

Application of Metal-Organic Frameworks (MOFs) in Carbon Capture

Litian Cao *

Shanghai Experimental School International Division, Shanghai, China

* Corresponding author: rspina82401@student.napavalley.edu

Abstract. The rising levels of CO₂ are unavoidably connected to climate change and its consequences on atmospheric temperatures throughout the world. Carbon capture and storage (CCS) is a dependable and practical method for capturing carbon emissions from industry. This article introduces the realms of direct air capture, post-combustion carbon capture, and pre-combustion carbon capture. Furthermore, the paper delves into the fascinating world of metal-organic frameworks (MOFs) materials with a high porosity, tunable structures, and exceptional adsorption capacities that can effectively absorb substantial quantities of CO₂, qualifying them as promising candidates for reducing greenhouse gas emissions. The synthesis methods and performance evaluation of MOF materials concerning carbon capture were introduced. Some of the challenges associated with MOFs are also discussed, including their reduced stability at high temperatures and sensitivity to moisture. This paper provides a comprehensive overview of carbon capture technologies, highlighting the potential of MOFs while addressing current challenges and opportunities in the field.

Keywords: Carbon capture, post-combustion carbon capture, metal-organic framework, pre-combustion carbon capture, direct air capture.

1. Introduction

Human activities, notably the combustion of fossil fuels in industrial settings, are the primary catalysts for global warming. This leads to elevated temperatures on Earth due to substantial emissions of carbon dioxide and methane, responsible for approximately 87% of human-induced CO₂. These emissions drive climate change and its adverse consequences. Furthermore, CO₂ emissions from mining and natural gas extraction worsen environmental CO₂ levels. In 2018, the IEA reported a 2.3% surge in global energy demand, driving heightened fuel consumption and a significant increase in total greenhouse gas emissions. The atmosphere bore 46 gigatons of emissions, with carbon dioxide contributing 33.3 gigatons. Oceans absorbed a quarter of this CO₂, while forests served as crucial carbon sinks. However, deforestation and wildfires caused the loss of 12 million hectares of forest in 2018, and the 2019 report is projected to show an increase in this number. These trends emphasize the urgent need to reduce emissions and implement effective capture measures [1, 2].

Carbon capture and storage (CCS) has emerged as a useful method in the fight against global warming, extreme weather and climate change. CCS entails removing carbon dioxide (CO₂) produced from the transportation and industrial sectors and transferring them to approved storage facilities. It is considered one of the practical approaches to combat global warming and its detrimental effects on humanity and the environment. Amine-based post-combustion capture, pre-combustion capture-fuel combustion, chemical looping, cryogenic capture, membrane separation, solid sorbent capture, alongside direct air capture (DAC), and mineralization are some of the current suites of carbon capture methodologies. These various strategies provide a range of options for collecting CO₂ emissions from various sources and look to be crucial in the battle against climate change. The efficiency and scalability of these technologies are continuously improving as a result of ongoing research and development, solidifying their status as essential elements of the movement towards a more sustainable, carbon-neutral future. In the search for efficient carbon capture, metal-organic frameworks (MOFs) have become a potential technique. Their exceptional surface areas and tunable properties make them a focal point of research and development in this field. Some MOFs are already

in use in the field of carbon capture, for example, HKUST-1 and UiO-66 [3,4]. While MOFs' great porosity and vast surface surfaces make them promise for carbon capture, they also present challenges. MOFs exhibit reduced stability at higher temperatures and are sensitive to moisture. Researchers are actively exploring solutions such as post-synthesis functionalization and creating open spaces on MOFs' metal parts to enhance their performance.

In this article, firstly, an overview of current technologies applied to carbon capture was introduced. Secondly, the synthesis and evaluation of MOFs used in carbon capture were highlighted.

2. Current Technologies for Carbon Capture

Carbon capture technologies have become a key weapon in our toolbox as we fight climate change on a global scale. These ground-breaking approaches are expertly designed to absorb carbon dioxide emissions from a variety of sources, such as power stations, industrial complexes, and even the environment itself. These technologies play a key role in lessening our carbon footprint by capturing CO₂ and limiting its escape into the atmosphere, so minimizing its contribution to the greenhouse effect. Carbon capture (CC), also known as CO₂ extraction from power plant emissions, transportation of the collected CO₂, and CO₂ sequestration are the three key steps in the CCS process used in power plants [5].

