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Review Article

**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 CO₂, SO₂, H₂S and NH₃ capture and in some cases, storage. Using the standard adsorbent properties (SAPs) such as adsorption capacity, selectivity, permeability/permeance, regenerability and reusability, ease of functionality 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.

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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_x, [6], CH₄ [7], NH₃, SO_x, NO_x, H₂S [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.

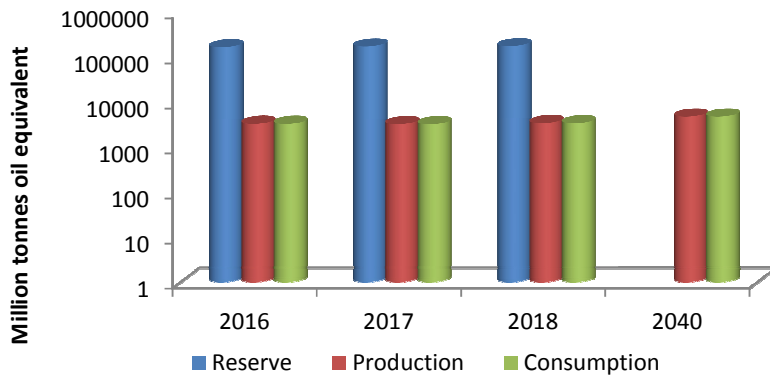


Fig. 1. Natural gas outlook (Source: [2-5])

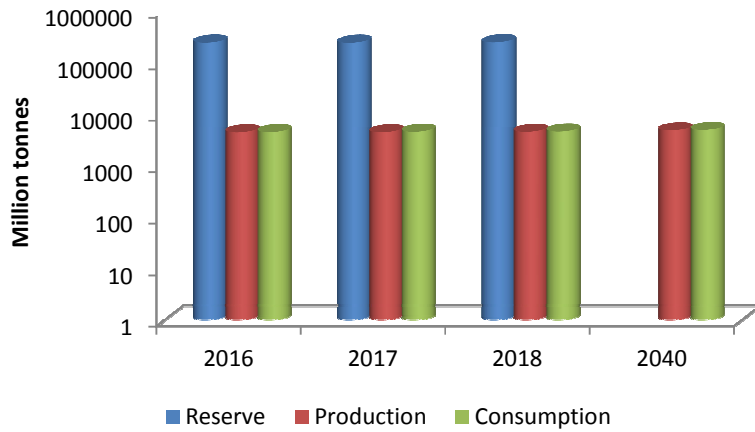


Fig. 2. Crude oil outlook (Source: [2-5])

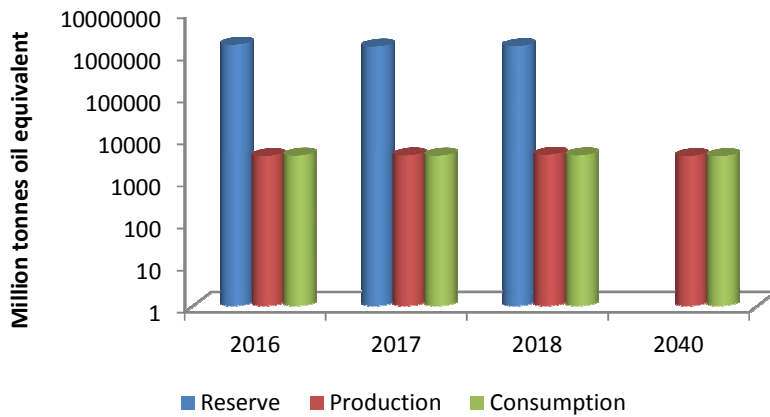


Fig. 3. Coal outlook (Source: [2-5])

1 Different materials and methods [11–18] have been reported for the separation and capture
2 of hazardous gases either from process systems or the environment. Amongst these
3 compounds, adsorbents such as metal organic frameworks (MOFs), polymers, activated
4 carbon (AC) and membranes, have been considered as promising candidates for gas
5 separation and storage, due to their large surface area and pore volume, good thermal and
6 chemical stability, ease of functionality and tunability, low regeneration cost and high
7 selectivity. These adsorbents can be easily modified for specific applications through pre-
8 and post-functionalization of the structure [19–21]. Adsorbent utilization becomes more
9 feasible when its CO₂ adsorption capacity is above 3 mmol/g [22].

