACs.

MOFs have been revealed to show exceptional selectivity for  $CO_2$  and  $SO_2$  in binary mixtures of  $CO_2/N_2$  and  $SO_2/CO_2$  respectively, making it a suitable candidate for  $CO_2$  and  $SO_2$  capture. Most membranes showed selectivity and permeance capacities suitable for industrial applications (>30 for selectivity and >2250 for permeance).

## 4.1 Perspective for Future Study

Most of the temperature conditions at which these adsorbents were investigated are below practical temperature conditions obtainable in post-combustion process systems. therefore, creates a challenge in their industrial deployment. It is, therefore, needful to investigate the capture and storage capacities of these absorbents at higher temperatures, to ensure industrial applicability for improved their environmental sustainability. Also, information on the selectivity, stability, regenerability and reusability of most of the adsorbents were not reported. It becomes imperative for these parameters to be adequately investigated and reported. The adsorption capacities of MOFs for CO<sub>2</sub>, Polymers, and ACs 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.

#### **COMPETING INTERESTS**

Authors have declared that no competing interests exist.

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