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Removal of carbon dioxide by adsorption using various adsorbents: A Review

Achugbu O.E.[1*], Nwabanne J.T.[1], Okey-Onyesolu C.F.[1] & Modozie B.U.[2]

*[1]Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, 420110, Nigeria. [2]Department of Pharmaceutical and Medicinal Chemistry, Nnamdi Azikiwe University, Awka, 420110, Nigeria. Corresponding Author Email: oe.achugbu@unizik.edu.ng**

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ABSTRACT

The purpose of this work is to put together a concise review of previous open access works on the removal of CO_2 using various adsorbents. Previous works on this focused on comparing the adsorption capacity of activated amine-modified and non-modified adsorbents. Most of the adsorbents used by previous researchers were thermally and chemically activated. Thermal and chemical activation play vital roles in the modification of the adsorbents by clearing their active sites of impurities and increasing the porosity of the adsorbents. For comparative analyses, some researchers enhanced part of their activated adsorbents using amine groups which have great affinity for CO_2. The following amine groups were used by previous researchers to enhance the adsorbents for higher CO_2 uptake: monoethanolamine (MEA), diethanolamine (DEA), Triethanolamine (TEA), Tetraethylenepentamine (TEPA), polyethylenimine (PEI), methyl-diethanolamine, pentaethylenehexamine or the combination, PEI/MEA or even NaOH. On wet impregnation, these amine groups subsequently occupy the active sites released during activation. During the adsorption experiment, the carbon dioxide gas is chemisorbed by these amine groups as it comes in contact with the adsorbents surfaces. Results obtained by previous researchers on the adsorption capacity of the plain and amine-enhanced adsorbents were not all in agreement. While majority claimed that the adsorbents modified with amine groups adsorbed better than the unmodified ones, few claimed the reverse was their results. Most of the adsorbents used showed good adsorption-desorption regenerability of 7-16 cycles. The review further showed that the Freundlich isotherm model was found to be the best for fitting the CO_2 adsorption isotherm.

Keywords: Carbon dioxide; Adsorbents; Amines; Removal; Adsorption; Desorption; Carbon capture; Global warming; Greenhouse gases.

1. Introduction

Carbon dioxide (CO_2) is the major greenhouse gas which causes global warming. Large amount of carbon dioxide emanate from burning fossil fuels such as petroleum, mineral coal, and natural gas by the power, manufacturing, and transport sectors [1]. The IPCC's 2018 report on warming of our planet states that CO_2 removal of 100-1000 gigatons (GT) will be needed in the next 100 years to prevent our planet's mean temperatures from rising beyond 1.5°C (2.7°F) its levels before the period of industrial revolution [2].

The primary source of energy used worldwide is fossil fuels, and this situation is probably going to persist for some decades to come. To allow for the continuous burning of fossil fuels while lowering CO_2 emissions into the atmosphere and so preventing climate change worldwide, carbon dioxide capture is crucial. Solvents or solid adsorbents are capable of capturing carbon dioxide (CO_2), with solid adsorbents appearing to have several advantages over solvents. The different limitations of using absorbents include the following: low CO_2 absorption capacity, high equipment deterioration rate, amine breakdown in the flue gases triggered by SO_2, NO_2 and O_2 leading to absorbent makeup rate, large equipment size, and excessive energy consumption during extremely high temperatures absorption [3]. Sequel to the above listed limitations, solid adsorption processes are preferred to absorption and equally studied to solve those characteristic setbacks in chemical absorption.

According to [4], in addition to this, adsorption is also a preferred method because desorption can be carried out under supportive conditions and the desorbed carbon dioxide stored in a container. Also, it has been suggested that amines can be impregnated or grafted on these adsorbents which have porous surfaces in order to increase the rate of mass transfer of CO_2 into them and improve their initial limited adsorption capacity.

1.1. Study Objectives

- To inform researchers on the various mitigation strategies that can be utilized in carbon capture.
- To guide researchers on the choice of adsorbents for effective carbon capture having classified them under various nanoparticles.
- To enable the use of fossil fuels while reducing the emissions of CO_2 into the atmosphere, and thereby mitigating global climate change.
- To reduce greenhouse gas emissions, allowing utilities to keep using abundant and efficient fossil fuels to generate reliable and affordable power as we gradually move to green energy generation.
- To guide researchers on how best to combine certain process variables for optimal carbon capture.

