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Membrane contactors for CO_2 capture processes – critical review

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Abstract:
The use of membrane contactor in industrial processes is wide, and lately it started to be used in CO_2 capture process mainly for gas purification or to reduce the emission. Use of the membrane contactor provides high contact surface area so the size of the absorber unit significantly decreases, which is an important factor for commercialization. The research has been caried out regarding the use of novel materials for the membrane production and absorbent solution improvements. The present review reveals the progress in membrane contactor systems for CO_2 capture processes concerning solution for ceramic membrane wetting, comparison study of different polymers used for fabrication and methods of enzyme immobilization for biocomposite membrane. Also information about variety of absorbent solutions is described.

Keywords: membrane contactors, CO_2 capture, polymeric membranes
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1 Introduction

The content of carbon dioxide in the atmosphere has increased since the industrial revolution (started in 1750) by 40 % according to The International Panel of Climate Change (Figure 1) [1]. The major human activity sources of CO_2 emission are power and industry sectors, which generate 60 % of total emission. Burning fossil fuels in power plants, oil refineries and other large industrial facilities release the biggest amount of carbon dioxide to the air. Besides the combustion, emission occurs during petrochemical processes, manufacture of metals from ores with use of carbon, thermal decomposition of limestone in cement production and fermentation process in alcohol making. Even if natural sources of CO_2 emissions are larger than human, increased content of carbon dioxide affects the balance in nature and causes the climate change [1]. More than 100 countries have adopted a global warming limit of 2 °C or below as a guiding principle for it mitigation efforts to reduce climate change risks, impacts and damages [2]. Unfortunately, simulations shows that even though the emission will stop, the consequences will be an irreversible change for 1,000 years after, such as atmosphere warming, precipitation changes or sea level rise [3].

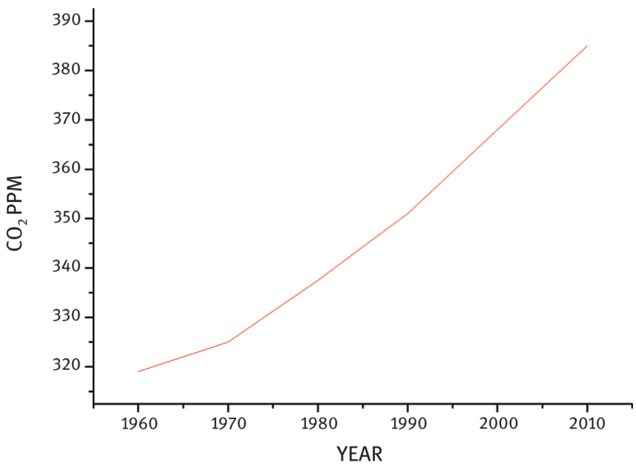

Figure 1: Chart showing the increase of atmospheric concentration during years 1958–2010 [1].

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The CO_2 capture is an efficient process if we are taking into consideration a CO_2 emission source with its high concentration. In order to contribute to the wellness of the environment, few ways of the elimination of the CO_2 excess from the air were proposed, like the use of algal cultures and sea weed as negative emission technologies [4] or use of CO_2 captured directly from the air as reagent in green synthetic strategy [5]. Due to low efficiency, the low-concentration carbon dioxide capture process is still a rarely discussed subject and requires development.

Very effective and widely commercially used during flue gas purification CO_2 capture method is the amine base scrubbing [6]. Amine-based system uses the chemical absorption of CO_2 into metanolamine. It takes place in a two-compartment system: first CO_2 from the flue gas stream is absorbed in the absorber and then desorbed in stripper as concentrated gas so the amine is regenerated. The heat needed for desorption is very high and it is the most expensive part of the process. Nevertheless, researchers are coming with new ideas constantly searching for improvements.