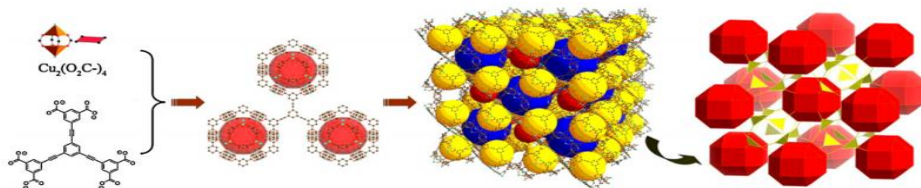
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11 For the purpose of this study, an up to date review of the performance of MOFs, polymers,
12 AC and membrane adsorbents are considered. The major focus of this study therefore, was
13 to identify the best performing adsorbents for noxious gas sequestration and then proffer
14 suitable areas for their application.
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16 2. ADSORBENTS FOR CAPTURE OF HARMFUL GASES

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

26 2.1 Metal Organic Frameworks (MOFs)

27
28 Metal Organic Frameworks (MOFs) are an emerging class of porous materials constructed
29 from metal-containing nodes and organic linkers [27]. Due to the strong bonds that exist
30 between the metal-containing nodes [also known as secondary building units (SBUs)] and
31 organic linkers, MOFs usually boast of a structure with permanent porosity and open
32 crystalline frameworks as shown in Fig. 4. The organic spacers or the metallic SBUs can be
33 altered to control the pore environment of the MOF [28]. Their inherent
34 characteristics/advantages such as large surface area, ease of functionalization, kinetic
35 diameter, electric properties, Open Metal Sites (OMS), high porosity and tuneable size of
36 pores [29] have made them very attractive compounds in applications such as gas storage
37 and separation, catalysis and sensing [30,31]. The ease with which SBUs and organic
38 linkers are changed and altered has led to the synthesis of thousands of various MOF
39 structures. As a result, the structures and properties of MOFs can be designed and
40 systematically tuned by the choice of building blocks used for the synthesis of the framework
41 [32]. Various strategies have also been reported for improving the performance of MOFs
42 [33].
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46 **Fig. 4.** Crystalline structure of Metal Organic Frameworks [32]

47 MOFs have been investigated for optimization of structure functionality. In this regard, MOFs
48 have been reported to exhibit promising potential for sequestration of gases such as CO₂,
49 H₂S, CH₄, NH₃, NO_x, SO_x etc. [8,14,34–39]. The works of [13,14,40–66] highlight MOFs for
50 CO₂, SO₂, H₂S and NH₃ sequestration at pre- and post-combustion conditions.

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52 **2.2. Polymers**

53

54 Porous Organic Polymers (POP) are composed of organic building blocks connected
55 through covalent bonds, exhibiting thermal and chemical stabilities, large surface area, ease
56 of synthesis and low density [67]. There are two classes of POP. They include; The
57 amorphous (conjugated microporous polymers (CMP) [68], covalent triazine framework [18],
58 porous aromatic framework [18], hyper-cross linked polymers (HCP) [69]) and polymers of
59 intrinsic [70] and crystalline types (covalent organic polymers) [71].

60 Different polymers have been synthesized for harmful gases sequestration at different
61 process conditions [72] and modification through pre-synthetic and post synthetic
62 functionalization [73] have been reported for improved performance for specific applications .
63 [15]. The agents used for functionalization are compounds that increase the affinity of porous
64 polymers for a specific noxious gas. For instance, for CO₂ adsorption, amino functional
65 groups [74], –N heterocycles [75], phenolic motifs [15] are utilized. The method of synthesis
66 plays a key role in the structure of a polymer which invariably affects the adsorption capacity.
67 The different monomers (building blocks) and methods of synthesis are explained by [76].
68 Polymers have also shown excellent reusability [75] and low heat of adsorption [77]. The
69 works of [11,15,18,69,73,78–85] highlight the use of polymers for CO₂, SO₂, NH₃ and H₂S
70 sequestration.

