



Research paper

Past, present and future of materials' applications for CO₂ capture: A bibliometric analysis

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ABSTRACT

The CO₂ emission, especially from the energy sector, has increased by 1.7% in recent years, which is an enormous increase. Therefore, various materials have been employed to capture the released CO₂. Although many studies have also been conducted to review the state-of-the-art of CO₂ capture technology, a quantitative review of the development of this field is still a novelty. Keeping this in mind, the present study aims to quantitatively review the available literature on this technology that has been published during the period of 1970–2020, by applying bibliometric and content analysis techniques. The bibliometric analysis reveals that 62.68% of the total articles indexed in Web of Science are published in the last five years. *International Journal of Greenhouse Gas Control* has been identified as the highest contributing journal, with 9.97% and 8.02% contribution in publications and citations, respectively. Further, China and USA are the main research hubs of this field. Again, by using content analysis techniques, chemical fixation, cycloaddition, cyclic carbonates, epoxides and mixed-matrix membrane are determined as the hot topics of this field. Moreover, the application of nanotubes and nanoparticles can be a promising option in future research.

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1. Introduction

Carbon dioxide, a greenhouse gas, plays a vital role in maintaining the temperature of the earth and primarily responsible for global warming (Duan et al., 2016; Jande et al., 2014). In absence of CO₂, the temperature of the earth's surface would have been –18 °C. The presence of CO₂ makes the earth's surface temperature 33 °C warmer. As a result of its presence and its ability to create greenhouse effect, the average surface temperature of the earth is maintained at 15 °C (Charney et al., 1979; Shapiro, 1990). The concentration of CO₂ in the atmosphere has seen a lot of variation over the entire course of history. It has evolved with the evolution of the atmosphere as a result of anthropogenic activities

(Azuma et al., 2018; Das Kangabam and Govindaraju, 2019; Ragnarsson et al., 2017). The Early Eocene Climate Optimum (EECO) that occurred about 51–53 million years ago is considered as the warmest interval in the past 65 million years, where the average surface temperature was over 10 °C as compared to the pre-industrial era; while, the CO₂ level averaged around 500–3000 parts per million (ppm) (Anagnostou et al., 2016; Hyland and Sheldon, 2013; Loptson et al., 2014; Zachos et al., 2008). The era that existed about 33.6 million years ago is considered as the Oligocene epoch period, when the development of ice sheets in Antarctica resulted in the cooling of the atmosphere (Anagnostou et al., 2016; Kurita and Miwa, 1998; Zachos et al., 2001). Evaluations on the analysis of air bubbles trapped under the snow have provided suitable data regarding CO₂. Until before the industrial revolution, the CO₂ concentration remained below 280 ppm level; while, in the 1950s, the CO₂ level was approximately 310 ppm (Inglis et al., 2015).

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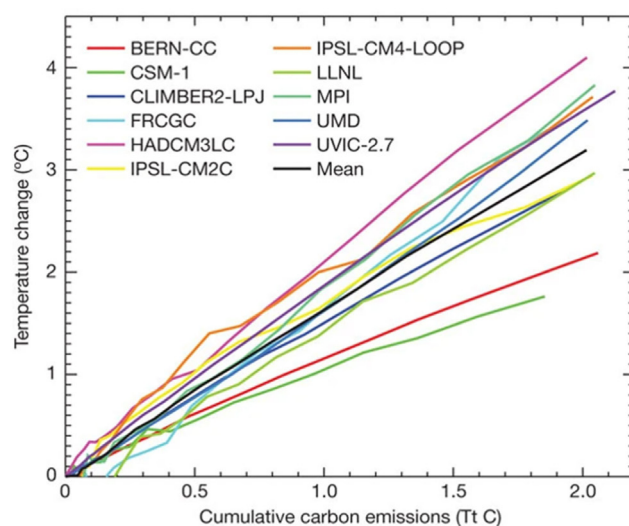
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With recent global shifts in the environment due to human activity, the Earth has entered into a new phase – the Anthropocene (Crutzen, 2006; Davis and Todd, 2017; Keys et al., 2019; Lewis and Maslin, 2015). The earth will witness the impact of today's activities for the upcoming million years (Lewis and Maslin, 2015). This threat to the sustainable future of humanity has led us to understand the earth system trajectories, climate change, biosphere, and the correlation of socio-economic balance with the environmental factors (Ripple et al., 2019; Steffen et al., 2018). The level and trajectory of the greenhouse gases (GHGs) is seen to be increasing in a quasilinear relationship, when plotted as level of CO₂ against global temperature rise (Ripple et al., 2019; Steffen et al., 2018), see Fig. 1(a). In fact, the CO₂ content in the atmosphere has shown drastic increment in the last decade (Gorus and Aydin, 2019; Lenton et al., 2019). In 2019, the global atmospheric carbon dioxide level was the highest (at 409 ppm). The global growth rate of CO₂ has shown an increasing trend, where it has grown by 2.3 ppm per year from 2009–2018; this, in comparison to the past 60 years, is about 100 times faster (Etheridge et al., 1998; Leite, 2020). Fig. 1(b) depicts an overview of the increasing CO₂ concentration.

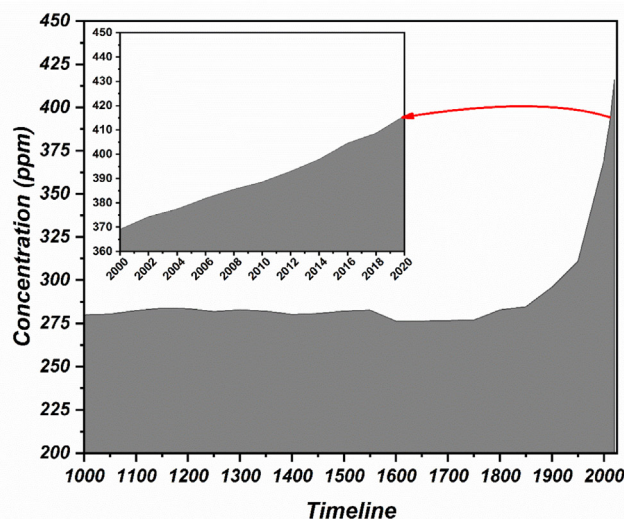
To combat the global climate changes, approaches to mitigate GHGs emissions are deemed essential. While considering various approaches, including afforestation (Huang et al., 2018; Suganuma et al., 2019), deployment of renewable energy (Mush-taq et al., 2016; Siddiqi et al., 2019), use of clean fuels (Kaffash et al., 2021; Zaidi et al., 2018), improvement in energy efficiency to reduce the detrimental effect of CO₂ (Berthelot and Bogaerts, 2017; Haugen et al., 2021), CO₂ capture and storage (CCS) and protection CO₂ sinks (Koivunen et al., 2021) have shown the highest potential in reducing the emissions (Haszeldine et al., 2018; Manan et al., 2017). The use of CCS, along with other mitigation techniques, can effectively contribute towards achievement of the targets of Intergovernmental Panel on Climate Change (IPCC), i.e., reduction of CO₂ by 50%–85% by the year 2050 as compared to the emission in 2000 (Leung et al., 2014).

CCS involves multiple processes for CO₂ emission control, including combustion, separation and storage. The combustion process is further divided into three categories, namely post-combustion, pre-combustion and oxyfuel combustion. In post-combustion systems, CO₂ is captured from the flue gases produced by the combustion of fuel; whereas in pre-combustion systems, the fuel is processed in a reactor to produce separate streams of CO₂ for storage and H₂ for use as a fuel. In the case of oxy-combustion, oxygen is used instead of air, which produces a flue mainly consisting of H₂O and CO₂, where CO₂ is readily captured (Metz et al., 2005). Out of these three categories, the gasification/pretreatment process facilitates formation of higher CO₂ concentration (Irfan et al., 2011). Moving forward to different separation technologies, the techniques of absorption (Tang et al., 2005), adsorption (Cinke et al., 2003), chemical looping combustion (Ishida and Jin, 1997), membrane separation (Adewole et al., 2013), and cryogenic distillation (Xu et al., 2014) are the promising ones. The captured CO₂ can be stored into geological formations, and can be transported to the industry for further utilization in for example ammonia and urea production, beverage industry, and fire extinguishers (Pan et al., 2012; Tomić et al., 2018).

