Carbon 126 (2018) 338–345

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

High capacity polyethylenimine impregnated microtubes made of carbon nanotubes for CO_2 capture

Laura Keller [a, b, 1], Burkhard Ohs [a, 1], Jelena Lenhart [a], Lorenz Abduly [a], Philipp Blanke [a], Matthias Wessling [a, b, *]

[a] RWTH Aachen University, Chemical Process Engineering, Forckenbeckstr. 51, 52074 Aachen, Germany
[b] DWI - Leibniz Institute for Interactive Materials, Forckenbeckstr. 50, 52074 Aachen, Germany

ARTICLE INFO

Article history:
Received 4 July 2017
Received in revised form
6 October 2017
Accepted 7 October 2017
Available online 10 October 2017

ABSTRACT

Anthropogenic carbon dioxide emissions cause global warming - one of the major challenges society faces today. Carbon capture technologies can mitigate this development and stabilize the global average temperature. However, to reach their potential, energy efficient processes and new materials are required. In this work, we present a new type of hollow fiber sorbents. Highly porous multi-walled carbon nanotube based (MWCNT) microtubes with a high internal surface area were functionalized with polyethylenimine (PEI) via a wet impregnation method. Their tubular geometry opens up the device design space to control gas distribution and residence time. For low PEI fractions in the impregnation solution, the high surface area and porosity of the microtubes is preserved, and the CO_2 uptake increases with increasing PEI fractions. We observed a maximum CO_2 uptake of 93 mg/g_{fiber} at 20 wt.-% of PEI in the impregnation solution. At higher PEI loadings the CO_2 uptake decreases. Due to the thermal and chemical stability of the PEI sorbent and the CNT matrix, we anticipate the applicability of these microtubes for a wide range of separation processes and operation conditions. Such tubular MWCNT geometries may serve as a scaffold platform to immobilize a functional surface coating inside a controlled nanoporosity.

1. Introduction

Globally, anthropogenic greenhouse gas emissions continue to increase. They were the highest in human history from 2000 to 2010 and reached approximately 49 gigaton carbon dioxide equivalent in 2010 [1]. In 2014, almost one-third of the world's primary energy supply was provided by coal while it accounted for almost half of the 32 Gt CO_2 emissions by fuel combustion [2]. The energy sector is expected to continue to be the primary source of greenhouse gas and CO_2 emissions [1]. Mitigation strategies for greenhouse gas emissions are necessary to hold the global average below +2 °C of pre-industrial levels. Since especially CO_2 emissions from the energy supply sector and the share of coal in the global fuel mix continue to increase [1] measures like the separation and storage of carbon dioxide become indispensable [1,3]. Carbon capture and storage (CCS) is considered a direct emissions mitigation option that buys enough time (around 50 years) for a transition away from fossil fuels [4].

Carbon dioxide can be separated from flue gas streams using sorption processes. Only absorption processes based on aqueous amine solutions are commercially used, but due to cost reasons mainly for CO_2 separation from natural gas [5,6]. Additional to high costs other disadvantages of liquid amine absorption exist, e.g. equipment corrosion or degradation of the solvent [5–8]. Consequently, adsorption processes are considered as an alternative. Solid adsorbents like zeolites [9,10], metal-organic frameworks (MOF) [11,12] or different amine-functionalized solid sorbents (e.g. silica [13,14], nanofibrillated cellulose [15], fly-ash or monolithic porous carbon [16–18], or polymers [19]) are being investigated extensively. MOFs and zeolites are hydrophilic and thus the presence of water in flue gases leads to a decreased CO_2 uptake [20]. Additionally, a large pressure and/or temperature gradient is needed to ensure near complete desorption of CO_2 and to achieve an efficient process performance [7]. Solid sorbents that consist of a supported polymeric amine can have high sorption capacities, fast

---

[*] Corresponding author. RWTH Aachen University, Chemical Process Engineering, Forckenbeckstr. 51, 52074 Aachen, Germany.

E-mail address: Manuscripts.CVT@avt.rwth-aachen.de (M. Wessling).

[1] Contributed equally to this work.

https://doi.org/10.1016/j.carbon.2017.10.023

ad- and desorption cycles and low energy consumption [6,7]. Due to their high selectivity towards CO_2 in mixtures with nitrogen, methane, oxygen or hydrogen even at low CO_2 concentrations [21,22], solid amines are particularly promising for carbon capture from low pressure streams such as flue gas or ambient air. Contrary to MOFs and zeolites, these sorbents exhibit an increased CO_2 sorption capacity when water is present in the gas stream [15,23]. Branched polyethylenimine (PEI) is a common choice because its branched chains have many CO_2 capturing amino groups [24] and it thus offers high CO_2 uptake capacities per molecule [25]. The main reaction occurring between PEI and CO_2 is believed to be the formation of a carbamate ion [26]. Similar to absorption of CO_2 to aqueous amine solutions, this formation is proposed to be a two-stage reaction: 2 mol of amine react with 1 mol of CO_2 via a zwitterion mechanism which is followed by base catalyzed deprotonation of said zwitterion via a second amine group [27–29]:

$$CO_2 + 2R_2NH \rightleftharpoons R_2NH_2^+ + R_2NCOO^- \quad (1)$$

$$CO_2 + 2R_3N \rightleftharpoons R_4N^+ + R_2NCOO^- \quad (2)$$

Typically, solid sorbents are regenerated using low pressures or high temperatures resulting in processes like pressure swing adsorption, temperature swing adsorption or vacuum swing adsorption [30]. In these processes, the gas mixtures usually flow through an adsorption column, i.e. a packed bed reactor, where the sorbent is present in the form of pellets or granules in the size range of several millimeters. A high pressure drop resulting from high gas flow rates at decreasing pellet diameter leads to high energy requirements. Furthermore, packed bed adsorption reactors suffer from a significant mass transfer resistance and undefined flow conditions resulting in reduced product purities and/or recoveries [31]. The delicate balance between desired high amine loading and depressed adsorption kinetics has recently been reported [32].