2.1. Pre-combustion Carbon Capture

During the process of pre-combustion carbon capture, fuel reforming is used to create syngas, a combination of carbon monoxide (CO) and hydrogen. The separation of CO₂ follows, as indicated in Fig. 1. Fuel reformation and partial oxidation, which produce the synthesis gas, are the primary phases in this process. For instance, in steam reforming, the fuel and steam undergo a partial oxidation process [6]. Additionally, the process includes a preliminary stage to remove sulfur and particulate matter. This is necessary to ensure that the catalyst remains functional and maintains its activity. The overall outcome of this procedure is the capture of both CO₂ and hydrogen gas. These captured gases can then be utilized as a fuel source, with the result of combustion being the production of water [1].

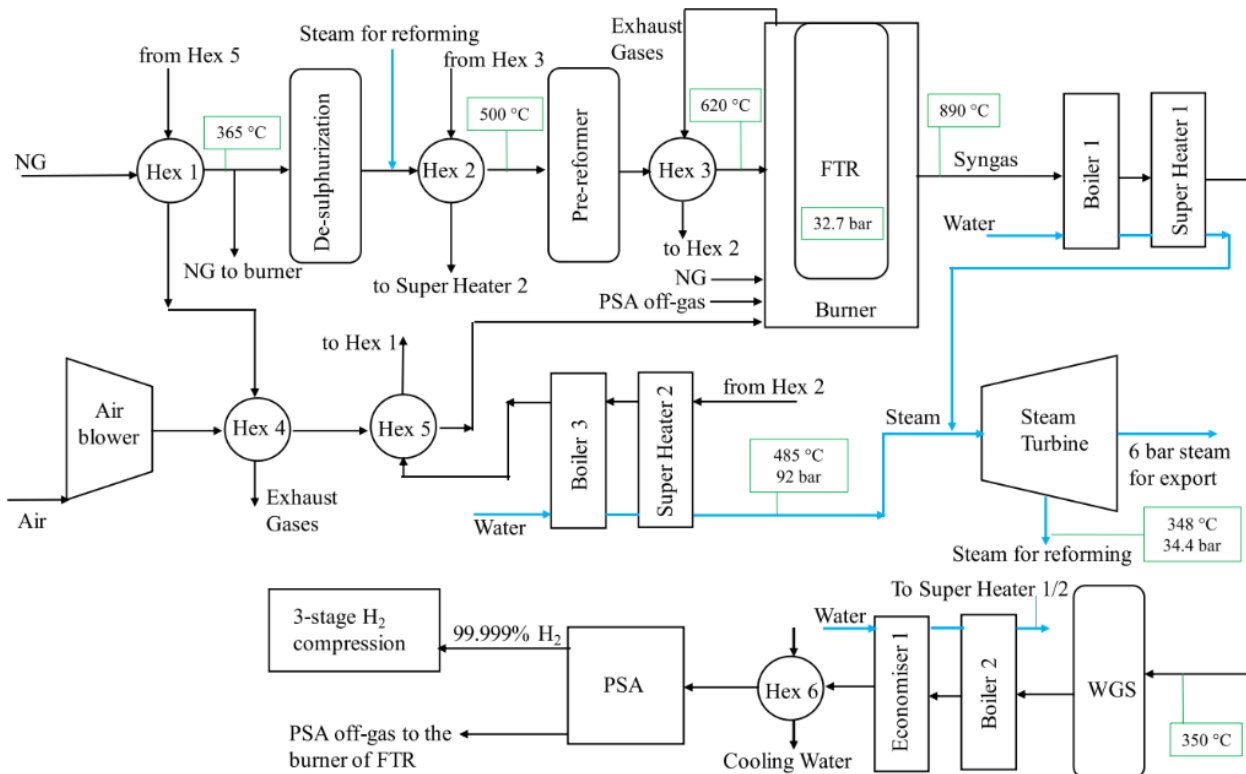


Figure 1. Reforming gas while carbon capture [6].