Owing to the cruciality of CO₂ capture, this topic has attracted much attention in recent years. Therefore, there is a need to quantitatively map the evolution of the field and determine the top trending research topics. In this regard, Xing et al. (2020) conducted a bibliometric review of CO₂ conversion, which was downright amazing with accurate, informative and timely conclusions. The review was conducted using the WoS database for the years 2010–2019. It was concluded by the authors that catalytic



(a)



(b)

Fig. 1. (a) Quasi-linear relationship between the level of CO₂ emissions against global temperature rise predicted by C4MIP simulations (Matthews et al., 2009). (b) Increasing CO₂ level in the atmosphere (Etheridge et al., 1998). Source: Reprinted by permission from (Matthews et al., 2009).

conversion technology, including thermal catalysis, photocatalysis and electrocatalysis, is the pivot to the research community (Xing et al., 2020). Osman et al. (2020) conducted a similar bibliometric study, covering the span of 2010–2020, with a main focus on decarbonization. Wong et al. (2020) studied carbon utilization technologies by conducting the bibliometric analysis of 1857 publications from the WoS database that were published within the period of 1995–2019. In this study, chemical fixation and epoxides were identified among the hot topics of the time. Omoregbe et al. (2020) conducted a bibliometric analysis of carbon dioxide capture technologies using the WoS database for the years 1998–2018. It was realized that the research activities in the field got boosted after 2008. However, a comprehensive quantitative review on material's applications for CO₂ capture is missing from the published literature. Therefore, this study aims at conducting bibliometric analysis of the literature published in the last 50 years (1970–2020), with the focus on materials' applications for CO₂ capture. For this purpose, content analysis

technique, in addition to bibliometric analysis, has been adopted and the research trends have been mapped.

2. Methods

There are numerous journal indexing databases, out of which Web of Science (WoS) is world's oldest, widely used and authoritative database of scientific publications and citations (Birkle et al., 2020). The core collection of WoS is comprised of a collection of 21,000 peer-reviewed high-quality journals, distributed across 250 fields, and accessible globally. In fact, more than 53 million publications can be accessed, along with 1.18 billion cited references (Clarivate, 2021b; Naseer et al., 2021). In this article, the core collection of WoS database has been employed to investigate the literature on CO₂ capture, along with analysis of materials' applications. From the WoS database, 39000 publications, relevant to the topic, were extracted. The extracted publications were primarily journal articles, and they were selected for content analysis.

One of the quantitative techniques to review the literature of a specific field is bibliometric analysis. This technique is used to evaluate the published literature statistically, and can also be used to draw a landscape of evolution in a particular field. (Hui et al., 2020; Iftikhar et al., 2019). In this article, bibliometric analysis is used to map the evolution of CO₂ capture and materials' applications. The obtained data was analyzed to find the trend in publication history, publication distribution, subject category distribution, leading journals, leading countries, leading organizations, leading authors and research themes.

Another quantitative literature review technique is content analysis. It is used to draw the landscape of the most frequent keywords used in a specific field. This technique is used to determine how a specific field has emerged through different eras, and what has been the correlation between any two specific keywords. In this article, this technique is used to draw a landscape of frequently used keywords. Besides, this article also presents the future directions in the field of CO₂ capture based on content analysis.

3. Results and discussions

3.1. Publication history

The very first article stating CO₂ capture was published in 1975 (Nagra and Armstrong, 1975). Until 1990, the topic of CO₂ capture failed to attract much attention, as evident from the publication of only 9 articles in these 16 years. In the following decade (1990–2000), this topic started to receive the attention of researchers and policymakers, resulting in 535 publications; and this amounts to 1.37% of the overall publications until 2020. The next decade contributed with 10.05%; while, the recent decade (2011–2020) has been the main era of research on this topic, as about 88.59% of the total publications belong to this period. Fig. 2 provides a comprehensive look of the evaluation of this field. It can be realized from the figure that although the number of publications has been increasing every year starting from 2000, a rapid rate of increase took place after 2007. The year 2017 witnessed a sharp rise in publications that amounted to an increase of 17.1% in one year. The year 2020 produced the highest number of publications, mainly because in the COVID-19 situation this topic has been of some interest to the research community. Various studies (Aktar et al., 2020; Andreoni, 2021; Chevallier, 2021; Liu et al., 2020; Peng and Jimenez, 2021; Wang et al., 2020) are available that particularly discussed the impact of COVID-19 on the environment, specifically the CO₂ concentration in the environment.

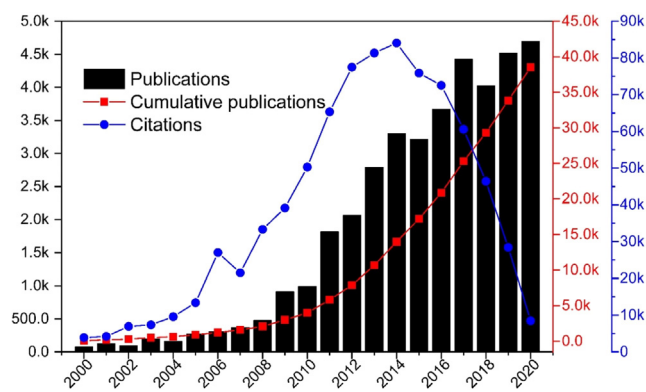


Fig. 2. Publication history of materials' applications for CO₂ capture.

Overall, the total number of publications has been increasing at a high rate, as depicted by the cumulative number of publications presented in the figure. In the case of the number of citations, 2014 has witnessed the highest output.

3.2. Publication distribution

There are 39,000 documents available in the WoS on CO₂ capture-material nexus. Most of the documents are articles, i.e., 31,880 (81.74%), followed by proceeding papers (see Fig. 3). The overall contributions of the different document types, including proceeding papers, reviews, book chapters, meeting abstracts, editorials and others are 14.67%, 5.04%, 1.42%, 1.14%, 0.7% and 0.68% respectively. Others include early access, news items, corrections, letters, books, data papers, notes, retracted publications and reprints, contributing respectively 0.33%, 0.13%, 0.06%, 0.05%, 0.04%, 0.03%, 0.03%, 0.01 and 0.001%.

3.3. Subject category distribution

The literature on the CO₂ research field is classified into 192 subject categories, as per the data available in WoS. The top 5 subject categories, along with their respective contributing percentage, are chemical engineering (33.32%), energy fuels (32.36%), chemistry multidisciplinary (15.03%), environmental engineering (13.80%) and physical chemistry (13.37%) (Fig. 4).

Chemical engineering couples principles of engineering with applied chemistry, industrial chemistry and chemical engineering. Fundamentally, it focuses on the chemical conversion of raw materials to useful products (Clarivate, 2021a). Energy fuels category is concerned with the production and management of combustible nonrenewable fuels and all renewable energy sources, except nuclear studies (Clarivate, 2021a; Naseer et al., 2021). Chemistry multidisciplinary looks at chemical sciences through the lens of multidisciplinary approaches (Clarivate, 2021a). Environmental Engineering sheds light on anthropogenic activities and their impacts on humans and the environment (Clarivate, 2021a; Naseer et al., 2021). Chemistry, Physical includes resources on photochemistry, solid-state chemistry, kinetics, catalysis, quantum chemistry, surface chemistry, electrochemistry, chemical thermodynamics, thermophysics, colloids, fullerenes, and zeolites (Clarivate, 2021a).