There are a number of patents released during the last decade with inventions concerning CO_2 removal from the gas streams by precipitation techniques [7–9] or by separation with membranes [10–14]. The absorbent systems for removing CO_2 from exhaust gases by precipitation consist of absorbents such as a mixture of amine and amino acid salts (AASs), metal oxides or bicarbonates which are contacted with CO_2-containing gas stream, what results in a precipitation of different solids. The bicarbonate salts are then withdrawn from the absorber compartment and regenerated in desorber by for example applying heat. The inventors claim that the CO_2 capture efficiency is higher than conventional amine scrubbing with higher CO_2 removal ability per cycle and less solvent vaporization loss. The membrane technology used for CO_2 capture is based on the separation processes in mixed gases – CO_2/N_2 and CO_2/CH_4 in flue gas and nature gas. The inventors have come up with new composite materials for the membrane preparation, e. g. polyimide-poly(ethylene glycol) copolymer membrane, polyvinylamine/polyaniline mixed matrix membranes or a metal organic framework membrane among the others. Membranes work as selective barriers which allow the passage of CO_2 and contribute to the formation of CO_2 reach permeate on the other side.

Fixed CO_2 can be later used for several applications and further processes depending on its form. For example, precipitated product can be used as a material for a construction, cement, or to produce aggregate so the CO_2 cannot escape back to the atmosphere. Whereas a pure, gaseous product is used in chemical synthesis. The scientific world notes the potential use of the CO_2 as a source of green energy production, especially being interested in recycling of the carbon dioxide by its conversion to the methanol or hydrocarbons and further use of it as a fuel in e. g. direct methanol fuel cell [15].

Lately, use of membrane contactors found interest due to a possible decrease of the absorber unit size and as a consequence, lower prize of the system production and exploration. This review focused on the use of gas–liquid membrane contactor systems in CO_2 capture processes. We summarize the state of art in the technology including novel materials and process improvement approaches. Three different membrane types – ceramic, polymeric and biocomposite, as well as variety of absorbents solutions – are presented.

2 Membrane contactors

Membrane contactors (Figure 2) are used in separation processes due to a number of advantages, e. g.: they provide large gas–liquid contact area which helps reducing the contactor size and weight, they are easy scale-up and have compact configuration, what's more the driving force is a difference in the concentration gradient; thus there is no need to apply pressure and this excludes flooding problem.

Selection of compatible membrane and absorbent is crucial for the efficiency of the system. The membrane has to be stable chemically and physically so it will not undergo degradation. But the most important factor is overcoming the wetting problem. It is true that high porosity and the open structure are good for the flux; unfortunately they can contribute to the membrane wetting. For a proper performance, membrane pores should stay dry and open for the gas, because it helps to keep the large contact area (Figure 3). Thus, the best solution is to choose the membrane with high hydrophobicity and the absorbent solution with high surface tension. Besides, absorbent should exhibit high affinity to the gas so its gas absorption capacity will be high as well as the selectivity and it should be also compatible with the rest components of the system having e. g. non-corrosive properties. Whereas, the membrane mostly has to provide high gas permeability by having large open spaces within the structure.

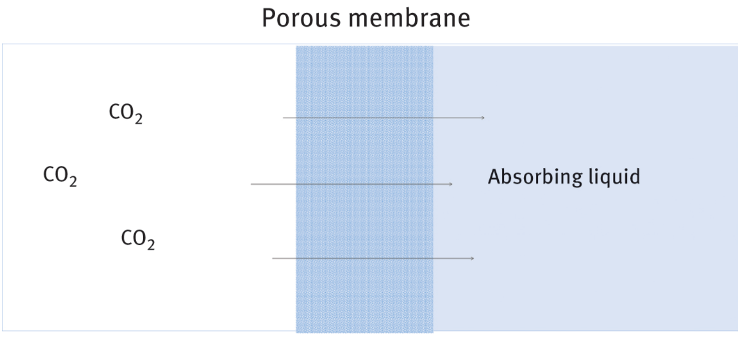

Figure 2: Schematic representation of gas–liquid membrane contactor for CO_2 capture.

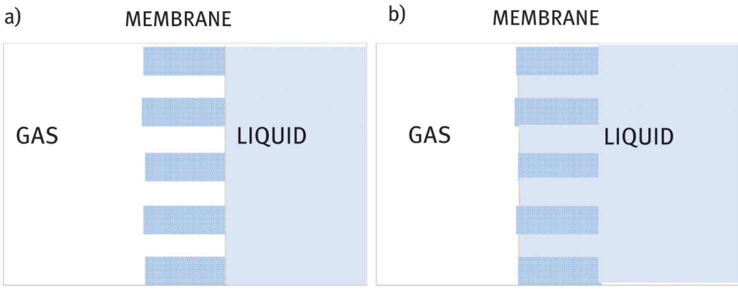

Figure 3: Gas–liquid membrane contactor in dry (a) and wet (b) modes. The contact surface area is marked with red color.