2.2. Post-Combustion Carbon Capture

Post-combustion carbon capture includes extracting CO₂ from exhaust gases produced by extensive fossil fuel burning., such as that which takes place in cement kilns, boilers, and industrial furnaces. Carbon capture is now applied in many power plants via the absorption approach, which makes use of chemical solvents like amines. As shown in Fig. 2, the high-temperature flue gas is sent through the absorber and cooled to a temperature of 40 to 60 °C. After that, CO₂ and the chemical solvent, frequently amine, in the absorber establish a bond. The solvent is then brought to a stripper and heated there between 100 and 140 °C. Now that CO₂ has been added, the solvent is improved. The heat causes the solvent to release the CO₂, generating it for future use [7]. Operating the necessary pumps, blowers, compressors, and heating mechanisms uses a significant amount of energy, causing a reduction in overall efficiency. The flue gas's chemical makeup, determined by the type of fuel used, affects the concentration of CO₂. In the carbon capture absorption process, it is possible to achieve a typical CO₂ recovery rate of 80 to 90%. Nitrogen oxides and sulfur oxides must be eliminated from the process to maximize CC since they can interact with the solvent. The utilization of solid sorbents for example CaO, pressure swing adsorption (PSA), MOFs, and membrane separation are only a few of the different techniques that have been researched for carbon capture [1].

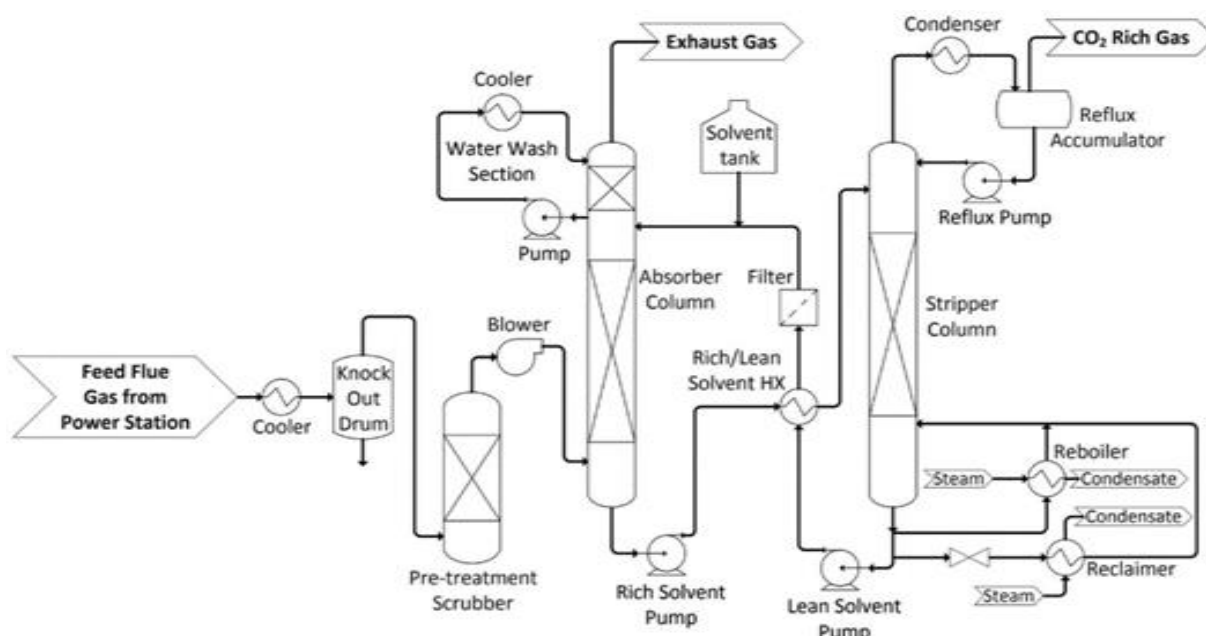


Figure 2. Flow diagram for the process of post-combustion carbon capture [7].

2.3. Direct Air Capture

Direct Air Capture (DAC) of carbon dioxide from the atmosphere has drawn a lot of scientific attention due to its potential to reduce the logistical challenges of moving amounts of CO₂ of considerable size to where it is needed. Unlike traditional capture methods, DAC, if broadly implemented, has the potential to actively lower atmospheric CO₂ levels in contrast to current policies, which primarily target large-point emissions and, at most, moderate the growth of CO₂ concentrations. Nevertheless, DAC presents formidable technological hurdles due to the air's incredibly low CO₂ content (approximately 400 ppm). Consequently, this technology demands materials with exceptional binding affinities, characterized by strong selectivity for CO₂ over nitrogen and quick CO₂ absorption at low partial pressures. In the pursuit of direct air capture applications, researchers have explored not only amine-functionalized metal oxides but also solid materials like alkali-supported carbonates, aqueous hydroxides and MOFs.