71 **2.3. Activated Carbon (AC)**

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73 AC has been investigated for capture of noxious gases [86,87]. This is due to reduced cost
74 of production, large surface area, ease of modification of pores, good thermal and chemical
75 stability, hydrophobic nature, stability in the presence of heat and chemical resistance [88].
76 AC shows promising potential for practical applications in terms of balance of performance
77 [89] considering cost of production, benign effect on the environment, availability of
78 precursor materials [90,91] and sustainability [92], and have been reported to exhibit
79 reusability, promising adsorption kinetics [26] and stability after several sorption cycles [63],
80 requiring low regeneration energy [93]. A key determinant to the adsorption performance of
81 AC is the type of precursor used in its synthesis. Different precursors have been reported in
82 the literature for the production of AC.

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84 They include bamboo [94], petroleum coke [95], rice husk char [26] wood [96], coconut shell
85 [97], sugarcane bagasse [91], argan fruit shells [98], pinewood shavings char, biochar [89]
86 etc. Amongst these precursors, biochar stands out as it exhibits high porosity and high
87 amount of fixed carbon that can be processed to AC with high micro porosity [89]. Therefore,
88 biochar precursors should receive further investigation in its use for the production of AC for
89 gas sequestration. It is imperative to state that these precursors should have low ash and
90 volatile matter content so as to produce AC with micropores on the surface of the structure
91 for adsorption abilities.

92

93 AC have been investigated for SO_x and NO_x [99,100], H₂S [101] and CO₂ [100] sequestration
94 at different process conditions. In order to optimize capture and selectivity of AC for specific
95 gases, modification of the structure to increase its affinity for specific gases have been
96 reported [102–108]. Various studies on the use of AC for CO₂, SO₂, NH₃ and NO_x
97 sequestration, have also been reported [90,91,93,98,108,109].

98 **2.4. Membranes**

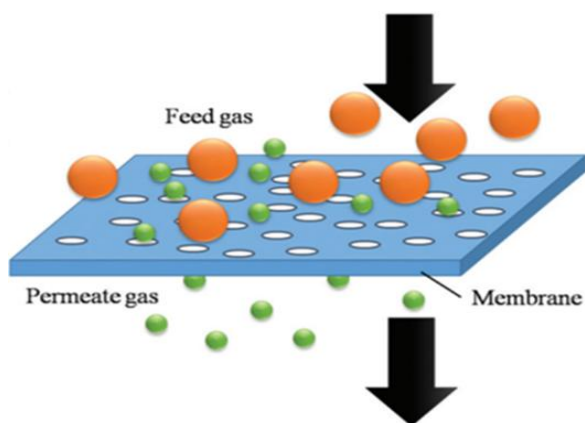
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100 Membranes basically function as filters as shown in Fig. 5. They are used for separation
101 [110]. Different researchers have reported membrane use for capture of harmful gases in
102 literature [17,111,112] as they are environmental benign and efficient in energy consumption
103 [113] and exhibit technical and cost-related merits [114]. Key parameters that determine
104 feasibility of membranes for industrial applications are *permeability and selectivity* [115].
105 Membranes should therefore possess high permeability, permeance, high selectivity, low
106 cost of production and regeneration, good chemical and thermal stability, and ability to resist
107 plasticization [116,117], in order for it to be feasible. Progress in this regard have been
108 recorded in literature where properties of membranes have been optimized even though
109 challenges such as high cost, low physical and chemical stability, low selectivity and low
110 hydrothermal stability still persist [118]. This structure optimization has resulted in the
111 synthesis of different class of membranes [110,119–122].

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113 Various studies on the use of membrane for the capture of CO₂ and H₂S, have also been
114 reported [110,112,122–126].

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

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

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3.1. CO₂ Adsorption capacity at pre-combustion conditions

Pre-combustion conditions typically occur at relatively high pressures and / or low 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. Polymers PPN-4 [128] and PAF-1 [129]

137 exhibited the highest adsorption capacities of 48.20 mmol/g and 29.55 mmol/g at pressures
138 of 50 bar and 40 bar respectively at ambient temperatures. ACs LSB3-800 [86] and SBL-
139 PNP-1-4-750 [130] also showed high adsorption capacities of 20.9 mmol/g and 19.65
140 mmol/g at pressures of 20 bar each at 298K. AC SBL-PNP-1-4-750 [130] was the only
141 adsorbent that showed high adsorption capacity of 16.2 mmol/g at a high temperature of
142 1023K, at 20 bar.