3 Membranes

3.1 Ceramics

Ceramic membranes possess superior chemical and thermal stability over polymeric ones. The most common materials used for the fabrication of ceramic membranes for the CO_2 capture systems are metal oxides, especially alumina and silica. Unfortunately, hydroxide groups situated on their surface results in high hydrophilicity of the material. Thus, the researchers are focused mostly on improvement of the membrane hydrophobicity in order to overcome the wetting problem and come with new superhydrophobic ceramic (SC) membrane contactors. The fluoroalkysilane (FAS) grafting is the method usually used for the hydrophobicity improvement. The FAS reacts with OH-groups from e. g. silica and increases the surface hydrophobicity (Figure 4).

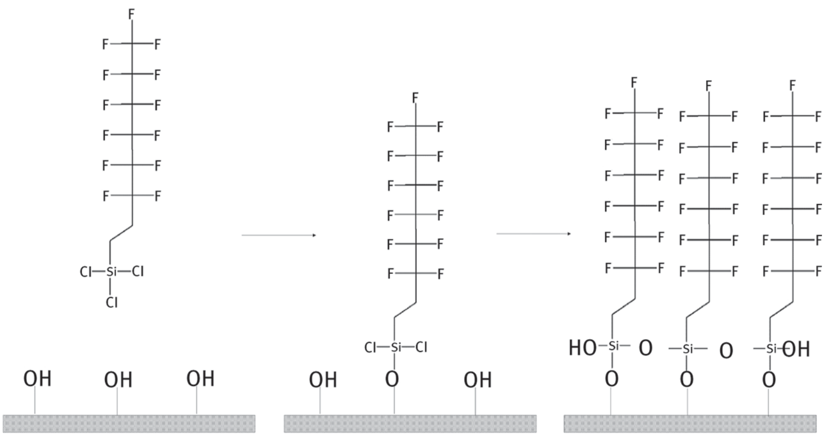

Figure 4: Exemplary reaction of surface hydroxyl groups with fluoroalkylsilane.

For instance, Magnone et al. [16] performed the grafting directly on an alumina hollow-fiber membrane contactor with a high-symmetric distribution of morphological elements. The modified membrane achieved a CO_2 absorption flux of about 5.4×10^{-3} mol/m^{2}s at room temperature with a single-symmetric ceramic membrane, which is considerably higher compared to other conventional polymeric membrane for CO_2 absorption into MEA solutions.

Lin et al. [17] reported that pore wetting by amine solution was decreasing CO_2 absorption flux into an alumina membrane. The author's approach consisted in coating the macroporous alumina tubular membrane surface with mesoporous silica aerogel by sol-gel reaction and shrinking of the pore size. Afterward, the membrane undergoes grafting with FAS. The achieved contact angle with four grafting reached the value of 139 degrees showing the improvement of the membrane hydrophobicity. Prepared membranes have high CO_2 flux 0.6 $mmol/m^2s$ and were stable for 24 h. Compared to the analogue flat membranes, the tubular membranes provide a larger surface area, which results in higher CO_2 recovery up to 100 %.

Another material for SC preparation is a mullite ($3Al_2O_32SiO_2$), which combines alumina and kaolin. Abdulmunen et al. [18] proposed the preparation of grafted kaolin–alumina hollow-fiber membrane. Using low-cost materials, provides obtainment of membranes with high porosity and hydrophobicity what contributes to a high performance. The membrane was prepared by extrusion and sintering technique from a suspension of kaolin and alumina mixture followed by grafting with FAS with a contact angle of 142 degrees.

In order to overcome the wetting and the fouling problem in liquid gas membrane contactor systems, Yu et al. [19] fabricated the SC membrane from alumina tube with ZrO_2 which was followed by grafting. The authors suggested also a periodic drying of the membrane to ensure constant and high CO_2 removal efficiency. The ceramic membrane is considered as a cheaper material, which gives improved results and has anti-wetting and anti-fouling features, thanks to the drying. After being grafted with FAS, the ceramic membrane exhibited a contact angle value of 153° and a slightly lower permeance because the grafted FAS reduces the pore size of the membrane.