2. Effects of Excess carbon dioxide in the globe

Due to the fact that it naturally occurs in the atmosphere as a byproduct of the carbon cycle, carbon dioxide helps to maintain a comfortable level of warmth on the planet. The amount of carbon dioxide released into the atmosphere by human activity was easily absorbed by the environment before the industrial revolution. However, due to industrial activity in recent years, our biosphere has become overwhelmed with carbon dioxide. This has caused a change in the climate worldwide. The effects of too much carbon dioxide in our atmosphere include rising temperatures, more frequent droughts, violent storms, rising sea levels, loss of species, and insufficient food supplies, among other things.

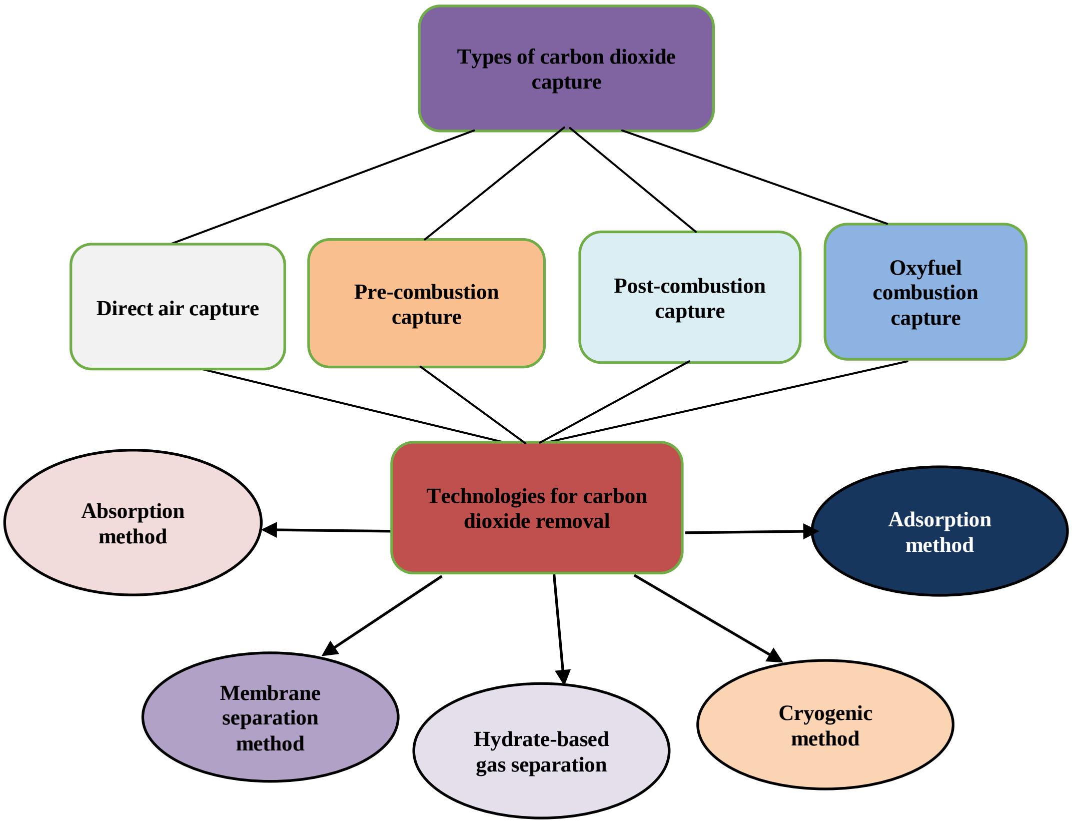

Figure 1. Carbon dioxide mitigation technologies

3. Overview of mitigation strategies

Figure 1 shows types of carbon dioxide capture which include direct air capture, pre-combustion, post-combustion and oxyfuel combustion capture. Each of these utilizes one of the five carbon dioxide removal technologies discussed below.

a. Absorption process

In this method, carbon dioxide which is more soluble in a particular liquid than other components of the gas mixture is absorbed from its mixture with an inert gas. According to [4], an absorption column and a stripping column, where the absorbent is thermally regenerated, make up a conventional absorption process. In this procedure, the carbon dioxide-rich flue gas is passed down the bottom of a packed absorption column and washed by a counter-current carbon dioxide-lean absorbent. Despite being commercialized for many years, this technique has the following drawbacks: equipment corrodes quickly, little CO_2 is absorbed, other gases in the flue gas damage the amine, regenerating absorbent requires a lot of energy, and the absorber needed is enormous in size [3].

