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To cite this article: V Indira and K Abhitha 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1114** 012081

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A review on polymer based adsorbents for CO₂ capture

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Abstract. Carbon dioxide (CO₂) is the essential ozone harming gas and its emissions ends up in worldwide temperature alteration that leads to climate change. CO₂ adsorption on solid materials such as zeolites, carbonaceous materials, metal organic frameworks and silicasone of the efficient method for carbon dioxide removal. This review focuses on polymer-based adsorbents for CO₂ capture. Porous organic polymers like hyper-cross linked polymers (HCPs), covalent organic frameworks (COFs), conjugated microporous polymers (CMPs) and covalent triazine-based frameworks (CTFs) display CO₂ catching limit of around 3 to 6 mmol/g at 273K and 1 bar. Polymer such as polyethyleneimine when incorporated with adsorbents offers improved CO₂ adsorption at higher temperature. CO₂ adsorbents developed from polymer waste can play a dual function in environmental pollution control. In industrial packed columns, polymer composites are considered as superior choice for CO₂ capture.

1. Introduction

Global warming is the major issue in current scenario worldwide, which leads to climate change. Among the greenhouse gases carbon dioxide plays major role and its emissions rose to a historic high peak in recent years. Fossil fuel emissions results in about 91% of total CO₂ release because of expanding energy demand. Carbon dioxide is the enduring greenhouse gas, which absorbs heat. The other greenhouse gases like methane and nitrous oxide absorbs more heat per molecule as compared to CO₂, which takes less. But CO₂ is available in the atmosphere in large quantities and exists for longer duration, as compared to other gases. This results in global warming. Earth's temperature is increasing due to increase in atmospheric CO₂, which causes 2/3 of energy imbalance. As per the report of National Oceanic and Atmospheric Administration (NOAA) and American Meteorological Society, the average global CO₂ amount in the year 2018 was 407.4 ± 0.1 ppm. As per the recent reports of NOAA, CO₂ level in the atmosphere is 413.72 ppm on 2020 July 29 which is higher than 408.96 ppm in 2019 July 29. The CO₂ level growth rate is close to 2.3 ppm per year, which was distinctly around 0.6 ± 0.1 ppm per year in 1960s [1].

The largest contribution to the greenhouse gases is CO₂. Major CO₂ emission is due to the combustion of fossil fuel while the remaining from the industrial emissions. Different mitigations followed worldwide to lower CO₂ emissions comprises of promote energy conservation efficiency, adopting renewable energy like solar, hydropower, wind & bio energy, using geo engineering approaches such as afforestation and reforestation, enhancing use of fuels with low carbon (natural gas, nuclear power), and CO₂ capture and storage[2][3][4]. Carbon Capture and Storage or Sequestration (CCS) is one of the method for solving climate change issue. Pre-combustion, post-combustion, and oxy-fuel combustion are different technologies for CO₂ capture [5][6][7]. CO₂ capture from atmospheric air is also getting popularity nowadays since it has the real world



application. This method is more challenging because it deals with very low concentration of CO₂ in the range of 400 ppm[8][9]. Major CO₂ separation methods used for the removal of CO₂ from flue gas includes absorption, adsorption, chemical looping combustion, membrane separation, and cryogenic distillation [10][11][12][13][14]. CO₂ capture using solid adsorbents considered as the most promising technology for CCS because adsorption process can reduce the cost and energy of the separation and capture. Sorption capacity, reproducibility, stability and selectivity are the major factors to be considered while selecting adsorbent for carbon dioxide removal. All these factors depends on the composition of gas mixture, especially the concentration of CO₂ [15]. The process conditions like temperature and pressure will affect the rate of adsorption. This review discusses the role of polymer-based adsorbents in CO₂ capture.