Not all high-performance materials that are appropriate for large-point source CO₂ collection convert well to DAC, principally because of the special difficulties presented by DAC's ultra-dilute CO₂ concentration. Given that at decreasing CO₂ concentrations the heat of adsorption and adsorbate

affinity rise, recent thermodynamic calculations have shown that the Temperature Swing Adsorption (TSA) technique is better than Pressure Swing Adsorption (PSA) for DAC applications [5].

3. Carbon Capture using Metal-Organic Framework Materials

A method for extracting CO₂ from various industrial gas streams that shows promise is the use of porous solid materials for CO₂ collection. Over the years, numerous adsorbents have undergone thorough evaluation for their efficacy in capturing CO₂ emissions from both precombustion and post-combustion gas effluents. These adsorbents can generally be categorized into high and low-temperature materials. Other substances that can act as adsorbents at high temperatures include hydrotalcite, alkali or alkaline-earth oxides (including alkali silicates), calcium oxides (CaO), zirconates, and double salts. High-temperature adsorbents, on the other hand, use chemisorption mechanisms. Low-temperature adsorbents, on the other hand, consist of molecular sieves, carbon-based substances like activated carbon, carbon nanotubes, graphene, and carbon nanofibers, as well as more recent inventions like MOFs, covalent organic frameworks, and porous polymer networks [8]. low-temperature adsorbents primarily rely on physisorption. One notable exception among the low-temperature adsorbents is supported amines, which exhibit chemisorptive characteristics and form strong interactions with CO₂ [1].

A solid substance known as a MOF, or metal-organic framework, has a high porosity and acts like a sponge to absorb large amounts of a particular gas molecule, such as carbon dioxide. They have been studied for around 20 years, but during the past ten years, study has exploded as scientists discover more and more useful uses. MOFs stand out because of their extraordinarily large interior surface areas. One gram of a MOF, or around the size of a sugar cube, has a surface area that is larger than a football field. Therefore, if appropriately engineered, a tiny amount of MOF may remove a sizable quantity of CO₂ released as exhaust from the combustion of fossil fuels.

3.1. Synthesis of MOFs

There are two categories of techniques for synthesizing MOFs including traditional and contemporary. Traditional methods include electrochemical, solvothermal (hydrothermal), mechanochemical, and sol-gel methods, while modern methods encompass spray drying/evaporation, flow chemical, microwave, and sonication approaches.

MOFs have often been synthesized using solvothermal methods. In an enclosed autoclave reactor, heating reagents dissolved in an all-purpose solvent is required. Pressure and temperature in the reactor have an impact on crystal size. Higher pressures and longer times lead to larger crystals. Solvents like ethanol or deionized water are used to clean crystals. However, using organic solvents presents issues with the environment. The focus has switched to aqueous techniques like hydrothermal synthesis, which employs water instead of organic solvents, to address environmental issues. The process includes cleaning and vacuum drying. Although it offers well-defined crystal structures and sizes, it's time-consuming and energy-intensive.

Mechanochemical synthesis employs mechanical methods like stirring for MOF crystal formation. It's time-efficient but yields predetermined crystal sizes. Sonochemical methods use sound waves to facilitate reactions. Ultrasonication, the preferred variant, completes synthesis rapidly but often leads to low yields. Electrochemical methods, driven by electricity, are quick but yield MOFs with lower surface areas and pore volumes.

Spray drying/evaporation techniques are simple but time-consuming. Chemical flow methods involve reactions occurring on their own, with synthesis time-varying. Microwave synthesis subjects reagents to microwave radiation, producing MOFs quickly, though scaling up is challenging. Microwave-assisted solvothermal synthesis, a novel technique, has the potential to produce MOFs with large pore volumes and surfaces.

There are drawbacks to the methods now in use, including low yields and energy-intensive procedures. Better yields and scalable manufacturing are possible with mechanochemical processes

supported by solvents and microwaves. Challenges in MOF production include a lack of cost-effective mass production methods, the absence of large-scale industrial production, energy-intensive processes, and intricate synthesis procedures.[2]

3.2. Carbon Capture Performance of MOFs

A crucial common physical characteristic of metal-organic frameworks (MOFs) is their exceptional Brunauer–emmett–teller (BET) surface areas (SA). These adaptable materials are used in carbon capture in three main ways, including functionalized materials, as pure materials and as combined with adsorbents. Each type has distinct capacities to handle carbon capture difficulties.