143

144 Membranes showed suitability for pre-combustion separation of CO₂. They have been
145 shown to function within pressure range of pre-combustion carbon capture. Membranes
146 COF 300/6FDA-DAM MMM and COF 300/Pebax MMM [131] can be applied in pre-
147 combustion conditions if their thermal stability at high temperatures is improved.

148

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

153

154 **3.2. CO₂ Adsorption capacity at post-combustion conditions.**

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156 Post combustion applications occur basically at approximately atmospheric pressure of 1
157 bar and high or low temperatures [132]. At practical post combustion conditions of flue
158 gases from systems such automobiles, petrol generators, motorcycles, gas turbine power
159 plants, oil turbine plants, coal fired plants, water pyrolysis and cement production, only a few
160 adsorbents were found to be applicable. Most of the adsorbents showed a decrease in
161 working capacity as temperature increased and ultimately resulted in the decomposition of
162 the structure which implied that the adsorbents cannot be used at relatively high temperature
163 conditions. This can be attributed to the fact that as temperature increases, adsorption
164 capacity of adsorbents such as AC decreases [133]. The low adsorption capacities of AC
165 with values between 0.2 mmol/g to 1.80 mmol/g at 1 bar and 373K [104] and that of
166 NORF700 [134] and NCLK3 [135] with adsorption capacities of 2.10 mmol/g and 2.00
167 mmol/g at 1 bar and 323K, support this claim. Polymers, AC and MOFs do not exhibit high
168 adsorption capacities for CO₂ in post-combustion conditions at high temperatures. MOFs 1-
169 een and 1-dmen [136], TAEA modified MIL-101 (Cr) [45] and 1-nmen [136] had the highest
170 adsorption capacities of 5.05 mmol/g, 4.34 mmol/g, 4.05 mmol/g and 2.92 mmol/g
171 respectively, at ~1 bar and 313K. Amongst these MOFs, 1-dmen [52] has shown promising
172 potential for practical applications due to its high selectivity of 554 for CO₂ in a binary mixture
173 of CO₂/N₂. It is therefore evident that these values for adsorption capacity are not as high as
174 those recorded in pre-combustion conditions as pressure increase results in increase in
175 adsorption capacities [137].

176

177 Most adsorbents showed good adsorption capacities for post combustion CO₂ capture at
178 ambient temperatures, with polymer and AC exhibiting the highest adsorption capacities.
179 Polymer IHBPA (TEPA) [138] and PI-COF-2 [80] had adsorption capacities of 7.65 mmol/g
180 and 5.8 mmol/g respectively at 1 bar and 298K while AC CuO NP-AC [108], ARG-K-Im [98]
181 and DAC-AC-CO₂ [98] had adsorption capacities of 6.72 mmol/g, 5.63 mmol/g and 5.52
182 mmol/g respectively at 1 bar and 298K. MOF UTSA-120a [46] was the highest performing
183 MOF in this regard with adsorption capacity of 5.00 mmol/g at 1 bar and 296K, all other
184 MOFs performed below this value in this study. Considering the working temperatures and
185 pressures of the adsorbents, they are mostly suited for pre- and post - combustion capture at
186 *ambient temperatures*.

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189

190 **3.3. CO₂ Selectivity of adsorbents at pre- and post-combustion conditions.**

191

192 In terms of selectivity for CO₂ in flue gas stream, MOFs have shown exceptional selectivity
193 that outperformed other adsorbents such as polymers, adsorbents and membranes. This
194 can be attributed to their ease of functionalization using CO₂-philic functional groups. MIL-
195 140 [41] and UTSA-120a [46] showed one of the highest selectivity of 1900 and ~600 for
196 CO₂ in binary mixtures (CO₂/N₂). An extremely high selectivity of 7531 for CO₂/N₂ binary
197 mixture was recorded for MOF MFUM-1(Cu) [139] without information on its adsorption
198 capacity. MOFs 1-dmen [136] and 1-ipen [136] have also been reported to exhibit
199 selectivities of 554 and 273 respectively.

