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Ambient CO_2 adsorption via membrane contactors – Value of assimilation from air as nature stomata

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ABSTRACT

Biomimetic systems represent one of the most attractive ways to produce artificial complex devices taking the best from nature in a simple and repetitive manner. Some of these systems can imitate trees in some of their functions, in this article, the objective is to imitate trees in their ability to fixate CO_2 and use it to produce organic compounds. As trees do that fixation after the penetration of the gas though the smart pores of the leaves, stomata, we call our pores as artificial stomata. The project aims to end up with compact systems for small size devices that would work with autonomy in the near future in energy systems. Polysulfone based membranes were prepared by a Phase Inversion Precipitation method using different polymeric solutions (N,N-Dimethylformamide or 1-Methyl-2-pyrrolidone). Obtained asymmetric fingerlike, droplike, or spongy morphologies were characterized: by SEM and ESEM equipped with EDX, while their surfaces were investigated by: AFM, dynamic and static contact angle, swelling measurement. Moreover, copper - ferrite nanoparticles, used for preparation of composite membranes was characterized by TEM, and X-ray diffraction. Their influence on material CO_2 solubility, membrane surface morphology and wettability were deeply investigated, and demonstrated influence of membranes roughness on their performance. Furthermore, generated results reveled higher CO_2 assimilation than the natural stomata and shown very high CO_2 absorption flux (67.5 mmol/m^2*s).

1. Introduction

The content of carbon dioxide in the atmosphere has increased by 40% since industrial revolution, which started around year 1750 and reached ta value of 400 ppm in 2010 [1]. CO_2 Emission occurs mainly during fossil fuel combustion, petrochemical processes, manufacture of metals from ores with use of carbon, thermal decomposition of limestone in cement production and fermentation process in alcohol preparation. Even if natural sources of CO_2 emissions are larger than human, increased content of carbon dioxide affects the balance in nature and changes the climate. Due to warming of the atmosphere, Earth surface and oceans, ice sheets are losing mass and see level is rising. On the other hand, oceans absorb most of CO_2 what cause its acidification [1]. There are few ways for reduction of the emissions like reducing the energy consumption or increasing use of natural renewable energy sources, but in order to eliminate or recirculate the CO_2 that already exists in atmosphere, it has to be captured. The best approach is to take the inspiration from the nature, which since billions of years is improving the CO_2 capture process in photosynthesis by leaves. The mean organs used to control the gas exchange in leafs are stomata. Stomata are small adjustable pores situated on the leaf surface and during photosynthesis it allows CO_2 to diffuse into the leaf [2]. According to Nature [3] stomata are small pores on the surfaces of leaves and stems, bounded by a pair of guard cells, that control the exchange of gases - most importantly water vapor and CO_2 - between the interior of the leaf and the atmosphere. Very recently Chi Hoon Park et al. [4] reported a study concerning a concept of self-humidifying membranes analogous to vapor exchange mechanism of stomata. By deposition of a thin hydrophobic layers with narrow water channels with controlled thickness and morphology, author obtained a nanocracked surface which opens under humidifying conditions allowing water and ion molecules to pass. Whereas, our approach is focused on the stomata role in CO_2 assimilation process. Currently CO_2 capture processes are using physical or chemical solvents and membrane technology. Recently, new hybrid systems that combine membranes and absorbent solutions have been developed [5,6]. These are a very compact systems, where the

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membrane contactor is a gas permeable barrier between liquid solutions and gas [7]. This hybrid system, named as membrane contactor, combines an advanced membrane with an effective absorbing aqueous solution. The selective sorbent performs as the separator function, while the membrane facilitates the mass exchange process by expanding the phase contact surface area [8]. This membrane contactor system mimics the leaf structure for carbon dioxide capture process, where the pores play the role of stomata. Moreover the membrane contactor system possesses the following advantages: (1) it provides large contact surface area between phases, without need to disperse one phase into another; (2) it is modular; (3) it is not sensitive to flooding, channeling or back-mixing; (4) its operational flow rates are wide; (5) the system footprint can be costume designed and modified; and (6) the overall system size is small.

Polysulfone (PSf) has been widely used as a membrane material due to its mechanical strength, thermo-stability, stability against chemicals and relative hydrophobicity [9,10]. Furthermore, the membrane internal morphology is easy to control by simply changing preparation conditions [11]. Because of the above properties, this polymer provides a potential application in the membrane gas absorption processes [12]. Several studies on PSf with different additives have shown that is possible improve CO_2 flux, by modifying morphology and characteristics of the membranes. M. Rahbari-Sisakht et al. investigated the effects of surface macromolecules on the morphology of PSf hollow fiber membrane contactor for CO_2 absorption. They used SMM, macromolecules with an amphipathic structure, with their main chain composed by polyurea or polyurethane polymer (hydrophilic part), which is end-capped with two low polarity fluorine-based polymer (oligomer) chains (hydrophobic part). In this case, also, the results shows that CO_2 absorption flux was enhanced [13].