Functionalized MOFs, where the addition of functional groups enhances their CO₂ capture capacity. Polyethyleneimine (PEI) is a popular choice. With PEI-MIL-101, it showed BET SA of 480 m²/g and a carbon capture performance of 2 millimole/g during research. [9] Another research on 5% PEI-MIL-101(Cr, Mg) yielded a high BET SA of 1258.330 m²/g carbon capture performance of 2,5 millimole/g [9].

In their pure form, MOFs stand as promising CO₂ traps. UiO-66 exhibited a notable carbon capture performance of 2.32 millimole/g [4]. In another research, HKUST-1 demonstrated a remarkable carbon capture performance of 3.3 millimole/g and alongside a BET SA of approximately 850 m²/g [3]. Cu₃(BTC)₂, another MOF, outperformed with a carbon capture performance of 4.4 millimole/g, boasting BET SA exceeding 1400 m²/g [4]. However, the pinnacle of carbon capture performance was witnessed with Cu-BTC, reported in a research paper [10], recording an astonishing 9.59 millimole/g at 273 K and 5.33 millimole/g at 298 K both under 1 atm due to its natural affinity for CO₂. In this work, aPPy(/GO) adsorbents were compared to Cu-BTC and its derivatives., with aPPy displaying CC performance of 4.03 millimole/g and 7 millimole/g for the same conditions. While Pure Cu-BTC exhibited a BET SA of 1760 m²/g, pure aPPy showed a remarkable value of 2420 m²/g. Both materials exhibited similar isosteric heats of adsorption, with Cu-BTC's slightly higher value attributed to its greater porosity, facilitating strong CO₂ adsorption via dispersive interactions.

The third approach combines MOFs with sorbents. Research on Cu-BTC combined with graphene oxide (GO) [10], revealed a carbon capture performance of 9.59 millimole/g, despite a reduction in BET SA compared to pure Cu-BTC. Similarly, MOF-200 and MOF-200/GO were compared [11], yielding CC performances of 1.17 millimole/g and 1.34 millimole/g, respectively, despite their high BET SAs. This indicated GO's strong affinity for CO₂.

3.3. Factors Affecting in Carbon Capture Using of MOF Material

3.3.1. Temperature

Most MOFs can capture a lot of CO₂s when it's cold, like between 273 K and 303 K. But when we increase the temperature during the capturing process, the amount of CO₂ they can capture goes down. This happens because their structure becomes less stable at higher temperatures. Research [12] found a similar thing with sod-ZMOF-chitosan. As the temperature went up, the amount of CO₂ it could capture went down from 978 mg/g at 298 K to 640 mg/g at 313 K, and even lower to 546 mg/g at 343 K.

3.3.2. Moisture

Another big problem with MOFs is that they don't like moisture. It makes their structure fall apart when they touch moisture. To tackle this problem and boost their CO₂ capture capacity, people are trying a few things. One idea from research [13] is to create more open spaces on the metal parts of MOFs. This makes them better at grabbing onto acidic gases, especially with metals that have multiple positive charges. There are also ways to change MOFs before making them, like using different liquids or temperatures. This can change how they look and how much CO₂ they can capture. After making MOFs, we can change them even more to work better for specific needs. This is called post-synthesis functionalization. It can make them better at repelling moisture and better at picking out CO₂ from other gases [13].

4. Summary

Carbon capture is of paramount importance in the fight against climate change. Capturing carbon dioxide from industrial operations and power generation before it is released into the atmosphere is of paramount importance for mitigating greenhouse gas emissions. This article provides a comprehensive overview of CCS, highlighting the potential of MOFs while addressing the current challenges and opportunities in the field. It serves as a valuable resource for researchers and policymakers working on strategies to reduce greenhouse gas emissions. Post-combustion carbon capture, while practical, requires a significant amount of energy and faces operational challenges, impacting efficiency. Alternative methods like solid sorbents and membrane separation are under exploration to mitigate these issues. Pre-combustion carbon capture, generating syngas and extracting CO₂ while producing hydrogen, holds promise for cleaner energy production. Direct air capture, despite technical and cost hurdles, presents a novel approach to reducing atmospheric CO₂. By extracting CO₂ directly from ambient air, it could complement existing methods and potentially reverse rising CO₂ levels. These approaches signify critical strides in mitigating CO₂ emissions and combatting climate change. Metal-organic frameworks (MOFs) excel in carbon capture due to their unique properties. MOFs possess exceptionally high porosity, offering an extensive surface area for gas adsorption. Their tunable structures allow for precise customization to target specific gas molecules like carbon dioxide. MOFs exhibit strong adsorption capacities, efficiently trapping CO₂ molecules within their framework. This combination of high porosity, tunability, and adsorption capacity makes MOFs ideal candidates for capturing and storing significant amounts of CO₂, particularly in industrial processes and direct air capture applications. However, MOFs have their own set of challenges, such as reduced stability at higher temperatures and sensitivity to moisture. Researchers are actively working on solutions, including post-synthesis functionalization and creating open spaces on MOFs' metal parts, to enhance their performance.