200

201 **3.4. Regenerability and reusability of adsorbents at pre- and post-combustion**
202 **conditions.**

203

204 Some of the adsorbents can be regenerated and re-used for CO₂ capture without losing their
205 adsorption capacities. MOF 1-een [136] has been reported to retain its adsorption capacity
206 after 600 sorption cycles, the highest recorded in this study. Other adsorbents such as AC
207 NSCS-4-700 [63], CNS-AC [90], DAC-AC-CO₂ [109], polymer (IHBPA (TEPA) [138] and
208 MOFs 1-dmen [52] and 1-een [136] have been shown to retain their adsorption capacities
209 between five to eleven sorption cycles.

210

211 **3.5. Thermal stability of adsorbents at pre- and post-combustion conditions.**

212

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

221

222 **3.6. Permeance and selectivity for CO₂ of membranes at pre- and post-**
223 **combustion conditions.**

224

225 Membranes have also shown promising permeance and selectivity for CO₂ in flue gas
226 mixtures. UiO-66CN@sPIM-1 [120] recorded the highest CO₂ permeance amongst reviewed
227 membranes with a value of 12063 Barrer and selectivity (CO₂/N₂) of 53.5 at atmospheric
228 conditions. MoS₂-SILM membrane [141] has been shown to exhibit the highest selectivity of
229 462 for CO₂. Also, membranes such as MOF-801/PEBA MMM [141] and COF-5/Pebax [126]
230 with selectivities of 66 and 49.3, respectively for SCO₂/N₂. Most of the membranes recently
231 synthesized exhibit high CO₂ permeance and promising selectivity for CO₂ separation which
232 exceeded the standard values for industrial use of 2250 for CO₂ permeability and >30 for
233 selectivity. The fact that most membranes have good permeance and selectivity for CO₂,
234 makes them well suited for industrial gas separation process applications.

Table 1. Selected CO₂ adsorbents with the highest adsorption capacity.

| Material | Adsorbent | CO ₂ Uptake (mmol/g) | P (bar) | T (K) | Slcty (CO ₂ /N ₂) | Stability | Cycles of Performance | Potential point of application |
|-----------------|-----------|---------------------------------|---------|-------|--|-----------|---|---|
| PPN-4 | Polymer | 48.20 | 50 | 298 | - | - | - | Pre-combustion capture of CO ₂ |
| PAF-1 | Polymer | 29.55 | 40 | 298 | - | - | - | Pre-combustion capture of CO ₂ |
| LSB3-800 | AC | 20.9 | 30 | 298 | - | - | - | Pre-combustion capture of CO ₂ |
| SBL-PNP-1-4-750 | AC | 19.65 | 20 | 298 | - | - | - | Pre-combustion capture of CO ₂ |
| SBL-PNP-1-4-750 | AC | 16.2 | 20 | 1023 | - | - | - | Pre-combustion capture of CO ₂ |
| HCP-1 | Polymer | 13.1 | 30 | 298 | - | - | - | Pre-combustion capture of CO ₂ |
| 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 ₂ |
| CNS-AC | AC | 8.36 | 30 | 303 | - | - | Adsorption performance remained unchanged after the 6 th sorption cycle | Pre-combustion capture of CO ₂ |
| HKUST-1 | MOF | 8.07 | 10 | 303 | - | - | - | Pre-combustion capture of CO ₂ |

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

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

1 **Table 2: CO₂ permeance and selectivity capacity of membranes**

2

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

3 1 Barrer = 10⁻¹⁰cc (STP)cm⁻² s⁻¹ cmHg⁻²

4 1 GPU = 10⁻⁶cc (STP)cm⁻² s⁻¹ cmHg⁻¹

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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 NH₃ 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 Cu₂Cl₂BBTA [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 NH₃ 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.

17

18 MOFs, polymers, AC and membrane have been reported to also sequester noxious gases
 19 such as SO₂, NH₃ and H₂S, considerably at pre-combustion and post combustion conditions,
 20 despite the chemical stability challenge posed by compounds such as SO₂ and H₂S to
 21 adsorbents. For SO₂ capture, MOF compounds such as MOF-3 [56], NH₂-MIL-125 (Ti) [144],

22 MFM-300 (Sc) [55] and MIL-160 [144], MOC-1 and MOC-3 [54] had better adsorption
 23 capacity at post combustion conditions at ambient temperatures, as shown in Table 4.
 24 Unfortunately, none of these compounds were investigated at temperatures consistent with
 25 Flue Gas Desulfurization (FGD) systems.