b. Membrane separation technology

Membrane functions as a filter. It permits some molecules to pass through its pores but prevents others. The membranes' pores are designed to have a smaller diameter than the unwanted material [5]. Typically, the driving force is a difference in concentration or pressure between the two sides of the semi-permeable membrane. However this method is based on differences in diffusivity and solubility. Membranes made of poly (ethylene oxide) are frequently used to separate carbon dioxide from mixtures of other gases. The reason for this is that carbon dioxide and oxygen have a great affinity for each other in the presence of polar ether. So, through them, carbon dioxide dissolves and diffuses.

c. Cryogenic method

This involves a physical separation process based on the differences between the boiling points and the desublimation properties of the components in the gas mixture [6]. Cryogenic carbon capture with compressed flue gas moderately compresses the flue gas to 5-7 bar before heat exchange and expands the flue gas after heat exchange to desublime CO_2 [7].

d. Hydrate-based gas separation

When the right temperature and pressure conditions are met, water can combine with tiny molecules like methane, ethane, hydrogen sulfide, and carbon dioxide to create crystalline formations known as gas hydrates [8, 9]. Crystalline lattices created by water molecules contain layers of carbon dioxide. In other words, it takes in environmental water molecules and incorporates them into its structure. This technique can be employed to separate CO_2 from its combination with methane.

e. Adsorption process

Adsorption is the process by which an element that was initially present in one phase is taken out of that phase by accumulating at the interface between that phase and a different (solid) phase. The chemical being removed, in this case, CO_2, is referred to as the adsorbate, while the solid material utilized in the process is known as the adsorbent.

4. Factors affecting adsorption of CO_2

According to [10], the following factors described below affect adsorption of carbon dioxide.

a. Effect of the temperature

With an increase in temperature, an adsorbent's ability to adsorb CO_2 declines. This is due to an increase in the mobility of adsorbed molecules into the adsorbent cavities, which may be brought on by higher thermal agitation, and a decrease in the contacts between the adsorbent and the adsorbate. Adsorption is an exothermic process, and in accordance with Le-Chatelier's principle, as the temperature rises, the amount of substance adsorbed decreases. Desorption sets in, as the molecules of the adsorbate are drawn away from the adsorbent. Consequently, adsorption decreases as temperature increases for physisorption. In chemisorption, the adsorption rate initially increases but subsequently decreases as temperature rises further.

b. Effect of pressure

When the partial pressure of CO_2 rises, the ability of CO_2 to adsorb on an adsorbent also rises. Over a constrained range of pressures, the amount of adsorption is exactly proportional to the gas pressure. The amount of adsorption is inversely related to pressure at low pressure. It grows more, slowly with pressure rise at moderate pressure. Finally, at high pressure, the amount of adsorption is constant since it is pressure independent.

c. Nature of adsorbent

Since adsorption is thought to be a surface phenomenon, its effectiveness grows as the surface area of the adsorbent does. Adsorbents that are more finely divided will have more surface area and, as a result, more adsorption. When adsorbents have increased surface area, chemisorption is more advantageous. Additionally, sufficient pore size is necessary for the carbon dioxide to easily penetrate the adsorbent.

d. Nature of adsorbate

Gases that are easily liquefiable and highly soluble in water, such as carbon dioxide, ammonia, chlorine, etc., are adsorbed by solids more quickly than elemental gases, such as oxygen, nitrogen, etc. This is due to the fact that easily liquefiable gases are more firmly adsorbed due to their larger intermolecular forces of attraction or Van der Waals forces.

e. Concentration of adsorbate

This has an impact that is comparable to that of pressure. At low concentrations of CO_2, the amount of CO_2 adsorbed increases. At a modest CO_2 concentration, it steadily rises, but at a high concentration, it reaches equilibrium and stays constant.