3.2 Polymers

Comparison between different polymeric membranes was done by Fabien Porcheron and the group. The authors studied a number of polymers: polypropylene (PP), nylon, polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF). Studies show that the membranes are hydrophobic; unfortunately, they notice the decrease of contact angle up to 0 degrees on nylon and PVDF after aging with absorbent solution in high temperature for 1 week. The results are in agreement with thermogravimetric analysis (TGA), thermomechanical analysis (TMA) and infrared spectroscopy (IR) analysis, where only PP and PTFE membranes did not reveal any changes caused by aging. Gas permeability test shows that the more porous is the material the better results it gives. According to the researcher, the PTFE membrane provides the best performance with high efficiency among the studied materials, due to its structure and stability [20].

The main studied section in the field are materials, mainly new materials for membrane preparation or improvements of existing ones. The most important membrane feature to improve in gas–liquid contactors operation is its hydrophobicity. A research group from China was trying to achieve it, incorporating graphene nanosheets into PVDF membrane. The modification induced a more porous sublayer structure, where the particles were visible and the surface roughness increased. Thus, contact angle increased only on the bottom surface. The hybrid membrane enhances the CO_2 absorption only when the more hydrophobic surface was facing the absorbent. The wetting problem was overcome so the long-term efficiency of system was achieved [21].

Fashand et al. [22] decided to use PVC for the first time in the gas–liquid contacting process for CO_2 capture. The relatively cheap material provides membrane with high hydrophobicity and a structure adequate for its use in the process, such as large macrovoids and reduced wall thickness. Thanks to good processability, high absorption efficiency was achieved by optimization of take-up speed during spinning process.

Besides concentrating about materials, researchers are concerning also the use of different modules. There is a theoretical study treating about the difference in CO_2 removal performance by flat-sheet membrane contactor (FSMC) and hollow-fiber (HFMC) polymeric membrane contactor with use of amine aqueous solutions. For the studied conditions, FSMC showed better results. Nevertheless, the authors admit that before choosing a suitable module a number of factors should be considered, such as membrane properties and operating parameters [23]. Francis Bougie and Iliuta [24] have studied the possibility of use of more than one FSMC for CO_2 removal from a gas mixture. The author designed an experiment, which consists of connecting up to three polymeric membrane contactors, so the outlet absorbent liquid was directed to the inlet of next compartment. Generated results indicated that there is a proportional increase in the CO_2 flux with the number of membranes. Moreover, the authors demonstrated that there is a possibility to add as many membranes as needed to achieve the absorbent solution saturation.

3.3 Biocomposite

According to Fick's law, increase of local CO_2 concentration on the membrane side will result in enhancing the CO_2 absorption by the system. To achieve it, scientists are modifying the membrane surface, by for example incorporation of biomolecules. Most commonly used enzyme for CO_2 capture studies is carbonic anhydrase. The protein is situated in leaf and it is responsible for catalysis of CO_2 hydration (1) for photosynthesis. Besides, we can find it in blood, where it helps to keep the pH balance. The catalyzed reaction involves two-step mechanism. The first step (2) is the nucleophilic attack of a zinc-bound hydroxide ion on CO_2. The second step (3) is the regeneration of the active site by ionization of the zinc-bound water molecule and removal of a proton from the active site.

$$CO_2 + H_2O \leftrightarrow HCO^{3-} + H^+ \tag{1}$$

$$Zn^{2+}OH^- + CO_2 \leftrightarrow Zn^{2+} + HCO^{3-} \tag{2}$$

$$Zn^{2+} + H_2O \leftrightarrow H^+ + Zn^{2+}OH^- \tag{3}$$

Unfortunately, the biomimetic systems suffer one main disadvantage: enzyme incorporation into a synthetic support usually results in decrease in its activity caused by, among the others, structural or functional changes. The researchers are applying different incorporation techniques to overcome this issue.

One option is use of nanoparticles to covalently bond the enzyme. This approach was investigated by Jingwei Hou et al. [25] Biocatalytic TiO_2 nanoparticles with covalently immobilized carbonic anhydrase were used to prepare superhydrophobic PP membrane by sol–gel coating and surface modification with perfluorodecyltriethoxysilane (PDTS). Results showed that enzyme remain high in activity and the biocatalytic membrane contactor exhibits reusability of 10 cycles.