So-called hollow fiber sorbents are a new modular solution to these limitations. They potentially outperform granular structures due to high geometric surface areas, faster cycle times and high packing densities [31]. Hollow fiber sorbents were first introduced by Feng et al. [33], who showed their potential resulting from lower pressure drops and a lower mass transfer resistance. Additionally, a better flow distribution leads to sharper breakthrough curves and thus higher recoveries. Lively et al. [34] dispersed adsorption particles inside of a hollow fiber consisting of a polymeric matrix. These fibers are produced by fiber spinning technology using both a polymer binder as well as high loadings of a sorbent filler such as zeolites. An additional sheath layer can be formed by a simultaneous co-extrusion process. Low permeability polymers, such as PVDC, are used to prevent a loss of the gas mixture to the shell or the bore side of the hollow fiber sorbent [35]. Finally, a temperature moderator can be used to thermally balance the heat of adsorption and desorption [36].

The impregnation of a functional liquid on a highly porous support structure with a high internal surface area offers several advantages: the high surface area ensures fast adsorption while the thin active adsorption layer leads to a lower mass transfer resistance. Amines have already been immobilized in hollow fibers to increase their sorption capacity [20,37]. However, these systems always comprise a polymer matrix with a) a low internal surface area, b) low adsorption capacity, c) low thermal as well as chemical stability and d) limited thermal conductivity for temperature control. To overcome these limitations and exploit the advantages mentioned before, a different support structure is needed.

We present the first microtubular sorbents based on carbon nanotubes (CNT) (see Fig. 1 (a)). The CNT form a strong and flexible structure [38], very similar to the flat equivalent (so-called buckypapers). Due to this no polymeric matrix with low sorption capacities and a low surface area, as in state-of-the-art hollow fiber sorbents, is required. CNT and thus the microtubes exhibit a high thermal and chemical stability. A functional liquid, in this work polyethylenimine, can be immobilized into the highly porous fiber wall to increase its sorption capacities. Bae et al. [39] proposed the interactions between CNT and PEI to be hydrogen bonding and weak electrostatic interactions. They determined the interactions to be spontaneous and stable under conventional experimental conditions [39]. Different studies have shown good CO_2 adsorption capacities with amine-functionalized CNTs, using multi-walled CNT as well as single-walled CNT [40–42]. Recently, a high sorption capacity of modified multi-walled CNT impregnated with tetraethylenepentamine of 5 mmoL/g (10 vol.-% CO_2 in N_2, 1 vol.-% H_2O) was achieved [43]. Due to the lower cost of multi-walled CNT and potentially similar sorption capacities, they were chosen for this work. In our amine impregnated hollow fibers, the small size of the CNTs ensures fast heat and mass transfer, which are essential for efficient swing sorption processes. The CNT microtubes can be assembled into hollow fiber modules, see Fig. 1(b), and when coated with a gas impermeable layer a temperature moderator can be used on the shell side. Fig. 1(c) shows a lab scale module of several microtubes. Additionally, shorter pieces of microtubes can potentially be arranged into packed beds (Fig. 1(d)). Thus, the shape of the microtubes (e.g. length, diameter) can be tailored as well as the material itself can be functionalized and tailored to a specific application. In this work, the properties of the PEI-impregnated microtubes based on CNT, such as specific surface area and the CO_2 sorption capacity, are reported.

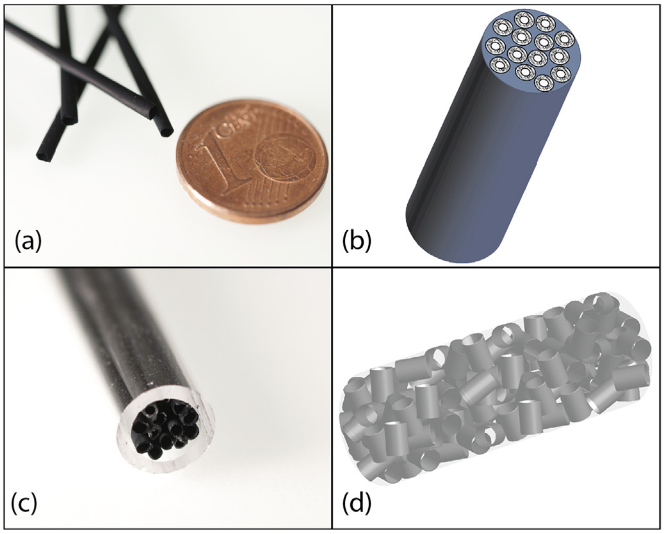

Fig. 1. (a) Photo of CNT microtubes with a coin for size reference, (b) schematic representation of a hollow fiber module with CNT microtubes, (c) photo of parallelized CNT microtubes, (d) schematic representation of a packed bed with short pieces of CNT microtubes. (A colour version of this figure can be viewed online.)

2. Experimental

2.1. Preparation of PEI-loaded CNT microtubes

As described in a previous study, we fabricated microtubes by filtrating a CNT suspension through a microfiltration hollow fiber membrane in dead-end filtration mode [44]. Suspensions of multi-walled carbon nanotubes (MWCNT; outer diameter of 6–9 nm and 5 μm length; purity >95%, Sigma-Aldrich) were prepared by mixing 1 g of CNT, 10 g of Triton-X 100 (Sigma-Aldrich) and 1 L of deionized