After 2011, the chemical engineering category has grasped much attention among researchers, while the other categories seem to correlate as there has been an increase in the number of articles published in these fields. Publications in the energy fuels category have faced ups and downs; however, the overall energy fuels category has also evolved over time. Detailed evolution of the top 5 research categories in the last two decades is depicted in Fig. 5.

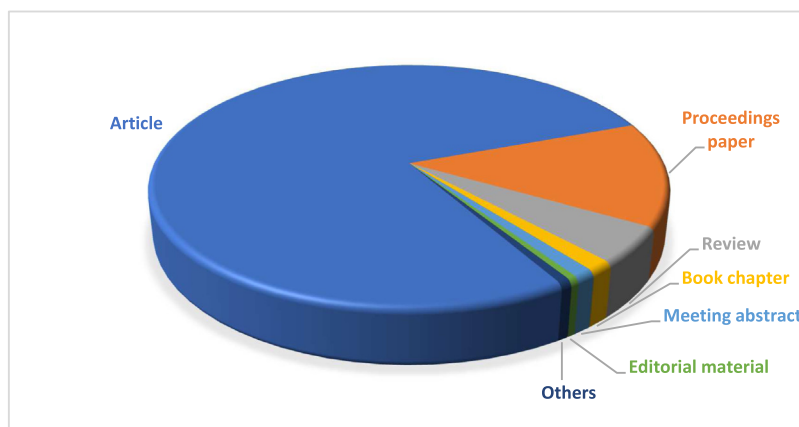


Fig. 3. Distribution of documents published in WoS.

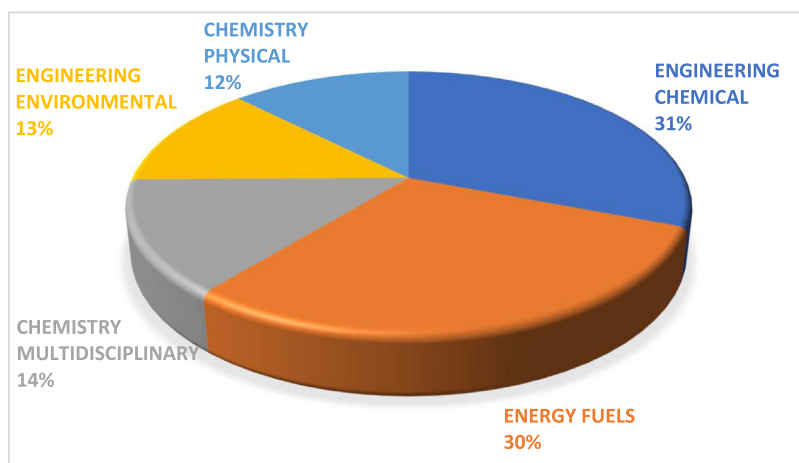


Fig. 4. Top five subject categories in CO₂ research.

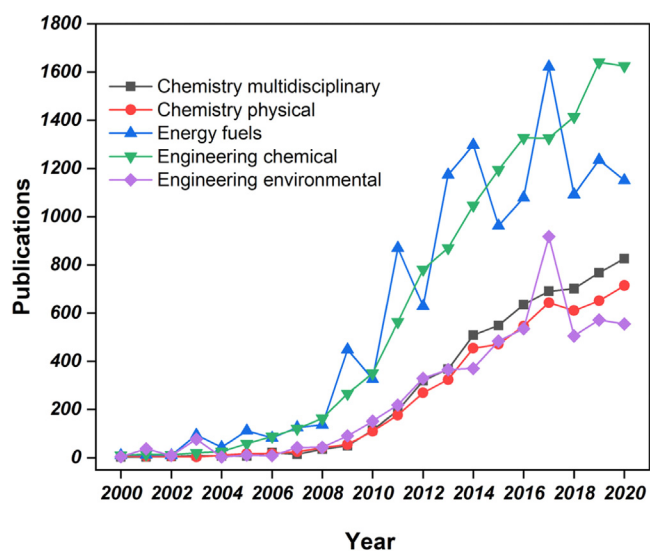


Fig. 5. Trends in top five research categories.

3.4. Leading journals

This analysis was performed to find the impact and contribution of different journals in CO₂ capture technology. There

are about 2485 journals found that published documents in this domain. Filtration was performed to find the journals with the most impact in the field. The minimum benchmark was set to be 100 document publications and 100 citations; and, as a result, only a total of 56 journals met the minimum threshold (see Fig. 6).

From Fig. 6, it can be observed that the *International Journal of Greenhouse Gas Control* has the highest contribution (i.e., 9.97% of publications and 8.02% of citations), followed by *Industrial & Engineering Chemistry Research* (i.e., 6.94% of publications and 6.37% of citations). Table 1 shows the individual contribution of the top 15 journals that cumulatively contributed about 56.81% and 53.38% of the overall publications and citations, respectively.

3.5. Leading organizations

A total of 10,165 organizations were found that are involved in CO₂ capture research. To highlight the leading organizations, a minimum benchmark of 100 publications and 100 citations was adopted, resulting in only 107 organizations passing the threshold (see Fig. 7). The size of the circle shows the influence of an organization in the field, while the connecting lines show the collaboration between organizations. Table 2 presents a list of the individual contribution of the top 15 organizations that cumulatively contributed about 29.83% of publications and 30.71% of citations. It was found that the Chinese Academy of Sciences is at the top of the list, followed by Tsinghua University.

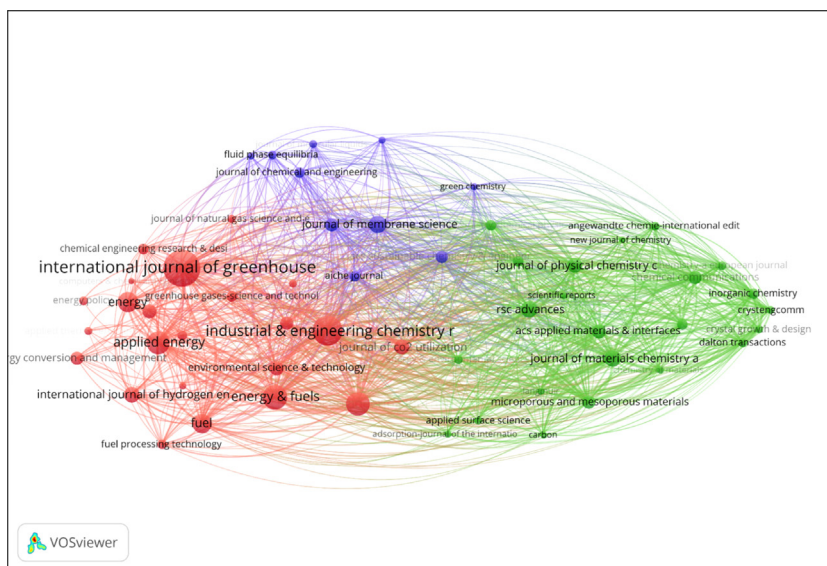


Fig. 6. Leading journals in CO₂ capture technologies.