2. Conventional adsorbents

Different adsorbents like carbonaceous materials, mesoporous silica, zeolites and metal organic framework exhibits significant CO₂ capture capability[16][17][18][19]. These adsorbents are responsible for CO₂ capture by physical adsorption and with suitable functional modification aids by chemisorption. Surface modification of activated carbon using chitosan as the nitrogen source shows improved CO₂ adsorption of 5.83 mmol/g at 273 K and 1 bar. Under the same condition, unmodified activated carbon has the capacity of 2.8 mmol/g. This enhancement is due to the affinity of CO₂ towards the N species incorporated by the modification. Here chemisorption plays the role along with physisorption [20]. Similarly, mesoporous silica with amine functionalization exhibits improved CO₂ adsorption due to increased interaction between carbon dioxide and amine source. These adsorbent could maintain 69% of adsorption capacity up to four cycles of adsorption-desorption[21]. Structural properties and CO₂ adsorption of various adsorbents are given in table 1. These types of adsorbents are in particulate form. For industrial application, these adsorbents have to convert into pellet or bead like structures so that they can be used in packed columns. Most of the adsorbents are inorganic and their processability is difficult which makes the structured adsorber production as challenging and expensive. In industrial packed columns, adsorbents in particulate form causes mass loss and pressure drop. These losses can overcome by supporting the adsorbents on polymer materials. Polymeric composites exhibit good mechanical stability, processability and are inexpensive [22]. Polymer based materials are being used currently for CO₂ capture.

Table 1. Surface structural properties and CO₂ adsorption capacities of different adsorbents

Adsorbent	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Maximum CO ₂ adsorption (mmol CO ₂ /g adsorbent)	Pressure (bar)	Temperature (K)	Reference
N enriched microporous activated carbon	1525	0.77	6.22 2.37	1 0.15	273 273	[23]
Graphene	716	0.66	3.13	1	298	[24]
Hierarchical zeolite 4A	126	0.45	3.09	1	298	[25]
NaX zeolite	695.1	0.4077	4.25	1	298	[26]
Zeolite 13X	405.2	0.294	4.75	2	305	[27]
Mesoporous silica (Tetraethylenepent amine modified)	4.24	0.06	5.82	-	348	[28]

3. Porous organic polymer

Porous organic polymers play a significant role as CO₂ capturing agent due to their low density, large specific surface area, better physicochemical stability, tunable pore structure and functionality. Various kinds of porous organic polymers like hyper-cross linked polymers, covalent organic frameworks, conjugated microporous polymers, and covalent triazine-based frameworks are used extensively for CO₂ capture [29]. HCPs can be prepared by Friedel-Crafts alkylation reaction of monomers. Chang et al. synthesized Indolo [3,2-b] carbazole-containing hyper-cross linked microporous organic polymers with monomer 6, 12-diphenyl-5, 11-dihydroindolo [3,2-b] carbazole for InCz-HCP1 and 6,12-bis(4-diphenylaminophenyl)-5, 11-dihydroindolo [3,2-b] carbazole for InCz-HCP2. InCz-HCP2 (specific surface area 1421 m²/g) shows a better CO₂ adsorption capacity of 3.58 mmol/g at 273 K and 1.13 bar. At the same condition, InCz-HCP1 provides 2.26 mmol/g of CO₂ capture capacity with a specific surface area of 750 m²/g [30].

Gao et al. prepared a number of HCPs based on pitch (PHCP) using trichloro-methane as an external cross linking agent. Among the prepared HCPs, PHCP-3 with anhydrous aluminium chloride/petroleum pitch weight ratio of 6 exhibits the higher value of CO₂ capture as 4.03 mmol/g at 1 bar and 273 K [31]. HCPs are synthesized without expensive monomers hence it is simple to produce at large scale. But the challenge is the synthesis of controlled pore structure suitable for CO₂ capture. COFs with pore size near to 3.3 Å exhibits higher CO₂ capture capacity. Tian et al synthesized 2D COFs (SIOC-COF-5, SIOC-COF-6) with varying pore dimensions. SIOC-COF-5 with pore size of 8.1 Å has higher CO₂ capture capacity of 4.5 mmol/g at 273 K and 1 bar as compared to SIOC-COF-6 which has 3.2 mmol/g at 273K, 1 bar [32]. CMPs can also be synthesized by reactions, like Suzuki coupling reaction, Yamamoto reaction, Sonogashira reaction and so on. CMP prepared from various precursors exhibits CO₂ capacity ranges between 3.28 to 3.9 mmol/g at 1 bar, 273 K [33][34]. Different types of CTFs based on fumaronitrile, triptycene and hexaazatriphenylene reported the CO₂ capture capacity of 3.49, 4.24 and 6.3 mmol/g at 1 bar and 273 K. Even though porous polymers exhibit enhanced CO₂ capture capacity, their industrial application is more challenging because of the cost of monomers and synthetic pathways.