Spinel materials, such as ferrites, attracted research interest because of their special properties, e.g. catalytic, magnetic, gas sensing, and electronic conductivity [14]. Positively charged copper particles have shown improving influence in copper surface activity what enhances CO_2 complexation. J.H. Lee et al. performed experiments, in which Cu nanoparticles in ionic liquid were applied to CO_2 separation membranes. Experimental results show their good selectivity and gas permeance, and revealed that partially positively charged Cu nanoparticles facilitate CO_2 transport [15]. It is expected that $CuFe_2O_4$ nanoparticles will facilitate membrane contactor absorption properties.

Published studies are mostly focused on CO_2 absorption from flue gas, thus in absorption experiments of pure CO_2 or its mixture with N_2. The approach of the present article is to capture CO_2 from atmosphere, such as photosynthetic organisms do. Therefore, we could describe our research as the development or artificial stomata's (the pores that are present in the leaves of the trees and are responsible from the exchange of gases). The novelty of this study is the use of MC in ambient CO_2 fixation. Flat sheet contactors are less frequently described in the literature than hollow fiber membranes. However, they possess some advantages compared with hollow fibers, for instants they are easy to prepare, characterize, and the module is easy to assembly and scale up. Some authors report the linear relationship between the absorption rate and the liquid flow rate within the module [16]. Besides, CO_2 flux increases directly with of the pore size, which is also related to a decrease in the membrane wetting and, therefore, asymmetric membranes are favorable [17]. The hydrophobic character of the membrane in gas/liquid contactor system was found to be highly important. Studies on influence of polymeric membrane hydrophobicity on CO_2 recovery show an increase of CO_2 flux when membrane hydrophobicity also grows [18]. Membrane wetting causes an enhance on membrane mass transfer resistance. Moreover, absorbents surface tension also has an effect on the membrane wetting, high surface tension can increase the water contact angle [19].

The scope of the work is revealing the influence of polysulfone membrane contactors on atmospheric CO_2 capture rate by chemical adsorption into absorbents aqueous solutions. In this study, polysulfone flat sheet membranes with vary in morphology and with the addition of copper - ferrite nanoparticles were prepared, characterized and tested as contactors for CO_2 absorption flux from ambient air into potassium hydroxide aqueous solutions.

2. Experimental

2.1. Materials

Polysulfone (Mw 35.000 Da) in transparent pellet form; N,N-Dimethylformamide (DMF, 99%); and 1-Methyl-2-pyrrolidone (NMP, ACS) were purchased from Sigma Aldrich and used for flat sheet membrane manufacture. Distilled water was used as coagulation bath in membrane preparation. 2- propanol (99.8%, extra dry) from Acros Organics was added to the coagulation bath in case of preparation of M5. Hollytex non-woven made of polyester with a density of 34 g/m^2 was acquired from *Servicios Tecnicos y Equipamientos para Museos* (Stem) and used as support in the module. Extra pure potassium hydroxide in pellets (Sharlab) was dissolved in deionized water to prepare absorptive solutions. Carbon dioxide ion selective electrode and all needed solutions were purchased form Thermo Scientific: 1000 ppm as $CaCO_3$ standard solution for the calibration, Carbon Dioxide Buffer Solution to adjust solution pH to the operating range of the electrode and the electrode internal filling solution. CO_2 used for permeability and solubility testes was provided Carburos metalicos company, Spain. All chemicals were used without any further purification.

2.2. Membranes preparation

All membranes were prepared by phase inversion precipitation in ambient conditions. The proper amount of polymer was dissolved in an organic solvent and mixed with additives if added. Copper ferrite nanoparticles were prepared according to literature [20]. The resulting solution was stirred for 48 h and left overnight for degasification. Solutions containing nanoparticles were sonicated for 1 h before the membrane preparation. Obtained mixture was cast on a glass with use of casting knife (knife thickness: 200 µm or 250 µm or 300 µm), and immediately immersed into coagulation bath. Membrane precipitates

Table 1
Polymeric solution compositions and membranes preparation parameters.

Membrane	Polysulfone content (%wt)	Solvent (80% wt)	Additive $CuFe_2O_4$ (%wt)	Coagulation bath	Casting knife [µm]
M1	20	DMF	–	Water	300
M2	20	DMF	–	Water	250
M3	20	NMP	–	Water	250
M4	20	NMP	–	Water	200
M5	20	DMF	–	i-propanol:DMF 2:1	250
M6	19	DMF	1%	Water	300
M7	19	DMF	1%	Water	250
M8	19	NMP	1%	Water	250
M9	19	NMP	1%	Water	200