Nanomaterials improving CO₂ removal efficiency in membranes: A systematic review

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Abstract: Separation processes with membranes stand out in applications for removing CO₂ from gaseous mixtures due to industrial, environmental and energy demands. The membrane must then be designed to allow high gas flow, high selectivity and chemical and mechanical stability under operating conditions of feed composition, pressure and temperature. Hybrid materials based on carbon materials - carbon nanotubes and graphene oxide - and polymers - cellulose acetate, polyamide, polyimide and polyether block amide - are presented as new types of studied membranes that present promising results in gas separation. An attempt to study a systematic analysis was carried out and despite not achieving adequate results in the literature, it is possible to infer a potential application of carbon nanotubes and graphene oxide in polymeric matrix as nanofillers that improve CO₂ removal.

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Keywords: “CO₂ separation”, Nanofillers, Membranes, MMM, Statistical analysis, Bibliometrics, Data analysis

Adherence to the BJEDIS’ scope: This work is closely related to the scope of BJEDIS as it presents bibliometric research and systematic-analysis regarding the nanofillers improving the CO₂ removal efficiency in membranes.

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1. INTRODUCTION

The rapid pace of global industrialization, the intense exploitation of fossil fuels, and the huge amount of CO$_2$ released into the atmosphere have drawn attention to environmental issues such as global warming, and rising sea levels (1). Currently, the removal of CO$_2$ from such gases is performed by pressure swing adsorption, amine-based absorption, and cryogenic separation, but these techniques have disadvantages such as high initial and operational investment (2).

Membrane technology has received attention due to its energy efficiency, economy, scalability, and manufacturing simplicity. Among the different types of membranes, polymeric membranes have several advantages. The most notable observation regarding polymeric membranes is their low cost, good permeability, and simple operation (3).

Figure 1 illustrates the gas separation provided by the gas concentration differential between the two sides of the membrane. This difference in concentration is typically expressed, and in practice is realized, in terms of a pressure differential between the high-pressure side ($P_{\text{feed}}$) and the low-pressure side ($P_{\text{permeate}}$) of the membrane. In this model, gases are adsorbed on the high-pressure side of the membrane, diffused through the membrane with thickness $l$, and then desorbed on the low-pressure side of the membrane (4).

![Figure 1](image)

**Figure 1.** Separation of gases in polymeric membranes through the mechanism of adsorption, diffusion and desorption of gas molecules through a membrane with thickness $l$ (4). Copyright, 2016, MDPI.

State-of-the-art polymer materials for carbon dioxide separation are cellulose acetate, polyamide, polyimide and polyether block amide (PEBAX). Among these materials, cellulose acetate has a high carbon dioxide to methane selectivity, but low carbon dioxide permeability. In general, polyamide, polyimide, and PEBAX membranes, when they present higher permeability values, are accompanied by a decrease in the selectivity of carbon dioxide in relation to methane or nitrogen. Thus, these two characteristics, permeability and selectivity, are fundamental for a better competitiveness of a membrane of the mixed matrix (MMM) in relation to polymeric membranes. The permeability of the polyimide to carbon dioxide, for example, can be further improved by the introduction of fluorne. Another example, poly(dimethylsiloxane) (PDMS) rubber polymer has excellent permeability as well as lower carbon dioxide selectivity. Copolymers such as polyurethane urea elastomer (PUU) and PEBAX also show high permeability and low selectivity of CO$_2$/N$_2$ and CO$_2$/CH$_4$ (4).

There is a demand to establish new polymeric membrane compositions that improve CO$_2$ removal performance. In this phase of pure polymer replacement, several types of nanomaterials, such as carbon nanotubes (CNTs), carbon molecular sieves, zeolites, graphene oxide (GO) and organic metallic structures have already been proposed in polymeric matrices, which resulted in MMMs (3). In MMMs, porous fillers can build fast gas transport channels, expand polymer chain spacing and increase CO$_2$ permeability. Commonly used porous fillers can be classified into 1D nanomaterials, as in the case of CNTs, 2D nanomaterials, as in GO, and 3D nanomaterials, as in the organic metallic structure (2).

As proved next in this work, CNT and GO are the most relevant nanofillers in this subject. These nanomaterials can contribute individually or simultaneously in a polymer matrix to remove CO$_2$. Figure 2 illustrates how the simultaneous incorporation of carbon nanotubes and graphene oxide in the polymer matrix Matrimid® facilitates the
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diffusion of CO$_2$ in detriment of CH$_4$ and N$_2$. This behavior is because CO$_2$ (3.30 Å) has a smaller kinetic diameter than N$_2$ (3.64 Å) and CH$_4$ (3.80 Å) (5).

Selectivity has a direct impact on the recoverability of a given component and an indirect impact on the required membrane area and the required feed rate. While permeability, on the other hand, determines the direct amount of membrane needed for a given flow rate (5).

Taking into account the increase in scientific publications by leading authors and journals on the subject recently, the understanding of membranes for CO$_2$ removal is promising. This work describes a systematic review and an attempt to perform a systematic analysis of nanomaterials that improve CO$_2$ removal through membranes. For this purpose, the available literature was collected following a specific search in the SCOPUS database, allowing to perform a bibliometric analysis. Different tools were used for document filtering and graphical representation of the obtained results. The results were classified as acceptable or unacceptable based on the CO$_2$ permeability and CO$_2$/ (N$_2$ or CH$_4$ or H$_2$) selectivity variables and how these two characteristics vary with the composition of MMM. In addition, the documents must present the standard deviation and the number of experiments to obtain the data provided. Limitations regarding the development of methodologies were observed. The obtained results drove up the conclusion that membranes filled with CNT and GO represent a considerable number of studies on improving membranes for CO$_2$ removal.