Another method, used by Joel K. J. Yong et al. [26], includes the electrostatic adsorption of carbonic anhydrase by layer-by-layer assembly on polimeric membrane surface. The films were applied to the shell side of the hollow-fiber membranes by static mode where membrane remains in solution and by forcing polyelectrolites across the membrane. Results show the formation of thin films only on the surface, without penetration to the inside pores. This caused another improvement – the pore wetting was significantly reduced and finally the CO_2 hydration was enhanced in all examined cases.

Ya-Tao Zhang et al. [27] studied the performance of membrane reactors consisting of PVDF hollow-fiber membranes aligned parallel with nanocomposite hydrogel with immobilized CA between them. As the porous network of the hydrogel contained free water, which is crucial for proper functioning of the enzyme, the enzymatic activity remained up to 76 %. The obtained reactor effectively separates CO_2 from mixed gas streams of low concentration with 30 h of durability.

4 Absorbents

Absorbents are playing a crucial role in membrane contactor systems as they are the only selective part of the compartment and the effectivity of the system depends mostly on the affinity of the liquid to CO_2. A number of solutions were studied (Figure 5), especially bases and amines and their salts, but monoethanolamine solution is still the most commonly used reference absorbent.

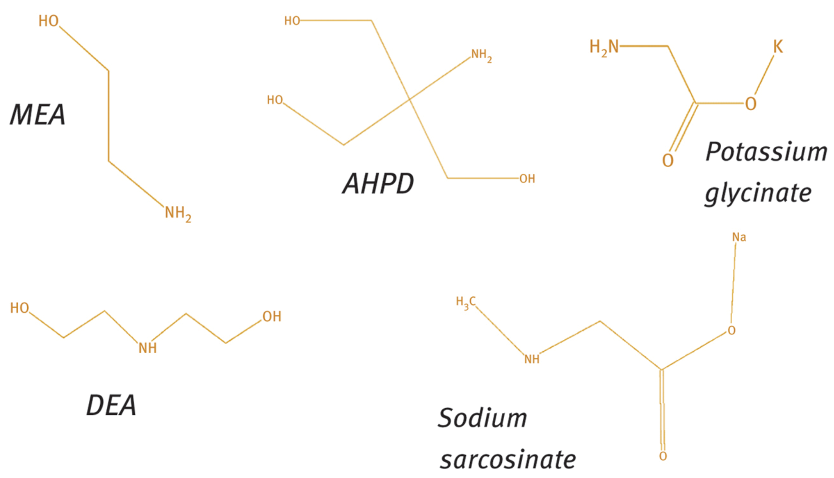

Figure 5: Amines used in CO_2 absorption studies.

The theoretical study conducted by Subham Paul and the group [23] about the use of single and blended amines, considering aqueous solutions of MEA, DEA, MDEA and AMP, as absorbent solutions for CO_2 capture by FSMC, proves that MEA has the highest absorption flux rate among single amines and the increase in its concentration in blends results in increase of absorbtion rate as well.

The use of aqueous amine solution was investigated also by Francis Bougie and Iliuta [24], who incorporated piperazine (Pz) as activator of CO_2 removal from CO_2/N_2 gas mixture by aqueous 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) in polymeric FSMC comparing his results with MEA solution. Pz is a secondary diamine activator, which has a good absorption and regeneration capacity and, thanks to its high surface tension, has a potential to decrease the membrane wetting. The activated absorbent solution showed better performance than single AHPD solution, but similar absorption flux for MEA solution.

AASs such as potassium glycinate, sodium glycinate, potassium sarcosine and sodium sarcosine, were compared with MEA and NaOH by Nihmiya Abdul Rahim and Al-Marzouqi [28]. The AAS solutions show better CO_2 absorption performance unfortunately only in low molar ratios, because decreased pH enhances the release of CO_2 reaction.

Muhammad Saeed [29] used zinc complex to promote the K_2CO_3 absorption in a contactor system. The Zn–cyclen complex is mimicking carbonic anhydrase (the enzyme mention in biocomposite membrane section), but according to the studies it is more stable and has a longer lifetime compared with the natural enzyme. Promotion of the absorbent results in a 10-fold improvement of the adsorption rate.

5 Conclusions

In this review, we revealed the current state of art of membrane contactors for CO_2 capture technology, covering different membrane materials, hydrophobicity improvements methods and process efficiency enhance approaches including the use of biological molecules and summary of absorbent solutions in use.

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