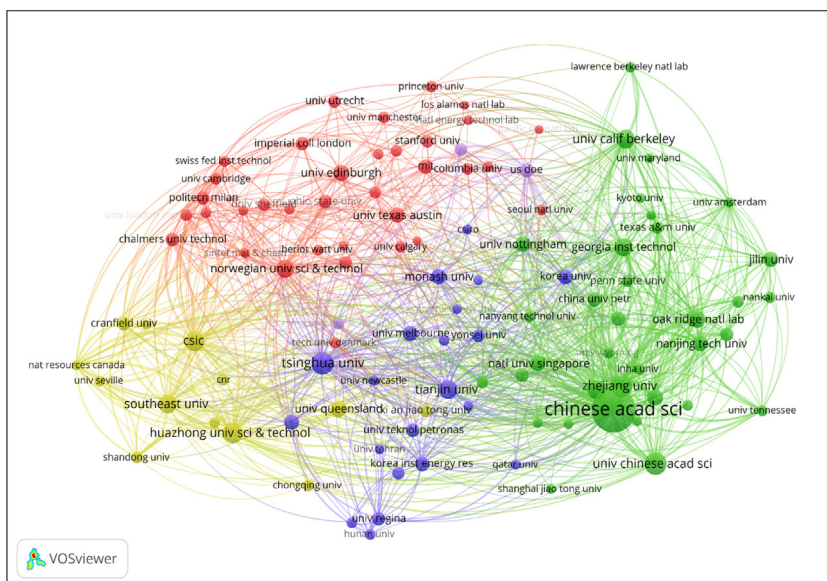


Fig. 7. Leading organizations in CO₂ capture technology.

Table 1
Top 15 leading journals in CO₂ capture technology.

| Journal Name | Documents | Citations | Documents contribution | Citation contribution |
|---|-----------|-----------|------------------------|-----------------------|
| International Journal of Greenhouse Gas Control | 1744 | 43328 | 9.79% | 8.02% |
| Industrial & Engineering Chemistry Research | 1236 | 34404 | 6.94% | 6.37% |
| Energy & Fuels | 860 | 22901 | 4.83% | 4.24% |
| Chemical Engineering Journal | 853 | 25805 | 4.79% | 4.78% |
| Applied Energy | 806 | 25028 | 4.52% | 4.64% |
| Energy | 632 | 16871 | 3.55% | 3.12% |
| Fuel | 616 | 20236 | 3.46% | 3.75% |
| Journal of Membrane Science | 491 | 18534 | 2.76% | 3.43% |
| RSC Advances | 486 | 8290 | 2.73% | 1.54% |
| Journal of Materials Chemistry A | 459 | 16898 | 2.58% | 3.13% |
| International Journal of Hydrogen Energy | 421 | 11408 | 2.36% | 2.11% |
| Journal of CO ₂ Utilization | 395 | 5098 | 2.22% | 0.94% |
| Journal of Physical Chemistry C | 394 | 10411 | 2.21% | 1.93% |
| Environmental Science & Technology | 367 | 18104 | 2.06% | 3.35% |
| ACS Applied Materials & Interfaces | 365 | 10878 | 2.05% | 2.01% |

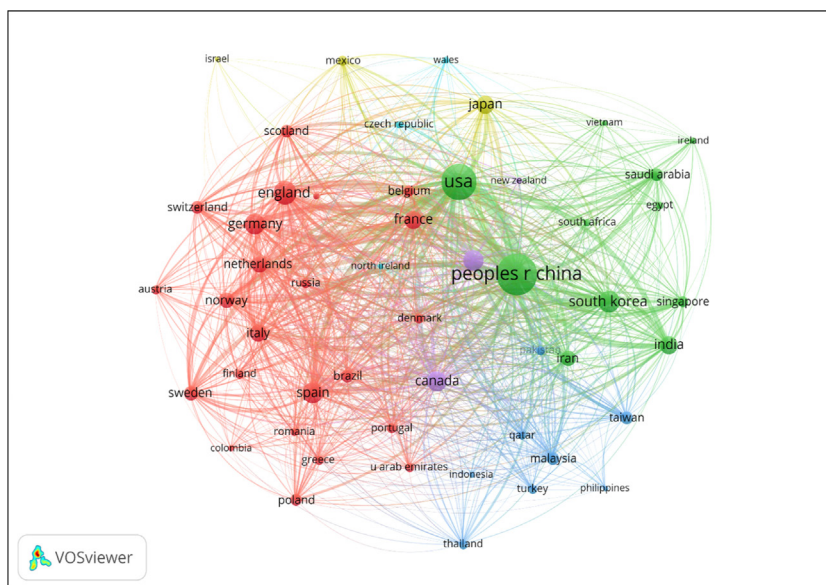


Fig. 8. Leading countries and their collaboration in materials' applications for CO₂ capture.

Table 2
Top 15 organizations in CO₂ capture research.

| Organization | Country | Documents | Citations | Document contribution | Citation contribution |
|---|----------|-----------|-----------|-----------------------|-----------------------|
| Chinese Academy of Sciences | China | 1290 | 36215 | 6.77% | 6.19% |
| Tsinghua University | China | 407 | 8996 | 2.14% | 1.54% |
| University of the Chinese Academy of Sciences | China | 403 | 7894 | 2.12% | 1.35% |
| Zhejiang University | China | 380 | 12739 | 2.00% | 2.18% |
| Huazhong University of Science & Technology | China | 354 | 7919 | 1.86% | 1.35% |
| Spanish National Research Council (CSIC) | Spain | 328 | 16662 | 1.72% | 2.85% |
| Southeast University | China | 309 | 6445 | 1.62% | 1.10% |
| Tianjin University | China | 308 | 6778 | 1.62% | 1.16% |
| University of California Berkeley | USA | 308 | 21965 | 1.62% | 3.76% |
| Dalian University of Technology | China | 300 | 8242 | 1.58% | 1.41% |
| Norwegian University of Science & Technology | Norway | 293 | 9756 | 1.54% | 1.67% |
| Georgia Institute of technology | USA | 281 | 11133 | 1.48% | 1.90% |
| University of Edinburgh | Scotland | 242 | 6270 | 1.27% | 1.07% |
| Oak Ridge National Laboratory | USA | 241 | 11549 | 1.27% | 1.97% |
| Beijing University of Chemical Technology | China | 237 | 7042 | 1.24% | 1.20% |

3.6. Leading countries

The country analysis technique is another widely used technique to determine the leading countries that are working on a certain research topic. In this article, this technique was used to determine the countries that have been working in the field of materials' applications for CO₂ capture. The collected data from WoS was analyzed, and it was observed that a total of 141 countries have been publishing articles related to the mentioned topic. The countries were filtered by using a minimum criterion of at least 50 articles 100 citations. This filtering process resulted in 51 countries of interest. The countries were further arranged based on the number of documents published to determine the top leading countries as depicted in Fig. 8.

In Fig. 8, the circle size represents a country's contribution, while the line thickness between any two countries represents the collaboration of the two countries. Fig. 8 reveals that, overall, the top three leading countries are China, USA and England. China leads with respect to the number of articles published, while USA leads in terms of the citations received. Quantitative analysis shows that the total number of documents published and the total number of citations received by the top 15 countries are 33477 and 966052, respectively. These two values contribute

Table 3
Top 15 countries in CO₂ capture research.

| Country | Documents | Citations | Document contribution | Citation contribution |
|-------------|-----------|-----------|-----------------------|-----------------------|
| China | 9140 | 212259 | 21.54% | 17.91% |
| USA | 6598 | 260811 | 15.55% | 22.01% |
| England | 2179 | 66261 | 5.13% | 5.59% |
| South Korea | 1896 | 40552 | 4.47% | 3.42% |
| Australia | 1746 | 53970 | 4.11% | 4.55% |
| Spain | 1614 | 49083 | 3.80% | 4.14% |
| Germany | 1608 | 49063 | 3.79% | 4.14% |
| Canada | 1545 | 49542 | 3.64% | 4.18% |
| India | 1238 | 21763 | 2.92% | 1.84% |
| France | 1128 | 36133 | 2.66% | 3.05% |
| Japan | 1113 | 28360 | 2.62% | 2.39% |
| Italy | 1086 | 28326 | 2.56% | 2.39% |
| Netherlands | 908 | 35278 | 2.14% | 2.98% |
| Norway | 846 | 23116 | 1.99% | 1.95% |
| Iran | 832 | 11535 | 1.96% | 0.97% |

about 78.88% of the total documents published and 81.52% of the total citations received. The individual contribution of the top 15 countries, based on the number of documents published and the number of citations received, is presented in Table 3.

