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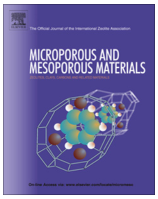

Post-combustion CO_2 adsorption on activated carbons with different textural properties

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ABSTRACT

Fixed bed CO_2 adsorption tests were carried out in model flue-gas streams onto two commercial activated carbons, namely Filtrasorb 400 and Nuchar RGC30, at 303 K, 323 K and 353 K. Thermodynamic adsorption results highlighted that the presence of a narrower micropore size distribution with a prevailing contribution of very small pore diameters, observed for Filtrasorb 400, is a key factor in determining a higher CO_2 capture capacity, mostly at low temperature. These experimental evidences were also corroborated by the higher value of the isosteric heat derived for Filtrasorb 400, testifying stronger interactions with CO_2 molecules with respect to Nuchar RGC30. Dynamic adsorption results on the investigated sorbents highlighted the important role played by both a greater contribution of mesopores and the presence of wider micropores for Nuchar RGC30 in establishing faster capture kinetics with respect to Filtrasorb 400, in particular at 303 K. Furthermore, the modeling analysis of 15% CO_2 breakthrough curves allowed identifying intraparticle diffusion as the rate-determining step of the process.

1. Introduction

CO_2 emission deriving from the power sector has become an environmental issue of great concern, due to its relevant contribution to the global climate change [1,2]. Carbon capture and storage (CCS) strategy has the potential to reduce the overall mitigation costs and to increase the flexibility in achieving a reduction in greenhouse gas (GHG) emissions [1,3]. According to the BLUE Map Scenario of the International Energy Agency (IEA), this route could contribute to a 19% reduction in CO_2 emissions by 2050 [4]. In this scenario, the implementation of post-combustion CO_2 capture processes into existing power plants seems to be the most promising strategy for a near-term emission mitigation [2]. Currently, CO_2 absorption into monoethanolamine (MEA) is considered as the benchmark technology within the post-combustion CO_2 capture options [5,6]. Nonetheless, numerous research studies are devoted to the development of high-efficiency CO_2 capture processes which can overcome the techno-economic limits associated with MEA use (such as equipment corrosion, high energy consumption for the solvent regeneration, solvent cost and regeneration) [5,7]. In this context, adsorption onto porous solids is an effective and versatile technique for the removal of different classes of pollutants from gaseous or liquid streams, thanks to the potentially high selectivity toward the target contaminant and its general low maintenance costs [8–17]. For CCS application, different classes of adsorbents, such as carbonaceous materials, zeolites, mesoporous silicas, metal organic frameworks, molecularly imprinted sorbents etc., are currently being investigated [8,13,16,18–22]. Numerous literature studies are focused on solids functionalization with basic nitrogen groups (mainly organic amines), able to favourably interact with acidic CO_2 molecules [8,16,23]. Activated carbons are highly attractive for CO_2 capture, due to their general low cost and composite structure, characterized by micropores which determine high surface area for adsorption, but also meso- and macropores which can facilitate the diffusion (fast kinetics) of the adsorbate to the inner porosity [24–26]. Furthermore, it has been underlined that activated carbons have a weaker physical interaction with CO_2, and consequently lower heat of adsorption, compared to zeolitic adsorbents, thus requiring less energy for the regeneration process [25]. Notwithstanding the described favorable features of activated carbons, their adsorption capacity toward CO_2 in simulated flue-gas streams (namely with a CO_2 partial pressure lower than 0.15 bar) has been only partially studied [19,27,28]. In particular, there is a lack of exhaustive information concerning the effects of

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Nomenclature

$1/n$	Freundlich heterogeneity parameter [–]
C	CO_2 concentration in the bulk gas phase [mol m^{-3}]
C^*	CO_2 concentration in the gas phase at the fluid–particle interface [mol m^{-3}]
C^{in}	CO_2 concentration in the gas phase at the fixed bed inlet [mol m^{-3}]
D_{ax}	axial dispersion coefficient [m^2 s^{-1}]
D_p	CO_2 intraparticle diffusivity [m^2 s^{-1}]
d_S	mean Sauter particle diameter [m]
K_F	Freundlich affinity constant [mol kg^{-1} bar$^{-1/n}$]
K_L	Langmuir equilibrium constant [bar^{-1}]
k_{ext}	CO_2 fluid film mass transfer coefficient [m s^{-1}]
L	packed bed length [m]
M_{CO_2}	CO_2 molecular weight [kg mol^{-1}]
m	sorbent amount [kg]
P/P_0	relative pressure [–]
Pe	fixed bed Péclet number [–]
P_{eq}	CO_2 equilibrium partial pressure in the gas phase [bar]
$Q^{in}_{CO_2}$	CO_2 volumetric flow rate at the fixed bed inlet [m^3 s^{-1}]
$Q^{out}_{CO_2}$	CO_2 volumetric flow rate at the fixed bed outlet [m^3 s^{-1}]
q_{st}	isosteric heat of adsorption [kJ mol^{-1}]
R	universal gas constant [kJ mol^{-1} K^{-1}]
R^2	determination coefficient [–]
R_S	mean Sauter particle radius [m]
r	radial particle coordinate [m]
S_{BET}	apparent surface area [m^2 g^{-1}]
T	temperature [K]
t	time [s]
t_b	breakpoint time [s]
t_b^{exp}	experimental breakpoint time [s]
t_b^{mod}	numerical breakpoint time [s]
t_{eq}	equilibrium adsorption time for which $Q^{out}_{CO_2}/Q^{in}_{CO_2} = 0.99$ [s]
u	gas superficial velocity [m s^{-1}]
V_0	micropore volume [cm^3 g^{-1}]
$Vads_{STP}$	specific N_2 adsorbed volume @ STP [cm^3 g^{-1}]
V_{meso}	mesopore volume [cm^3 g^{-1}]
V_n	narrow micropore volume [cm^3 g^{-1}]
V_t	total pore volume [cm^3 g^{-1}]
z	fixed bed axial coordinate [m]

