



Evaluation of CO₂ adsorption dynamics of polymer/silica supported poly(ethylenimine) hollow fiber sorbents in rapid temperature swing adsorption



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ABSTRACT

Rapid temperature swing adsorption (RTSA) using polymer/silica supported amine hollow fiber sorbents is a new post combustion CO₂ capture methodology that facilitates CO₂ adsorption under nearly isothermal conditions with improved energy efficiency via heat integration. In this work, the dynamic CO₂ adsorption characteristics of polymer/silica supported poly(ethylenimine) hollow fiber sorbents (CA-S-PEI-PI) are evaluated in a bench scale RTSA system. Non-isothermal fibers have breakthrough and pseudo-equilibrium CO₂ capacities of 0.67 mmol/g and 1.03 mmol/g at 35 °C, respectively, under humid simulated flue gas conditions (100% R.H.). Prolonged exposure of the fiber sorbents to water vapor enabled the breakthrough and pseudo-equilibrium CO₂ capacities to increase by 60% and 43%, respectively. Upon the removal of the heat of adsorption by flowing cooling water in the bores of the fiber sorbents, there is a substantial increase in the CO₂ breakthrough capacity, reaching 1.16 mmol/g using simulated humid flue gases. The breakthrough capacity is found to increase 5% upon increasing the adsorption temperature from 35 °C to 45 °C, suggesting improved mass transfer in the fiber sorbent at the higher temperature. The CO₂ adsorption and desorption rates are shown to be very rapid, with CO₂ breakthrough occurring in less than 72 s and the majority of the adsorbed CO₂ desorbing in 5 min. Extensive cycling studies demonstrate that the CA-S-PEI-PI sorbents have good dynamic swing capacities, stabilizing over 60 cycles. A newly developed rechargeable post-spinning amine infusion technique provides the feasibility of recovering the CO₂ adsorption performance of deactivated CA-S-PEI-PI fiber modules, by allowing for straightforward re-infusion of PEI into the deactivated sorbents. Amine-incorporated hollow fiber sorbents have good potential for practical use as scalable, adsorbing heat-exchangers.

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1. Introduction

CO₂ emissions from the combustion of fossil fuels are key contributors to global climate change. To maintain a growing world economy, society will continue to rely on fossil fuels for the next several decades, and therefore CO₂ capture and storage is needed to reduce CO₂ emissions from industrial facilities. The current benchmark technology for CO₂ capture from large point sources, liquid amine absorption, has been extensively studied (Choi et al., 2009;

Rochelle, 2009; Rubin et al., 2012; Song, 2006). However, the corrosive properties of the amine solutions and intensive energy needs of this process drive the search for alternative approaches with lower costs. Solid amine adsorbents have been considered as components of alternative separation processes (Belmabkhout et al., 2010; Bollini et al., 2011b; Hedin et al., 2013; Hicks et al., 2008; Tsuda et al., 1992; Xu et al., 2002) but conventional gas–solid contactors offer significant disadvantages, such as poor heat transfer and high pressure drops in fixed beds (Farooq and Ruthven, 1990a,b; Rezaei and Webley, 2010), as well as high sorbent attrition in looping bed systems (Bollini et al., 2011b).

Structured sorbents of various types based on zeolites and activated carbons have been developed to address the challenges typical of fixed beds, such as activated carbon monoliths (Menard et al., 2005, 2007), laminates (Ojuva et al., 2013; Rezaei et al., 2010) and hollow fiber sorbents (Labreche et al., 2013; Lively et al., 2009, 2012; Rezaei et al., 2013a). A monolithic composite made

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of activated carbon derived from natural graphite was developed by Menard et al. (2005, 2007) to improve thermal management during the CO₂ adsorption process. At lower CO₂ partial pressures, this conductive structured sorbent did not display better adsorption performance than a conventional granular packed bed. In a more recent study, zeolite 13× monoliths with a laminate structure were demonstrated to have high CO₂ capacity as well as fast CO₂ uptake kinetics (Ojuva et al., 2013). Nevertheless, difficulties associated with manufacturing such sorbents make their application in large-scale industrial processes a challenge.

In typical post-combustion capture conditions for coal fired power plants, a scalable, continuous technology must be considered to capture the large volume of flue gases produced. Rapid temperature swing adsorption (RTSA) using structured hollow fiber sorbents, as reported by Lively et al. (2009, 2012), is a novel CO₂ capture technology. There are several advantages associated with this approach. First, compared to conventional cyclic operation processes (e.g.: PSA, VSA, and TSA), the RTSA process employs unique, highly porous structured hollow fiber sorbents that have very rapid CO₂ adsorption/desorption kinetics and high working capacity per unit system volume (Lively et al., 2009, 2012). Consequently, fast cycling times could be achieved in the entire process, thereby reducing equipment size and allowing for efficient utilization of the adsorbents. Second, hollow fiber sorbents act as structured sorbents, and pressure drop through the adsorber column will be lower than for a traditional fixed bed (Lively et al., 2011a). Third, the unique design of hollow fiber sorbents allows for the flow of cooling agents in the bores of the hollow fibers, which is achieved by coating the bore-side of the fiber with a low permeability barrier layer (Lee et al., 2012; Lively et al., 2009, 2011b). The exothermic effects of CO₂ adsorption on the sorbent performance can thereby be minimized (Lively et al., 2012), thus achieving nearly isothermal adsorption in the RTSA process. In addition, the sensible heat of the fiber sorbent module can be substantially recovered, thus driving down the energy cost of capturing the CO₂. This highly heat integrated technique using hollow fiber sorbents results in an overall parasitic load that decreases dramatically compared to liquid amine and chilled ammonia solution sorption systems (Lively et al., 2010).