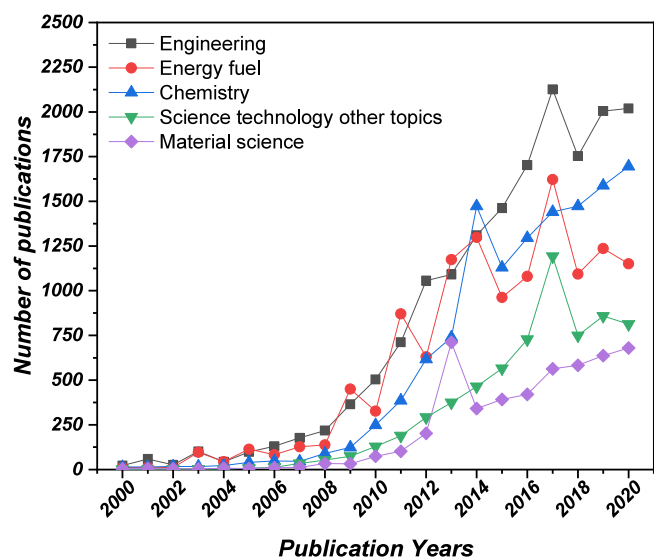


Fig. 9. Evolution of the top five research areas over time.

Table 4
Top 15 areas in CO₂ capture research.

| Research area | Publications | % Contribution |
|------------------------------------|--------------|----------------|
| Engineering | 17073 | 43.78 |
| Energy fuels | 12621 | 32.36 |
| Chemistry | 12609 | 32.33 |
| Science technology other topics | 6543 | 16.78 |
| Materials science | 4830 | 12.39 |
| Environmental sciences ecology | 4794 | 12.29 |
| Thermodynamics | 2201 | 5.64 |
| Physics | 1857 | 4.76 |
| Polymer science | 1098 | 2.82 |
| Geology | 913 | 2.34 |
| Meteorology atmospheric sciences | 711 | 1.82 |
| Electrochemistry | 682 | 1.75 |
| Mechanics | 652 | 1.67 |
| Biotechnology applied microbiology | 567 | 1.45 |
| Agriculture | 514 | 1.32 |

3.7. Research directions

3.7.1. Major research areas

All the documents available in WoS can be classified into 117 major research areas. Out of these, the top five areas are engineering, energy fuels, chemistry, science technology and materials science, contributing respectively 43.78%, 32.36%, 32.33%, 16.78% and 12.39%. A list of top 15 research areas is displayed in Table 4. Fig. 9 presents the evolution of the top five research fields as a function of time. It was observed that the engineering field has almost always been at the top, followed by chemistry.

3.7.2. Research trends

Research directions of a field can be analyzed by various techniques. In this paper, a data mining technique was employed to extract keywords that are used in CO₂ capture research. The author's keyword analysis is based on analyzing certain portions of an article, such as abstract and title; whereas, keyword plus analysis is based on analyzing the whole article, followed by collection of frequently used keywords. In this paper, keyword plus analysis was performed to map the trend of CO₂ capture research. The results show the most frequently used keywords and their co-occurrence. Therefore, this technique is a great option to have

Table 5
Most frequent keywords that have been used in CO₂ capture research.

| Keyword | Occurrences | % Occurrences |
|--------------------------|-------------|---------------|
| CO ₂ capture | 5135 | 6.91 |
| Adsorption | 3422 | 4.60 |
| Performance | 3198 | 4.30 |
| Separation | 2990 | 4.02 |
| Storage | 2241 | 3.02 |
| Absorption | 2027 | 2.73 |
| Kinetics | 1690 | 2.27 |
| Flue-gas | 1611 | 2.17 |
| Temperature | 1582 | 2.13 |
| Metal-organic frameworks | 1300 | 1.75 |
| Methane | 1279 | 1.72 |
| Solubility | 1167 | 1.57 |
| Energy | 1145 | 1.54 |
| sorption | 1072 | 1.44 |
| simulation | 994 | 1.34 |

an idea about how a specific field has evolved over time. The employed technique generated a total of 28,264 keywords that have been used related to materials' applications for CO₂ capture, out of which 240 keywords are those that have been used at least 150 times (see Fig. 10).

In Fig. 10, the circle size represents the frequency of keyword occurrence and the line thickness between any two keywords represents the frequency of their co-occurrence. The colors represent the specific time at which a specific keyword has emerged. From Fig. 10, it can be realized that the three most frequently used keywords are CO₂ capture, adsorption and performance. The collected data upon analysis and calculation demonstrated that the top 15 frequently used keywords accounted for 32048 occurrences, which is about 41.51% of the total keyword occurrences. The individual contribution of the top 15 keywords is listed in Table 5.

From keyword analysis, it got revealed that among all the technologies used for CO₂ capture, adsorption is the most popular followed by separation and absorption technologies. Moreover, deliberate analysis of the most frequent keywords revealed that the application of the following materials for CO₂ capture has been in the forefront of research – these materials are monoethanolamide, mesoporous silica, polymers, epoxides, graphene, cyclic carbonates, porous carbons, zeolites and alkanolamines. Recently, nanotubes and nanoparticles are also introduced in this field, and are appearing among the most frequent keywords. In addition, it was found that among the different sources of CO₂ emission, the energy sector is the mostly discussed, and among the different sources used for energy generation, coal appears at the top of the list. Furthermore, chemical fixation, cycloaddition, cyclic carbonates, epoxides and mixed-matrix membrane are found to be some of the recent hot topics of this field. It was also noticed that carbon conversion and storage technologies are being actively studied recently.

To further understand the research directions of this field, recent trends in frequently used materials for CO₂ capture are highlighted in the coming section

(i) Mesoporous materials-based adsorbents: Currently, industries are in the race of reducing their CO₂ emissions owing to increasing environmental threats. For this purpose, traditional CO₂ capture technologies, such as cryogenic distillation, membrane purification and adsorption, are getting widely used by the industrial sector (Azmi and Aziz, 2019; Leung et al., 2014). However, there are few factors that limit the advantages associated with the application of these technologies. These factors include high capital cost, low absorption capacity, equipment corrosion, poor stability and solvent loss (Yu et al., 2012). In order to overcome these problems and develop efficient CO₂ capture

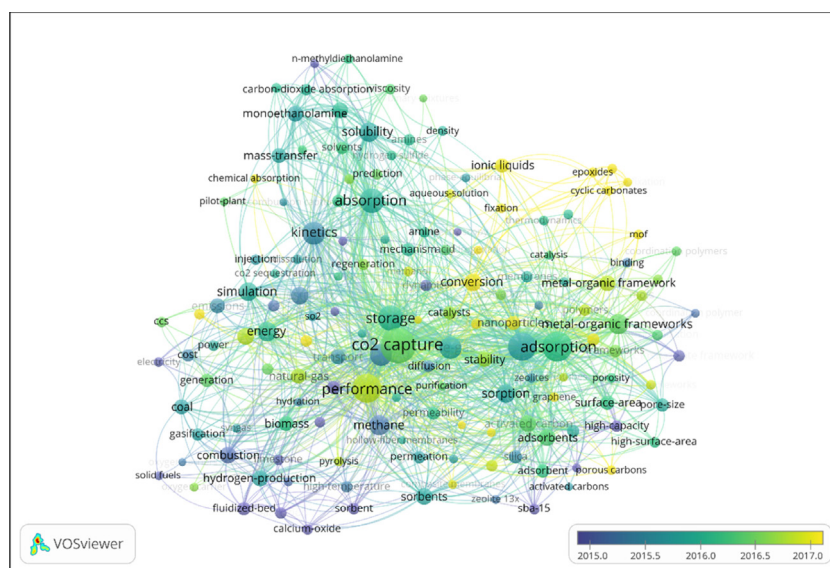


Fig. 10. Research trends in the materials' applications for CO₂ capture.

methods, the research community has shifted its attention to porous adsorbents (Olajire, 2017). Porous adsorbents have superior characteristics in terms of providing high surface area and high pore volume for capturing CO₂ that ultimately increases the CO₂ capture efficiency. Literature reports suggest that mesoporous materials-based adsorbents are among the most studied in this regard (Azmi and Aziz, 2019).