Greek symbols

ε	fixed bed voidage fraction [–]
ρ_{CO_2}	CO_2 density [kg m^{-3}]
ρ_p	adsorbent particle density [kg m^{-3}]
Ω_{ext}	film diffusion resistance [s]
Ω_p	intraparticle diffusion resistance [s]
ω	adsorption capacity in the adsorbent particle [mol kg^{-1}]
$\bar{\omega}$	adsorption capacity averaged over an adsorbent particle [mol kg^{-1}]
ω_{eq}	equilibrium adsorption capacity [mol kg^{-1}]
ω_{max}	Langmuir monolayer adsorption capacity [mol kg^{-1}]

activated carbon textural properties and surface chemistry on their CO_2 sorptive performances, mostly under dynamic conditions [26,29]. For example, it has been highlighted that the presence of narrow micropores in activated carbons plays a major role in determining high CO_2 capture capacities [26,30,31]. Liu and Wilcox [29] performed an interesting theoretical study in which they adopted grand canonical Monte Carlo simulations to predict CO_2 adsorption isotherms onto model carbon slit pores with different surface functionalities embedded. Numerical calculations showed that the presence of oxygen heteroatoms in hydroxyl or carboxyl surface functional groups allows an enhancement of CO_2 adsorption performance with respect to non-functionalized graphite slit pores, due to a modification of the surface electronic properties, which induces a more effective packing of the adsorbate molecules.

Based on the aforementioned preface, this paper intends to provide further insights on the role played by the microstructural features of activated carbons on their CO_2 adsorption properties under typical flue-gas conditions. To this end, equilibrium and kinetic CO_2 adsorption tests were carried out on two commercial activated carbons in a fixed bed apparatus at different temperatures (303 K, 323 K and 353 K) and CO_2 inlet concentrations (1–30% by vol., balance N_2). Relationships between adsorbent textural properties and their CO_2 capture behavior were outlined by means of CO_2/N_2 pore size analyses on solids and by mathematical modeling of both adsorption isotherms and breakthrough curves.

2. Materials and methods

2.1. Activated carbons textural characterization

Two activated carbons were chosen for the experimental campaign, in order to assess the effect of different pore structure on CO_2 capture capacity: Calgon Carbon Filtrasorb 400 (particle size 600–900 μm, sample denoted F600–900) and Mead Westvaco Nuchar RGC30 (particle size 600–1000 μm, sample denoted RGC30). The mean Sauter particle diameter (as obtained by laser granulometry) was 766 μm and 843 μm for F600–900 and RGC30, respectively. The textural characterization of the selected adsorbents was carried out in a N_2 Gsorb-6 adsorption equipment (www.g2mtech.com), working at 77 K and 273 K for N_2 and CO_2, respectively. Samples were previously degassed under vacuum at 373 K, in order to remove humidity before the analysis. The main microstructural parameters for F600–900 and RGC30 adsorbents were obtained from post-processing of CO_2/N_2 adsorption isotherms according to the models commonly applied in the literature [26]. The volume of narrow micropores (V_n, pore width up to 0.7 nm) was determined from CO_2 adsorption isotherm at 273 K using the Dubinin–Radushkevich (DR) equation. The apparent surface area (S_{BET}) was derived by applying the BET equation to N_2 adsorption data in the P/P_0 range = 0.01–0.15. The total micropore volume (V_0) was obtained from N_2 adsorption isotherm adopting the DR equation. Finally, the mesopore volume (V_{meso}) was derived as the difference between the total pore volume (V_t), corresponding to the amount adsorbed at P/P_0 = 0.97, and V_0.

2.2. Lab-scale apparatus and adsorption experiments

A detailed description of the plant adopted for the execution of adsorption tests can be found elsewhere [19]. Briefly, the feed gas composition ($N_2 + CO_2$) was determined via mass flow controllers (series El Flow Bronkhorst 201-CV). CO_2 adsorption runs on the investigated activated carbons were performed in a fixed bed column (total available length = 0.13 m; inner diameter = 0.02 m) made up of Pyrex glass. The fixed bed temperature was controlled by means of cylindrical shell Watlow band heaters connected to EZ-PM PID controllers (Watlow). The measurement of CO_2 percentage volumetric concentration during adsorption tests was carried out by a continuous ABB NDIR AO2020 Uras 26 gas analyzer. Data

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