5. Overview of various adsorbents utilized in CO_2 removal

Clay-based adsorbents: Clay minerals are notable among porous materials because they possess distinctive physical characteristics due to their stratified structure, tiny particle size, and high surface-to-volume ratio. A wide range of clay minerals, including halloysite, kaolinite, montmorillonite, nanosepiolite, and bentonite, have been utilized to remove CO_2 [11]. Authors in [12] examined the process by which various alkali and alkaline earth metals absorb mono-, di- or tri- ammonium cations. The samples under examination demonstrated a greater capability for CO_2 uptake when bentonite clay modified with monoethanol ammonium cations was used, as opposed to those modified with secondary and tertiary ethanol ammonium cations. An increase in temperature resulted in a decrease in the uptake capacity of the monoethanol ammonium cations, indicating that heat is liberated in the adsorption process. [13] utilized natural halloysite nanotubes (HNTs) and one coated with polyethylenimine (PEI). The treated sample's pore volume recorded as $0.499m^3/g$ and specific surface area recorded as $340.61m^2/g$ were roughly 2.5 and 7 times each the natural counterpart. The adsorption capability was found to rise with pressure but fall with temperature. For a sample impregnated with 30 wt% PEI, the greatest uptake capacity of 7.84 mmol per gram was achieved at 20 degrees Celsius and 9 bar.

Silica-based adsorbents: Today, due to its special qualities, such as high surface area, pore volume, ease of surface functionalization, superior mechanical and thermal durability, and low cost, porous silica-based materials have now come to light as outstanding contenders for CO_2 capture methods [14]. Authors in [15] studied the adsorption of CO_2 with four amines i.e., primary amine (MEA), secondary amine (DEA), tertiary amine (TEA) and a primary alkyl amine (ODA) impregnated on silica dioxide particulates. In comparison to the virgin SiO_2 sample, the 15 and 25 wt% MEA-impregnated and 25 wt% ODA-impregnated samples demonstrated higher CO_2 removal capabilities. Owing to the alkyl branch on DEA and TEA and the rising steric obstruction of long chain ODA, MEA/SiO_2 has the best ability to capture CO_2. [16] investigated the separation of carbon dioxide (CO_2) from flue gas by utilizing N-[3-(trimethoxysilyl)propyl]ethylenediamine (EDA) solution to modify mesoporous sphere-shaped silica particles (MSPs) for the purpose of separating carbon dioxide (CO_2) Both unmodified and modified MSP showed a rise in CO_2 adsorption capability between 20 and 60 °C, but a fall between 60 and 100 °C. When compared with EDA-enhanced zeolite and various silica adsorbents discussed in previous works, the MSP (EDA) exhibits an excellent adsorption efficiency. It was equally reported that there was regeneration and reuse of the spent modified adsorbent for 16 times. [17] captured CO_2 from synthesized biogas by employing commercial silica known as FNG-II silica (FS) impregnated on polyethyleneimine (PEI) and ethanolamine (MEA). When compared to silica impregnated only with MEA or PEI, silica impregnated with mixtures of the two showed improved CO_2 adsorption capacity as well as excellent thermal stability. With a flow rate of 100 mL/min at 25^oC and 0.2 MPa, FS-10%MEA -10%PEI demonstrated an ability to adsorb 64.68 mg per gram of CO_2 representing a value which is 81 per cent higher than FS-20%PEI.

Zeolites-based adsorbents: Zeolite is distinguished by its outstanding adsorption affinity, huge surface area, rapid ion exchange ability, and hydrophilicity. It is consequently used in CO_2 adsorption [18]. [19] prepared adsorbents using zeolite and used a fixed-bed flow reactor to study CO_2 removal from a synthetic flue gas mixture. To produce the adsorbents, base materials were coated with MEA, ethylenediamine, diethylenetriamine, and triethylenetetramine (TETA). Observations revealed that, up to a particular concentration of amine loading, the CO_2 adsorption capability increased. The 30 wt% TETA-enhanced zeolite showed the highest carbon dioxide removal capability of about 53 g of CO_2 for every kilogram of it used. Authors in [20] evaluated the CO_2 adsorption capacities of three different sorbents: zeolites, layered double hydroxides (LDH), and zeolites coated LDH composites. Investigations were done to ascertain how the zeolite Si/Al ratio and the presence of mesopores affected the sorption capacity of zeolites. The more hydrophilic zeolites, which have more Al-atoms in the frame, were used to achieve the higher CO_2 sorption capacity. [21] utilized zeolite 13X functionalized with amino groups. Grafting with varying concentrations of monoethanolamine (MEA) was the method used to functionalize the adsorptive material. It was discovered that adding more amine to the adsorbent block the pores and tends to decrease the pore volume of the resulting adsorbents. While some of the loaded MEA is efficiently covalently attached to the zeolitic structure, there is equally excessive MEA that is physically adsorbed and will eventually be desorbed when the temperature is raised above the boiling point of MEA as reported in literature.