In a study (Chen et al., 2018), application of a novel hybrid material containing MIL-101(Cr) and mesoporous silica was analyzed for CO₂ capture. The material was synthesized by in-situ hydrothermal method. Also, a comparative study of the absorption efficiency of MIL-101(Cr) and mesoporous silica integrated with MCM-41 was performed. According to the study, MIL-101(Cr)@MCM-41 was more efficient than MIL-101(Cr) alone towards CO₂ capture at 298 K and 1 bar. The CO₂ absorption was found to be 2.09 mmol g⁻¹ for MIL-101(Cr) integrated with MCM-41, which was approximately 79% higher than that demonstrated by MIL-101(Cr) alone. It was concluded that the addition of MCM-41 (mesoporous material) provided more sites for CO₂ absorption by increasing the surface area of the material.

Sánchez-Zambrano et al. (2018) emphasized the importance of amine-coated adsorbents for CO₂ capture, as liquid amines have large energy requirements for capturing CO₂. Some important features of amine impregnated silica adsorbents are that they can bear moisture, cause faster CO₂ absorption, and exhibit higher capacity of absorption. Also, regeneration of the amine impregnated adsorbent led to overall reduction of the energy requirement. Here, mesostructured silica foam (MF) was coated with different amine compounds, and the effect of varying concentration of imidazole (Im) was studied. Blending ratios of materials and the adsorption temperature served as variables in this study. Only those commercial amines were selected that have high boiling points and are less volatile, such as tetraethylenepentamine (TEPA). It was observed that the CO₂ adsorption capacity, working capacity, amine efficiency and the energy requirement of sorbents were improved significantly by adding Im to TEPA. The MF, coated with 30% MIm (Methylimidazole) and 40% TEPA, exhibited the highest efficiency among all the tested sorbents in the study, which implies that mesoporous materials are highly efficient in capturing CO₂.

In another study (Zhang et al., 2019a), extraction of mesoporous silica foams (MSFs) from alkali fusion of the acid-treated

industrial fly ash was performed to study the possibilities of CO₂ capture. In this process, Pluronic P123 was used as a structure-directing agent and trimethyl benzene was used as a swelling agent. The results showed that at 75 °C and at 1 bar the MSFs coated with 63.2 wt% polyethyleneimines demonstrated an absorption capacity of 4.7 mmol g⁻¹ for CO₂. The authors inferred that the performance of the said material, owing to the addition of mesoporous characteristics, was well above the other materials studied.

Recently, a polyamine-based protic ionic liquid sorbent was synthesized, supported by mesoporous silica (Zhang et al., 2019b). This novel adsorbent showed excellent properties toward CO₂ capture in the rate determining step (reaction rate: $147 \times 10^{-3} \text{ mmol g}^{-1} \text{ s}^{-0.5}$), which was three times better than exhibited by amine-modified and ionic liquid-functionalized support systems.

Hence, based on the recent experimental studies (Chen et al., 2018; Sánchez-Zambrano et al., 2018; Zhang et al., 2019a,b), it can be concluded that integrating various materials with mesoporous materials increases their capacity to capture CO₂. This increment in the capacity owes to the increased surface area for CO₂ capture. (ii) **Graphene:** Graphene has recently emerged as a very useful material that finds applications in several industries. Its utilization for CO₂ capture and conversion to utilizable materials is a hot topic at present. Graphene is highly promising and is also very inexpensive. Especially, the new grades of electrochemically exfoliated graphene are cheap because these involve electrochemical exfoliation of large blocks of graphite electrochemical exfoliation at very low cost (Parvez et al., 2014; Islam et al., 2021). The capability of graphene to capture CO₂ at low temperatures is a unique characteristic that makes it as a promising future material.

Temperature has a direct correlation with the CO₂ absorption capacity of a material. In fact, materials may fail to find their application in the industrial sector due to their temperature sensitivity. In order to study the temperature behavior of graphene, a study was conducted by Ekhlesi et al. (Ekhlesi et al., 2018). Carbonization of Populus wood biomass was conducted under a nitrogen atmosphere, and graphene was synthesized by chemical activation of the obtained carbon. The chemical used for the chemical activation was potassium hydroxide (KOH). The variables against which CO₂ absorption efficiency was tested were KOH and carbon ratios, heating temperature and heating time. It

was observed that the CO₂ absorption on graphene got decreased with the increase in temperature, and vice versa. The graphene samples prepared with a KOH/C ratio of 3:1 showed the highest absorption rate of 7.2 mmol g⁻¹, with an activation time of 60 min and an activation temperature of 850 °C. This was the highest ever recorded CO₂ absorption value, observed at room temperature and at 1 bar pressure, for porous carbon. Further, when the activation time was changed to 90 min and the pressure was increased to 10 bar, the absorption efficiency got increased up to 12.68 mmol g⁻¹. In addition, this process was reported to be exothermic (Ekhiasi et al., 2018).

Mixed matrix membranes, in combination with graphene oxide (GO), were evaluated in another study (Rodríguez-García et al., 2019), for capturing CO₂ that got emitted due to combustion. The wt% of GO used in the membranes varied from 0.02% to 1%. GO functionalized with polyetheramine (PEAGO) and porous graphene oxide (PGO) were also considered in this experimentation, with a fixed loading of 0.02 wt%. The results showed that for copolymer Pebax 2533 matrix, the addition of GO did not increase the CO₂ permeability when the GO filler content is greater than 0.02 wt%. This implies that the CO₂ permeability gets increased for the Pebax 2533 based membranes only if the GO nanofiller content is lesser than 0.02 wt%. Higher loadings, such as 1 wt%, significantly decreased the permeability of the mixed matrix membranes from 364 barrer to 54 barrer. Further, PEAGO and PGO were tested with the same loading of 0.02 wt%, showing improvement in the CO₂ permeability. In this regard, while pristine Pebax 2533 exhibited a permeability value of 364 barrer, it got increased to 371 barrer with GO loading and to 380 and 397 barrer for PEAGO and PGO loading, respectively (Casadei et al., 2020).

Hence, graphene is considered as a potential future material for CO₂ capture. It promises to serve as a low cost and highly efficient CO₂ capture material in the days to come (Huang et al., 2021).

(iii) Polymers: Polymers are among the most studied materials used for CO₂ capture, and they are also among the materials that show the highest potential to capture CO₂. In a study by Abdelmoaty et al. (Abdelmoaty, Tessema, Choudhury, El-Kadri, & El-Kaderi, 2018), 1,4-bis-(2,4-diamino-1,3,5-triazine)-benzene was used to derive nitrogen-rich porous polymers (NRPPs) for CO₂ capture. Two porous polymers, obtained by the co-polymerization of 1,4-bis-(2,4-diamino-1,3,5-triazine)-benzene with terephthalaldehyde and 1,3,5-tris(4-formylphenyl) benzene in dimethyl sulfoxide at 180 °C, were named as NRPP-1 and NRPP-2. These two polymers, at 1 bar pressure, showed CO₂ absorption capacities of 6.1 and 7.06 mmol g⁻¹, respectively. The latter value that was obtained for NRPP-2 polymer is the second-highest value ever reported in the literature for NRPPs (Abdelmoaty et al., 2018).