4. Polymer incorporated adsorbents

Polyethyleneimine (PEI) is an organic, cationic and polyamine polymer [35]. PEI has specialized application in biomedical, CO₂ capture and in electronics. PEI modified mesoporous adsorbents are used specially for CO₂ adsorption [36][37]. 70 weight% PEI impregnated mesoporous silica (prepared with pore expansion agents) shows better CO₂ adsorption of 4.955 mmol/g at 75 °C. This silica was prepared from bottom ashes of power plants and they have prepared zeolite 13X from the same source. These zeolite exhibits CO₂ capture capacity of 3 mmol/g of adsorbent which was found to be less than that prepared from pure chemicals (4.25 mmol/g) [38]. Similar experiment were done with zeolite 13X where it was impregnated with PEI and given improved CO₂ capture capacity at higher temperature. CO₂ adsorption of meso-13X-PEI was in the range of 11 to 58 mg/g adsorbent when the temperature changes from 25 to 125 °C. But it reported a maximum value of 80 mg/g at 100 °C [39]. When PEI incorporated into zeolite apart from physical adsorption, chemical adsorption plays the role in CO₂ adsorption. Recent studies were conducted on mesoporous metal organic framework incorporated with PEI and polystyrene for carbon dioxide adsorption. At 1 bar, 298 K CO₂ adsorption for MOF with 20% PEI is 1.41 mmol/g and with 20% polystyrene is 0.77 mmol/g. Under the same condition, as compared to unmodified MOF (1.3 mmol/g) PEI modified MOF has improved CO₂ adsorption due to the basic polymer PEI and relatively low performance by neutral polystyrene [40].

5. Polymer based hollow fiber sorbent

Hybrid materials are getting more demand in all field of engineering and application. Polymer based hybrid materials are new approach to carbon dioxide capture. Ryan et al. put new idea in the adsorbent development in hybrid form based on polymer-sorbent hollow fiber. Cellulose acetate and polyvinylpyrrolidone were the polymers and zeolite 13X was the adsorbent used for the study. These

hybrid adsorbent has the advantages like high sorption efficiency, rapid heat and mass transfer [41]. PEI modified glass fiber cross-linked with epichlorohydrin has studied for CO₂ adsorption and found to have the capture capacity of 4.12 mmol/g of adsorbent [42]. PEI impregnated silica/carbon nanotube composite hollow fibers are also developed and studied for CO₂ capture. Prepared micro-tube like structure exhibits the surface area of 203.6 m²/g to 283.2 m²/g and carbon dioxide capture capacity of 1.92 mmol/g at 0.15 bar partial pressure of carbon dioxide [43].

6. Waste polymer based adsorbents

Plastics are polymers, which have wide commercial application. At the same time, their waste management is one of issue. Research is going on the field of plastic or polymer recycling. One of the waste polymer is polyurethane (PU), especially in the form of polyurethane foam (PUF). As per the recent studies, PUF converted into porous carbon by precarbonization and potassium hydroxide activation. The porous structure obtained possess the CO₂ capture capacity of 6.67 at 0 °C and 4.33 mmol/g 25 °C under 1 bar. This porous carbon materials prepared possess improved selectivity and recyclability towards CO₂ capture from carbon dioxide and nitrogen mixture [44]. Plastic wastes like polyethylene terephthalate (bottle), polypropylene (cup), polyvinyl chloride (plastic pipe) and scrap tire (rubber) were used as template with carbide slag pellets. These materials were used for CO₂ adsorption and found to have capacity of 0.277 g/g and it can go up to 25 cycles [45]. Similarly porous carbon adsorbents were prepared from waste polyethylene terephthalate (PET) by carbonization and activation using potassium hydroxide [46].

7. Conclusions

Carbon dioxide can be captured by utilizing appropriate adsorbents. It was discovered that CO₂ capture capability of conventional adsorbents can be upgraded by surface modification and by polymer incorporation. Porous organic polymers and polymer-based hybrid materials have high carbon dioxide sorption efficiency. Waste polymer-based adsorbents provide promising results in terms of greenhouse gas removal. Waste polymer based adsorbents can offer dual benefits for reduction in environmental pollution. This plastic waste shows effective utilization in CO₂ expulsion. Accordingly, polymers play a significant role in carbon dioxide capture.

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