Carbon-based adsorbents: Carbon-based substances that are obtained from organic materials, plant matter, and agricultural waste may effectively and preferentially adsorb CO_2 [22]. [23] studied the CO_2 removal on commercial activated carbon enhanced with different wt% of MEA to obtain two samples rich in nitrogen (ACN10 and ACN20). The unmodified AC exhibited greater ability to adsorb at ambient temperature (298 K) and high pressure in comparison to the enhanced samples. The CO_2 removal abilities of the modified samples at 298 and 348 K were negatively affected by the decrease in surface area, with the exception of adsorption on ACN10 at 348 K, which indicates the possibility of chemisorption. [24] employed activated carbon fibers (ACFs) based on polyacrylonitrile that had been altered with tetraethylene pentamine (TEPA) or potassium hydroxide (KOH). Microporosity and surface oxygen functionalities have been reported to be strongly correlated with CO_2 intake suggesting the presence of O-C coordination in conjunction with physical adsorption. [25] investigated the CO_2 adsorption efficiency on carbon activated by physical and chemical treatments using single and multi-fixed bed column. Physical treatment involved carbonization of palm oil shell at temperature of 600°C. Multi-fixed bed column showed higher removal of CO_2 than single fixed bed column with 31.47% increased performance. Result showed that activated carbon from the chemical treatment is more efficient after washing it by distilled water. [26] employed KOH-activated microporous carbon compartments (MCCs) at 700 degrees Celsius, with mass ratios of KOH/C ranging from 1 to 5. MCC activated with a KOH/C ratio of 3 (MCC-K3) was reported to have had the greatest CO_2 removal abilities of 5.70 $molkg^{-1}$ at 0°C and 3.48 $molkg^{-1}$ at 25°C. The pseudo-second-order kinetic model was reported to be the best fit for the data. [27] employed coconut shells activated carbon (AC) to investigate the impacts of activation temperature and activation time on the fundamental properties of AC, such as iodine uptake, pH value, total volume of pores, BET specific surface area, ash content, and charcoal output. It was reported that the AC's charcoal yield falls with increasing time spent on activation and temperature. Conversely, as activation temperature rises, so do iodine uptake, ash content, pH level, and total volume of pores. The AC sample with the greatest BET specific surface area and total volume of pores, and thus the best CO_2 uptake efficieny, was activated at 1000°C for 120 minutes. Coconut AC has greater quick uptake ability when compared to another 30-mesh commercial AC. [28] employed activated carbon from coconut shells for methane and carbon dioxide removal from biogas. The carbon dioxide and methane uptake abilities of the sorbents are reportedly determined as 1.86 and 0.52 mol per kilogram accordingly, at 30°C and 1 bar. However, at 30°C and 10 bar, it increased to 8.36 mmol per gram and 4.63 mmol per gram, respectively. Palm kernel shell (PKS) and coconut shell (CS), which were physically activated (with steam) and chemically activated were utilized by [29]. It was reported that 800°C is the ideal activation temperature for physical activation, and 550°C is the ideal temperature for chemical activation. Additionally, various metal oxides (BaO, MgO, CuO, TiO_2, and CeO_2) were loaded onto the samples. It was discovered that the activated carbons made from PKS by chemical activation (PCAC) and from CS by physical activation (CPAC) had significantly larger BET surface areas and pore volumes than their counterparts. The modified and plain samples were used to remove CO_2 from synthetic flue gas. [30] utilized modified Jatropha activated carbon (JAC-TEA) and unmodified Jatropha activated carbon (JAC). A cylindrical glass column fitted with a digital mass balance was used to assess the CO_2 removal abilities of the two adsorbents. The impact of temperature (30–60°C) and adsorbent dosage (0.5–1.5 g) with due consideration to time, was examined. The adsorbents' abilities to adsorb CO_2 were found to improve with rise in amine concentration and the amount of adsorbent (bed height), but declines with temperature rise. The adsorption capacities of JAC and JAC-TEA were found to be 66 and 78 mg/g, accordingly. The technique by which CO_2 is adsorbed onto JAC and JAC-TEA was reported to be by physical adsorption with JAC-TEA having the ability to be reused for about 7 times. At temperatures between 303 and 333 K, adsorption on three enhanced activated carbon samples (B, C, and D) and an unmodified activated carbon sample (A) was studied by [31]. It was reported that the modified carbon samples removed significantly more CO_2 than the unmodified carbon sample. The best fit for the adsorption on carbon samples C and D was the Freundlich model, while the Dubinin-Radushkevich (DR) isotherm model was best for carbon samples A and B. The results showed that the heat of adsorption ranged from 10.5 to 28.4 KJ/mol, with sample D exhibiting the greatest value across all examined surface coatings.