The favorable properties of porous polymers for CO₂ capture have made them an excellent candidate in this technology arena. In a study by Mohamed et al. (Mohamed et al., 2020), para, meta and ortho arrangements of silicon-containing porous organic polymers were synthesized for CO₂ capture. The polymers were synthesized by using 2-, 3- and 4-hydroxybenzaldehyde and phenyltrichlorosilane, with a base in the process. It was concluded that at 323 K temperature and 40 bar pressure, the meta-arrangement structure showed the maximum CO₂ capture potential due to high surface area and pore volume.

(iv) Zeolites: According to statistics, fossil fuel burning is the primary source of CO₂ in the atmosphere (Boden et al., 2009; Kumar et al., 2020b; Rotty, 1987). Thus, the most effective way

to reduce CO₂ concentration from the environment is to reduce its emission from fossil fuel incineration. In this regard, various techniques have been developed and implemented, but the use of zeolite presents the most energy economic method for CO₂ capture (Kumar et al., 2020b; Makertihartha et al., 2017). In a study by Du et al. (2018), a new hybrid honeycomb monolith, composed of 70% 13X zeolite and 30% activated carbon, was synthesized for CO₂ capture applications. The single isotherm equilibrium generated for both CO₂ and nitrogen was measured by gravimetric method. It was observed that the synthesized novel hybrid honeycomb monolith exhibited a CO₂ adsorption capacity of 2.63 mol kg⁻¹ at 303 K temperature and 1 bar pressure.

In another study (Yan et al., 2019), a slurry was prepared (zeolitic imidazolate framework-8+2-methylimidazolate-glycolic water solution) for the adsorption of CO₂. This slurry was continuously cycled in a pilot scale sorption bubble column. The height of the adsorption column was 3.7 m and the inner diameter was 60 mm. Factors, such as sorption temperature, regeneration temperature, regeneration pressure and gas velocity, were also considered. It was observed that low sorption temperature, low superficial gas velocity, high regeneration temperature and low regeneration pressure produce excellent results in CO₂ capture. Under the above-mentioned conditions, 92% CO₂ capture efficiency was achieved. From a concentration of 24.9 mol% in the influent gas, 0.5–2.5 mol% of CO₂ was obtained in the effluent (Yan et al., 2019).

A separate report (Kumar et al., 2020a) demonstrated the synergistic effect of zeolite 5 A, monoethanolamine (MEA) and activated carbon (AC) towards CO₂ capture from the exhaust of internal combustion engines. The results obtained were excellent when an aluminum wire mesh was dipped in the slurry of MEA, zeolite 5 A and AC, dried and then employed at the exhaust pipe. The observations suggest that this adsorbent has an ability to significantly reduce not only the CO₂ concentration, but also CO by 5%, NO_x by 20% and hydrocarbons (HCs) by 30% (Kumar et al., 2020a).

(v) Porous Carbons: The need to find out the potential of porous carbons for CO₂ capture is due to the high cost of amine adsorbents and low CO₂/N₂ selectivity for typical adsorbents. In a study by Shao et al. (Shao, Li, Huang, & Liu, 2018), nitrogen-enriched porous carbons (NPCs), with a nitrogen content of 5.56–11.33 wt%, had been shown to demonstrate high CO₂ uptake, in the range of 120–207 mg g⁻¹. The reasons for high efficiency of porous carbons towards CO₂ uptake are the presence of nitrogen in the porous carbons and the diameter of nanoparticle (i.e., $d \leq 0.8$). In this experiments, it was realized that the NPC-4-600 derived from triazine-based porous organic polymer, with a nitrogen content of 9.71 wt%, showed the highest uptake at 1 °C temperature and 1 bar pressure (Shao et al., 2018).

Qi et al. (2019), on the other hand, had laid emphasis on the recycling of carbon. A heavy carbon waste (Mesitylene) product, which is achieved in the processing of C1 technologies, was utilized to prepare porous carbons to close the carbon loop. This study showed that attaching mesitylene polymers with flexible methylene groups gave it the properties of biomass-based material, which imparted the desired properties in porous carbons for high CO₂ uptake. It was demonstrated that at 0 °C temperature and 1 bar pressure the absorption can reach up to 6.61 mmol g⁻¹. This capacity was reported to be highest in comparison to other standard materials, when analyzed at 0 °C temperature and 1 bar pressure (Qi et al., 2019).

Nitrogen doped porous carbon (NDPCs) have been previously synthesized from nitrogen-containing polymers for efficient CO₂ capture. The synthesis of nitrogen-based polymers by solvent method has been the mostly considered method (as per the literature), while the difference between liquid-phase and solid-phase

synthesis is not well-defined. A study by Lou et al. (2020) had put emphasis on the solvent-free synthesis of nitrogen-containing polymers for NDPCs production. The NUT-71-F polymer, prepared by the solvent-free process, was found to generate better N-doped porous carbon for CO₂ capture. In this regard, the CO₂ uptake value reached up to 8.1 mmol g⁻¹, which was 33.34% higher than the value exhibited by its counterpart NUT-71-S (that was produced in a liquid phase) (Lou et al., 2020).

3.7.3. Nanoparticles and nanotubes: Emerging research area

The published literature contains numerous reports on the CO₂ capture technologies (Babar et al., 2019; Bartosik and Mastny, 2009; Bolland et al., 2001; Hill, 2005; Kim et al., 2014; Lackner, 2009; Li et al., 2014; Putra et al., 2017; Shen et al., 2017; Smid, 2009; Zhou et al., 2009). These reports can be broadly classified into two categories: (i) reductive CO₂ conversion technologies and (ii) non-reductive CO₂ technologies (Olajire, 2018). The reductive conversion technologies focus on the conversion of CO₂ to low oxidation state carbon (+2 or +1) at the expense of an immense amount of energy (Martín et al., 2015; Olajire, 2018). On the other hand, non-reductive technologies aim at converting CO₂ to high oxidation state carbon (+4 or +3), using a relatively lesser amount of energy (Martín et al., 2015; Olajire, 2018). A major portion of the literature comprises of studies that have been conducted using bulk materials. These bulk materials have relatively less active area; therefore, they demonstrate low catalytic reactivity (Mohamed et al., 2012; Roth et al., 2013). In this regard, application of nanoparticles and nanotubes has recently emerged as a hot topic, as these materials promise high active area, high catalytic reaction and high CO₂ capture rate (Martín et al., 2015; Mohamed et al., 2012) (see Table 6).

4. Conclusion

In summary, this study reported bibliometric and content analyses of about 39,000 publications, extracted from the Web of Science database, which focused on materials' applications for CO₂ capture. The research trends within this topic for over the last 50 years have been traced, and the following conclusions are drawn:

- With respect to timeline, the last decade (i.e., 2011–2020) has served as the main era of research concentration in this field, producing 88.59% of the total publications. The year 2017 had shown a rapid increase (17.1%) in publications. The period of 1991–2000 and 2001–2010 contributed 1.37% and 10.05%, respectively, of the total publications. Overall, it was observed that this topic received immense attention after 2007.
- Majority of the publications available in WoS are research articles, followed by reviews. It was realized that the research articles alone constituted about 81.4% of the total publications.
- Out of the total 192 subject categories that are active within CO₂ research, chemical engineering, energy fuel and chemistry multidisciplinary are the leading ones with contributions of 33.32%, 32.36% and 15.03%, respectively.
- The scope of about 2845 journals lies in line with carbon emission and control. Out of these, *International Journal of Green House Gas Control*, emerged as the leader with 9.79% and 8.02% contributions in the total publications and citations, respectively.