2. MATERIALS AND METHOD

All the steps of this study were derived from a question: “Do nanomaterials improve CO$_2$ removal efficiency in membranes?”

2.1. Articles search

Research articles containing the search key: TITLE-ABS-KEY (membrane AND nano* AND improv* AND "CO2 separation") AND (LIMIT-TO (DOCTYPE, "ar")) were collected using the SCOPUS database, all review articles were excluded from the search under this key. More specifically, 155 scientific articles were collected between 2008 and 2021. The number of articles published per year was plotted using the QtiPlot software. For this graph, articles published in 2021 were excluded, as the final number of articles has not yet been consolidated for the whole year. The survey was performed on July 5, 2021.

2.2. Scientific scenarios evaluation with VOSviewer

The documents were classified by their number of citations. The bibliographic information of the documents containing the abstract, the author's keywords, and the index's keywords were exported as RIS files and opened in the VOSviewer software (version 1.6.10). Different trending topics and themes were identified. Then, the search was refined using the following search key: TITLE-ABS-KEY (membrane AND nano* AND improv* AND CO2 AND separation AND graphene OR "carbon nanotub") AND (LIMIT-TO (DOCTYPE, "ar")), the terms "graphene" and "carbon nanotube" were inserted. This research produced 112 documents from 2007 to 2021.
2.3. Data Extraction

The articles were analyzed according to the following criteria: presence of CO₂ removal efficiency data, varying with the membrane composition. Besides, the documents must present the standard deviation, and the number of experiments to obtain the presented data. Based on the inclusion criteria, information from all eligible publications would be extracted. However, the objective with this data search was not achieved due to the lack of data contained in the tables, graphs under conditions of the same membrane composition or due to lack of information regarding the standard deviation or the number of repetitions of each experiment or the same conditions of operation to obtain the CO₂ removal efficiency curves. Therefore, no meta-analysis was conducted and this study is limited to presenting the trends observed in the analyzed field of study.

3. RESULTS AND DISCUSSION

Searches in the database followed the previously presented flow of criteria. The first generic search returned 153 scientific publications in the research article format. Figure 3 demonstrates the incipient but growing interest in the topic. Furthermore, after 2013, there is a trend toward a linear increase in interest in this topic, indicating that, in a few years, someone will be able to return to this subject, extracting new data and performing a meta-analysis for a better understanding of the structure-property relationships of these materials as a function of matrix/nanofillers combinations.

Figure 3. Number of publications per year according to the first search criteria indicated in item 2.1.

3.1 Evaluation of scientific scenarios with VOSviewer

A second search key including the terms "graphene" and "carbon nanotube" was tested. This analysis was possible due to the identification of keyword clusters in the bibliographic map provided by the VOSviewer software (version 1.6.16), as shown in Figure 4.
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Figure 4. Word map generated by VosViewer by the first search key pointed out in item 2.1.

VOSviewer made easier the understanding and interpretation of the network patterns related to the topic studied. A network map of trending topics was prepared using keywords and abstracts. The size of the circle represents how often a keyword appears. The distance between circles indicates their correlation. Fifty items, among the three clusters, were found. Figure 5 complements Figure 4 by presenting the densities of each word or term highlighted in the cluster map.

Figure 5. Density map generated in VOSViewer according to the search performed in item 2.1.
The visualization of Figures 4 and 5 evidenced studies focused on evaluating the permeability of CO$_2$, the use of MMMs, possible materials used in matrix membranes such as GO, CNT, PEBAX, as well as characterization techniques such as XRD, FTIR, SEM, TGA and involved gases in the separation of CO$_2$ as N$_2$ and CH$_4$. We opted for a new search consisting of the terms: “graphene” OR “carbon nanotub*” and retrieved 112 articles (Table 1). These articles compose the results of bibliometrics, which were analyzed in the systematic review phase.

From the bibliometric results, a systematic review step was conducted in each of the 112 articles, following the criteria previously established in the methodology section. This phase tried to identify useful statistical data for systematic analyses, such as CO$_2$ removal efficiency, membrane composition, either by the increment of GO or CNT, standard deviation or error bars. At this stage, however, no articles were found containing the necessary data, avoiding proceeding to the systematic analysis.

Gas separation processes require low energy consumption for processing large volumes of gases. MMMs are able to simultaneously improve the high gas flow without losing the selectivity of the main component of the process: the membrane. Thus, mixed matrix membranes containing graphene oxide and carbon nanotubes present very promising studies for CO$_2$ removal processes.

CONCLUSION

This work describes a systematic review and an attempt to perform a systematic analysis on nanomaterials that improve CO$_2$ removal using membranes. The search for scientific articles was standardized and evaluated according to the most frequent terms, which led to a more restricted search result. All 112 studies were systematically analyzed and classified according to data to assess the removal of CO$_2$ in polymer matrices consisting mainly of graphene oxide and carbon nanotubes. With this search for articles, it was impossible to obtain enough data to carry out the proposed systematic analysis. It is clear that the studies and proposals of membranes modified with graphene oxide and carbon nanotubes are in their initial phase of the study, but the impossibility of conducting the systematic analysis does not distort the importance of these nanomaterials it shows that it is a study front, which will grow even more in the coming years.

Sample CRediT author statement

Vinicius Freitas Caetano: Conceptualization, Methodology, Data analysis and Writing-Original draft preparation.
Priscila Simões Teixeira Amaral Paula: Methodology, Data analysis and Revision. Fernando G. de Souza Junior: Conceptualization, Methodology, Data analysis, Revision and Supervision.

Conflict of interest: None

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ANNEX

Table 1 – 112 articles were selected in the search with the terms: "graphene" OR "carbon nanotube*".


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