Alumina-based adsorbents: Given their significant environmental interactions, metal oxide powders, such as alumina, are getting a lot of attention for their ability to retain CO_2 [32]. It was reported that [32] prepared a number of γ-Al_2O_3 sorbents using ball-milling and solution-combustion techniques. A maximum of 1.94 mmol/g was achieved by γ-Al_2O_3, which was produced by the solution-combustion method and ball milled for 10 hours. This material outperformed the other adsorbents in the removal of CO_2 at 60^0C and 1.5 MPa due to its unique microstructure along with morphological characteristics.

Authors in [33] reported to have utilized sodium hydroxide (NaOH)-modified activated alumina in a fixed-bed column. Though they had surface areas of 203 and 207 m^2/g, respectively, the adsorption capacities of the plain activated alumina (PAA) and optimally modified adsorbent (3MAA) were 51.92 and 19.61 mg/g respectively. The reason for the improved adsorption on 3MAA was that its total pore volume and mean pore width were higher when compared to those of PAA.

Authors in [34] employed composite materials made of mesoporous γ-alumina and poly(ethyleneimine) to capture CO_2 at room temperature from power plants powered by coal. When in direct contact with steam, the amine adsorbents supported by alumina outperformed other sorbents based on silica. Commercial mesoporous alumina and one enhanced with chitosan were utilized by [35] to remove CO_2 from synthetic flue gas (CO_2 + N_2). The uptake capacity at 55°C was found to be 29.4 mg CO_2 per gram of adsorbent, which is four times higher than that of the commercially available counterpart at the same temperature. It has been reported that the improved CO_2 uptake was attributed to the basic nature of alumina and the inclusion of N_2 in the matrix. Furthermore, in the presence of oxygen, the CO_2 uptake capability was maintained; nonetheless, moisture had a negative effect on it, causing it to decrease to almost half its original value.

6. Adsorption performance of different adsorbents

Table 1 shows a summary of how various adsorbents performed on combination of different process parameters in the presence of different modifiers. Some of the adsorbents were modified with various amines while others were not. The modifiers used previously include primary, secondary and/or tertiary amines. However, sodium hydroxide, potassium hydroxide and piperazine were employed in few cases. The optimal process parameters that resulted to the maximum adsorption capacity recorded were equally indicated in the Table. The maximum adsorption capacity recorded in the previous studies is 64.68mg/g at 0.2Mpa and 25°C.

Table 1. Summary of adsorbents performance for CO_2 removal

Adsorbent	Modifier	Best performance	Removal efficiency (%)	q_{max} (mg/g)	Pressure	Flow rate (ml/min)	Temp. (°C)	Ref.
Activated carbon fibres	KOH & TEPA	KOH		2.74 mmol/g	1atm		25	[36]
Plain & modified activated alumina	NaOH	NaOH		51.92		90	35	[33]
Solution combustion & ball-milled alumina, Al_2O_3				1.94 mmol/g	1.5 MPa		60	[32]
Silica	MEA/PEI	10% MEA-10% PEI		64.68	0.2 MPa	100ml/min	25	[17]
MgO	TEPA	40% TEPA						[37]
Zeolite 13X	MEA, ED, IPA	Isopropanol amine (IPA)		22.78				[38]

7. Conclusion

In this paper, methods of carbon dioxide removal were briefly discussed. The method of adsorption was thoroughly discussed. Works that have been done on carbon dioxide removal by adsorption were reviewed. From the previous works reviewed, the maximum carbon dioxide adsorption capacity obtained was 64.68 mg/g. It was also observed that most researchers used solid sorbents as supports for amine for the carbon dioxide removal. In spite of numerous researches that have been conducted on carbon capture, there is still need for improvement as well as areas open for future researches. Firstly is on how to improve the recyclability of the spent adsorbents. Secondly is to explore possible ways of incorporating these nanoparticles, just like the catalytic converter of cars, in the exhaust system of these power plants. Thirdly, there is need to scale up the adsorption method of carbon capture. Finally, there is need to search for more suitable adsorbents for carbon capture, possibly ones that chemisorb carbon dioxide.

Declarations

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Competing Interests Statement

The authors declare no competing financial, professional, or personal interests.

Consent for publication

The authors declare that they consented to the publication of this study.

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