- Chinese Academy of Sciences and Tsinghua University are the leading research institutes in the mentioned field, with 6.77% and 2.14% contributions, respectively, in the total publications.
- China, USA and England are the main research hubs of the mentioned field, with 21.54%, 15.5% and 5.13% contribution in the total publications, respectively. In terms of citations received, USA leads China.
- Top research fields within the CO₂ capture domain are engineering, energy and fuel and chemistry.
- Over the last 50 years, adsorption technology has been a preferable technique for CO₂ capture, followed by separation and absorption technology. The most promising materials (arranged in descending order of importance) for CO₂ are monoethanolamide, mesoporous silica, polymers, epoxides, graphene, cyclic carbonates, porous carbons, zeolites and alkanolamines.
- Among the fossil fuels that responsible for CO₂ emission, coal is the most widely discussed.
- Use of various nanoparticles and nanotubes is being seen as a very potentially promising topic in future studies in this field. However, scaling up the nanotechnology-based CCS methods is excruciatingly difficult, and so precludes their industrial scale usage. Therefore, a special attention towards up-scaling of nanotechnology-based CCS methods is mandatory.

CRediT authorship contribution statement

Muhammad Nihal Naseer: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Validation, Visualization, Writing – original draft. **Asad A. Zaidi:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – review & editing. **Kingshuk Dutta:** Data curation, Formal analysis, Investigation, Methodology, Resources, Supervision, Validation, Visualization, Writing – review & editing. **Yasmin Abdul Wahab:** Data curation, Formal analysis, Investigation, Project administration, Resources, Supervision, Validation, Visualization, Writing – review & editing. **Juhana Jaafar:** Data curation, Formal analysis, Investigation, Project administration, Resources, Supervision, Validation, Visualization, Writing – review & editing. **Rabia Nusrat:** Formal analysis, Investigation, Software, Visualization, Writing – original draft. **Ibrar Ullah:** Investigation, Resources, Software, Validation, Visualization, Writing – original draft. **Bumjoo Kim:** Funding acquisition, Investigation, Project administration, Resources, Software, Validation, Visualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 6
Recent developments in application of nanoparticles and nanotubes in CO₂ capture.

| Material | Main findings | Ref |
|---|--|--|
| ReO ₂ nanoparticles (NPs) | This study focused on hydrogenation of CO ₂ into methanol, with the main aim of maximizing CO ₂ conversion rate by modifying TiO ₂ catalyst using ReO ₂ NPs. At 200 °C, a conversion rate of 18% and methanol selectivity of 98% were reported. With increasing temperature, the conversion rate was found to increase, while the methanol selectivity got decreased. At 250 °C, the conversion rate and the selectivity of 41% and 64% respectively, was reported. | Gothe et al. (2020) |
| Pd NPs | This study focused on non-reductive CO ₂ conversion process. Pd NPs were synthesized, in the presence of CO ₂ , in glycerol. The study concluded that the presence of supercritical conditions provides the most favorable environment to enhance the catalytic activity (for hydrogenation) of the Pd NPs. | Garg et al. (2020) |
| CeO ₂ NPs integrated with carbon nanotubes | This study proposed a novel integration of CeO ₂ NPs and carbon nanotubes to reduce CO ₂ to formic acid. The study revealed that formic acid can be formed at a pH (0.1 M, HNO ₃) with a historically low overpotential of −0.02 V and Faradic efficiency of 65%. The proposed integration study stands out in terms of low overpotential, low toxicity and cost effectiveness. | Valenti et al. (2020) |
| Fe ₃ O ₄ NPs | In this study, the author employed Fe ₃ O ₄ NPs on amines in different configurations to study the CO ₂ adsorption characteristics. The study revealed that introduction of Fe ₃ O ₄ NPs increased the CO ₂ absorption capability by 34.23% in comparison to water and 17.61% in comparison to nonfunctionalized Fe ₃ O ₄ . Additionally, the observations suggested that functionalization using NPs caused enhancement of the overall stability of Fe ₃ O ₄ , as compared to the unfunctionalized Fe ₃ O ₄ . | Elhambakhsh and Keshavarz (2020) |
| TiO ₂ NPs | In this study, TiO ₂ NPs were introduced in monoethanolamine to conduct the feasibility check of the reaction for CO ₂ capture. Rotating packaged bed reactor was used in this study to quantify the mass transfer coefficient, and ultimately enhance the CO ₂ capture efficiency. The study revealed that augmentation of the said NPs was in favor of mass transfer and CO ₂ capture. The authors observed that TiO ₂ NPs caused enhancement of the CO ₂ capture efficiency by 26.9–47.8%, while the mass transfer was found to increase by 7.5–96.1%. The study concluded that the application of these NPs to capture CO ₂ is feasible, as it enhances the efficiency. | Dashti and Abolhasani (2020) |
| CaCO ₃ NPs | In this report, a CO ₂ sequestration study was conducted with the aim to produce nano precipitated CaCO ₃ by utilizing industrial waste water. In order to store CO ₂ within the NPs, CO ₂ was bubbled through the solution of CaCO ₃ . | Bayoumi et al. (2019) |
| CeO ₂ NPs | In this study, cordierite ceramics incorporated with CeO ₂ NPs were studied for catalytic conversion of CO ₂ . Five different samples of cordierite were prepared, based on talc, kaolin and vermiculite, with different compositions of the NPs. The study showed that the overall photocatalytic activity of the CeO ₂ NPs was greater than that of the commercially available TiO ₂ P25. | Ambrožová et al. (2019) |
| Sn NPs | This study focused on the of CO ₂ reduction to formate by employing Cu embodied with Sn NPs. The main aim of the study was to increase the catalytic reactivity and selectivity. It was observed through a series of experiments that Cu incorporated with Sn NPs caused substantial increase in the overall CO ₂ reduction rate. In this study, a Faradic efficiency of 92% at pH (0.1 M KHCO ₃) and −0.95 V overpotential was observed. Additionally, the stability of the reaction was observed for about 12 h, and the proposed catalyst was declared as feasible. | Jiang et al. (2019) |
| Chitosan-grafted multiwalled carbon nanotubes | This study, for the very first time, reported a novel method for CO ₂ capture and chemical fixation. The study was conducted in a series of experiments to find the best CO ₂ capture method, using untreated chitosan, chitosan-grafted multiwalled carbon nanotubes and functionalized chitosan-grafted multiwalled carbon nanotubes. The experimental results proved that the CO ₂ capture capacity of the chitosan-grafted multiwalled carbon nanotubes was much higher than that of chitosan alone, while the capacity of the functionalized chitosan-grafted multiwalled carbon nanotubes was much higher than its unfunctionalized version. | Hsan et al. (2020) |
| Titanate nanotubes | In this study, titanate nanotubes modified with amines were analyzed for their possible applications in the selective absorption of CO ₂ . In this modified absorbent, nanotubes serve as a mesoporous material that caused significant increase in the CO ₂ uptake, capture and selectivity. At 1 bar pressure and 313 K temperature, a CO ₂ uptake of 44.5 mg g ^{−1} and a selectivity of 55% was observed, which was substantially high as compare to the literature. | Heo et al. (2019) |
| N-doped carbon nanotubes | In this study, N-doped carbon nanotubes were developed and analyzed for their possible applications in the CO ₂ capture domain. These nanotubes were developed by coating 3-aminophenol/formaldehyde resin on the external surface of silica tubes. The experimental investigation revealed that the proposed adsorbent caused an increase in the CO ₂ capture capacity by 50%. Additionally, these nanotubes were found to be stable and possessed high aseptic ratio, which shall be very useful in their future applications. | Wang et al. (2019) |

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