In the initial proof-of-concept demonstration of this approach, polymer/zeolite composite hollow fiber sorbents were developed (Lively et al., 2009). However, as most zeolites are highly hydrophilic, they do not perform well in hydrated flue gases, with water adsorbing preferentially over CO₂ in most cases (Brandani and Ruthven, 2004; Liu et al., 2010). In this work, we apply the RTSA concept with polymer/silica supported amine hollow fiber sorbents to yield a process that combines the favorable aspects of the RTSA approach with aminosilica adsorbents, which show not only higher tolerance to water, but also higher CO₂ capacities in the presence of water (Bollini et al., 2011b).

There are two classes of polymer/silica supported amine hollow fiber sorbents that have been developed for use in the RTSA process (Labreche et al., 2013; Rezaei et al., 2013a). The acronyms for these fiber sorbents are based on the following format: Polymer-Silica-Amine group-Synthesis method, e.g., CA-S-PEI-PI, where CA represents cellulose acetate, S for silica, PEI stands for poly(ethyleneimine), and PI for post-spinning amine infusion method (Labreche et al., 2013). *Class 1* fiber sorbents (CA-S-PEI-PI) are based on polymeric amines (PEI) that are physically impregnated into the pores of porous CA-S bare fibers (Labreche et al., 2013). *Class 2* fiber sorbents are based on covalently grafted organosilanes, with past examples being (3-aminopropyl)-trimethoxysilane-functionalized polymer/silica fiber sorbents (CA-S-APS-PI) (Rezaei et al., 2013a). All these amine-containing fiber sorbents were made by post-spinning amine infusion techniques (Labreche et al., 2013; Rezaei et al., 2013a), i.e., hollow fibers were first spun using commercial cellulose acetate

and mesoporous commercial silica with a silica loading of 57 wt%, and were subsequently treated with an amine solution using an infusion process as described in our prior papers (Labreche et al., 2013; Rezaei et al., 2013a). Previous work (Labreche et al., 2013) has illustrated that the open pore structure of the CA-S bare fibers allowed entry of PEI polymers containing primary, secondary and tertiary amines. These fiber porous structures were maintained during the following post-spinning amine infusion process, as demonstrated by SEM images and helium permeance measurements. Thus, internal mass transfer resistances through the fiber wall were minimal. Both class 1 and class 2 amine adsorbents have favorable CO₂ sorption kinetics and are therefore potential candidates for use in RTSA processes.

The present work primarily concerns the dynamic performance of poly(ethyleneimine) fiber sorbent modules (*Class 1*, CA-S-PEI-PI) under simulated dry or simulated wet flue gases. A fully automated RTSA system was designed to evaluate the hollow fiber sorbent CO₂ dynamic adsorption/desorption behavior. The CO₂ breakthrough capacity, q_b , is one crucial parameter that represents the dynamic capacity in a practical swing operation process, but less attention in the literature has been focused on this parameter (compared to equilibrium capacities). In this paper, the CO₂ breakthrough capacity, which is defined as the amount of adsorbed CO₂ per unit mass of fiber sorbents at the point where CO₂ begins to appear in the effluent gas, is used to compare the fiber sorbent performance under varied operating conditions. The cyclic adsorption/desorption characteristics of CA-S-PEI-PI fibers are compared at different temperatures. Moreover, the CO₂ dynamic capacity of CA-S-PEI-PI fiber modules containing fibers with low permeability bore side lumen layers with flowing cooling water is investigated. The modules are shown to give stable adsorption capacities after 60 adsorption/desorption cycles, allowing for long term, steady operation.

2. Experimental

2.1. Hollow fiber fabrication and barrier layer formation

Hollow fiber sorbents used in this work were spun and functionalized using the post-spinning amine infusion techniques described in our previous work (Labreche et al., 2013). The fiber sorbents were a hybrid matrix of cellulose acetate (CA) (Mw 50 000, Sigma-Aldrich) and commercial silica (C 803, W.R. Grace), with a silica loading of 57 wt%. The average pore diameter of the silica powder is 18.5–20 nm and the average particle size is 3.8 μm. The fibers are approximately 1100 μm in diameter with a bore diameter of 300 μm. Poly(ethyleneimine) (PEI) (MW 800, Sigma-Aldrich) was used as the amine source in the post-spinning amine infusion step (Labreche et al., 2013).

A mixture of Neoprene® (poly(chloroprene), DuPont Elastomers) and crosslinking agents (TSR-633, Tiarco Chemical) was used to form a barrier lumen layer in the bores of fibers via a post-treatment method (Lee et al., 2012; Lively et al., 2009, 2011b). The experimental set-up has been described in the literature previously (Lively et al., 2009). CA-S-PEI-PI fiber sorbents were potted into a 10 in. stainless steel module. The module was connected to a post-treatment system in a vertical position. A 180 mL latex mixture of Neoprene, TSR-633 and water with a weight ratio of 76/9/15% was extruded into the bores of the six-fiber module at a flow rate of 600 mL/h using an ISCO syringe pump (Model 1000D, Teledyne Isco). The fiber end was immersed in a hexane bath during the post-treatment process to inhibit the rapid drying of the latex (Lee et al., 2012). The opposite end of the fiber module was post-treated using a similar procedure. The barrier layer was then dried in “toluene-assisted” mode by flowing toluene-water

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