26
 27
 28 MOF MIL-53 (Al) TDC [57] was found to be the highest performing adsorbent for H₂S
 29 capture at post combustion conditions at ambient temperatures, more than Polymers
 30 PM₀₁₂@Ui-66@H₂S-MIPsM [145] and BPP-5 [146] as shown in Table 5. Furthermore,
 31 Polymer BPP-5 [146] had a better chemical stability and potential for regenerability and
 32 reusability. MOF MIL-101@M-0.5-0.5 [147] was found to be the only adsorbent with high
 33 potential for H₂S capture at pre-combustion conditions with adsorption capacity of 36.1
 34 mmol/g at 10 bar and 298K. Membrane NbOFFIVE-1-Ni/6FDA-DAMMM [146] showed
 35 capacity to simultaneously separate CO₂ and H₂S from methane (CH₄), with a selectivity of
 36 48 for CO₂+H₂S over CH₄ and a permeance of 950 CO₂+H₂S. This compound has potential
 37 for natural gas sweetening if the permeance property is improved.

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Table 3. Selected NH₃ adsorbents with the highest adsorption capacity

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

43 Table 4: Selected SO₂ adsorbents with the highest adsorption capacity

44

| Material | Adsorbent | SO ₂ 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 ₂ capture at ambient conditions. |
| NH ₂ -MIL-125(Ti) | MOF | 10.8 | 0.95 | 293 | SO ₂ /CO ₂ – 47-55 | - | Shown irreversible adsorption capacity; working capacity reduced at 2 nd cycle of performance. | SO ₂ 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 ₂ capture at ambient conditions |
| MIL-160 | MOF | 7.2 | 0.95 | 293 | SO ₂ /CO ₂ – 124-128 | Thermal and chemical stable | Exhibited good adsorption stability with slight reduction in sorption capacity after 5 sorption cycle | SO ₂ capture at ambient conditions |

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Table 5. Selected H₂S adsorbents with the highest adsorption capacity

| Material | Adsorbent | H ₂ 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 ₂ S from syngas stream. |
| MIL-53 (Al)-TDC | MOF | 18.1 | 1 | 303 | Chemically stable in the presence of H ₂ 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 ₂ 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 ₂ S capture at ambient conditions |

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63 4. CONCLUSIONS AND PERSPECTIVES

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

69
70 In terms of adsorption capacity, Polymers, AC and MOFs are suitable for CO₂ adsorption at
71 pre- and post – combustion conditions. Some polymers and ACs were found to have very
72 high adsorption capacities compared to MOFs. MOFs on the other hand, having the highest
73 adsorption capacities are best suited for SO₂ capture. For H₂S and NH₃ adsorption, MOFs
74 and Polymers had the highest adsorption capacity, making them more suitable than ACs.

75
76 MOFs have been revealed to show exceptional selectivity for CO₂ and SO₂ in binary
77 mixtures of CO₂/N₂ and SO₂/CO₂ respectively, making it a suitable candidate for CO₂ and
78 SO₂ capture. Most membranes showed selectivity and permeance capacities suitable for
79 industrial applications (>30 for selectivity and >2250 for permeance).

80
81 Most of the temperature conditions at which these adsorbents were investigated are below
82 practical temperature conditions obtainable in post – combustion process systems. This
83 therefore creates a challenge in their industrial deployment. It is therefore needful to
84 investigate the capture and storage capacities of these adsorbent at higher temperatures, so
85 as to ensure their industrial applicability for improved environmental sustainability. Also,
86 information on the selectivity, stability, regenerability and reusability of most of the
87 adsorbents, were not reported. It becomes imperative for these parameters to be properly
88 investigated and reported. The adsorption capacities of MOFs for CO₂, Polymers and ACs
89 for SO₂, as well as ACs for H₂S and NH₃, should be further investigated and improved upon.

92 COMPETING INTERESTS

93
94 Authors have declared that no competing interests exist.

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