In summary, the pursuit of effective CCS technologies is crucial when it comes to addressing climate change. While current methods and materials show promise, ongoing research and innovation are essential to overcome existing challenges and pave the way for a sustainable and greener future. To address climate change and safeguard the planet for future generations, it is imperative to integrate these technologies into a comprehensive strategy aimed at reducing CO₂ emissions.

References

- [1] Tabbi Wilberforce, A.G. Olabi, Enas Taha Sayed, et al. Progress in carbon capture technologies. *Science of The Total Environment*, 2021, 761: 143203.
- [2] Aniruddha, R., I. Sreedhar, and Benjaram M. Reddy. MOFs in carbon capture-past, present and future. *Journal of CO₂ Utilization*, 2020, 42: 101297.
- [3] Chungjung Choi, Rahul L. Kadam, Sanjit Gaikwad, et al. Metal organic frameworks immobilized polyacrylonitrile fiber mats with polyethyleneimine impregnation for CO₂ capture. *Microporous and Mesoporous Materials*. 2020, 296: 110006.
- [4] Kasra Pirzadeh, Kourosh Esfandiari, Ali Asghar Ghoreyshi, et al. CO₂ and N₂ adsorption and separation using aminated UiO - 66 and Cu₃ (BTC)₂: A comparative study. *Korean J. Chem. Eng*, 2020, 37: 513 - 524.
- [5] Ahmed Al-Mamoori, Anirudh Krishnamurthy, Ali A. Rownaghi, et al. Carbon capture and utilization update. *Energy Technology*. 2017, 56: 834 - 849.
- [6] SM Nazir, JH Cloete, S Cloete, et al. Efficient hydrogen production with CO₂ capture using gas switching reforming. *Energy*, 2019, 185: 372 - 385.
- [7] Mai Bui, Indra Gunawan, Vincent Verheyen, et al. Dynamic modeling and validation of post-combustion CO₂ capture plants in Australian coal-fired power stations. *Energy Procedia*, 2013, 37: 2694 - 2702.
- [8] Xiancheng Ma, Liqing Li, Shaobin Wang, et al. Ammonia-treated porous carbon derived from ZIF-8 for enhanced CO₂ adsorption. *Applied Surface Science*, 2016, 369: 390 - 397.

- [9] Sanjit Gaikwad, Seok-Jhin Kim, Sangil Han, CO₂ capture using amine-functionalized bimetallic MIL-101 MOFs and their stability on exposure to humid air and acid gases, *Microporous Mesoporous Mater*, 2019, 277: 253 – 260.
- [10] Szczęśniak, Barbara, and Jerzy Choma. Graphene-containing microporous composites for selective CO₂ adsorption. *Microporous and Mesoporous Materials*, 2020, 292: 109761.
- [11] Sami Ullah, Mohamad Azmi Bustam, Abdullah G. Al-Sehemi, et al. Influence of post-synthetic graphene oxide (GO) functionalization on the selective CO₂/CH₄ adsorption behavior of MOF-200 at different temperatures; an experimental and adsorption isotherms study. *Microporous Mesoporous Mater*, 2020, 296: 110002.
- [12] Muofhe C. Singo, Xitivhane C. Molepo, Olugbenga O. Oluwasina, et al. Chitosan-impregnated SOD-Metal Organic Frameworks (SOD-ZMOF) for CO₂ capture: Synthesis and performance evaluation. *Energy Procedia*, 2017, 114: 2429 - 2440.
- [13] Mohamedali, Mohammed, Devjyoti Nath, Hussameldin Ibrahim, et al. Review of recent developments in CO₂ capture using solid materials: metal organic frameworks (MOFs). *Greenhouse Gases*, 2016, 115 - 154.