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Adsorption of carbon dioxide on solid amine-functionalized sorbents: A dual kinetic model

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ABSTRACT

Developing efficient technologies for carbon capture is one of the biggest challenges of the future. Therefor, adsorption-based processes are considered to be very promising methods and amine-functionalized solid sorbents emerge as the most suitable materials for this task. To judge the techno-economic viability of such new materials, the investigation of process performance is necessary. Yet accurate but simple models representing the thermodynamic and kinetic properties of these materials are still lacking. For instance, the kinetics of CO_2 adsorption on amine-functionalized sorbents are still widely discussed. Common pseudo-first-order and pseudo-second-order models cannot describe the corresponding adsorption kinetics accurately. In comparison, Avrami's kinetic model and the generalized fractional-order kinetic model are more suitable to describe experimental data. Unfortunately, for these models the adsorption kinetics are a power function of the adsorption time. But, the fitted parameters of Avrami's kinetic model and the generalized fractional-order kinetic model often depend on the specific operation conditions, e.g. CO_2 mole fraction or temperature, and any reasonable correlation between the operation conditions and adsorption parameters can be derived. Furthermore, the time dependence makes the models unsuitable for the simulation of dynamic and periodic processes such as temperature swing adsorption. Too overcome these severe limitations, we present a dual kinetic model (DKM). We show that the model can describe the adsorption and desorption kinetics for different amine-functionalized materials surprisingly well, even more accurately than time-dependent adsorption models. This new model can now be easily incorporated into dynamic swing adsorption simulations to investigate new carbon capture processes.

1. Introduction

The reduction of CO_2 emissions is one of the most important technological challenges of the future [1]. Several technologies such as absorption [2], adsorption [3–6] or membrane-based processes [7] have been proposed for the separation of CO_2 from flue gas, natural gas and even from ambient air [8]. Pressure and temperature swing adsorption processes are considered to be a promising alternative for this task because they can produce high purity streams at low energy consumption [9]. However, commercially available sorbent materials often lack either high adsorption capacity or selectivity, in particular when humid streams are separated [10,11]. Consequently, researchers are actively exploring more efficient CO_2 sorbent materials. In particular, amine-functionalized solid sorbents are very promising materials. They show very high CO_2 adsorption capacities [12], are tolerant to moisture in the feed [13] and are very selective towards CO_2 in mixtures with nitrogen, methane, oxygen or hydrogen even at low CO_2 concentrations [14,15]. In comparison to absorption-based aqueous amine CO_2 separation, solid sorbents require less heat for regeneration because there is no need to heat the bulk solvent [16].

Besides the above mentioned extensive synthetic efforts, research focuses on structured sorbents [17,18] and holistic process studies [19–21]. Accompanied with life cycle analysis methods, viable process concepts can be identified [22]. Yet, the rigorous design and optimization of such processes require thermodynamic and kinetic models. In this regards, simple but precise kinetic models for amine-functionalized solid sorbents are needed to describe their behavior and fully exploit their potential. However, these simple yet accurate models are still lacking.

Depending on their preparation method, solid amine sorbents can be divided into three classes [9]: (i) chemical grafting of amines or amine-functional groups on the surface of the solid support (ii) physical amine impregnation on solid sorbents and (iii) a hybrid of the two other classes, where the amines are physically loaded on the solid support and then polymerized in-situ. Recently, an increasing number of studies regarding the influence of functionalization methods on adsorption

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capacities and adsorption kinetics have been published [14,23–26]. The functionalization method, the amine type, the amine loading as well as the porous solid support are among the most critical parameters for adsorption capacity and kinetics [27–29]. To judge the techno-economic viability of such new materials, process design investigations are necessary [30]. However, only limited studies regarding models for the adsorption as well as desorption kinetics of CO_2 on amine-functionalized materials exist [24,26,31,32]. Thus, we developed a new, simple and versatile model that describes adsorption kinetics of CO_2 on amine-functionalized solid sorbents. To show its general usability we tested the model for different types of solid support materials and functionalization methods.

The kinetics of CO_2 adsorption on solid sorbents are affected by several molecular processes occurring simultaneously such as film diffusion, intra-particle diffusion and adsorbate interaction with active sites (physisorption and/or chemi-sorption with reactions of higher order) [32,33]. Bollini et al. used Toth and Langmuir isotherms to account for the different adsorption sites [34,33], but used linear driving force expressions to describe the mass transfer rate assuming that the rate limiting processes are based on diffusional mechanisms. But, these studies did not provide any information on the desorption kinetics [35]. Recently, detailed mechanistic kinetic models have been discussed, but they are too complex for process simulation and optimization [35]. In fact, a large number of kinetic parameters and their temperature dependencies have to be determined. To avoid (a) the uncertainty in the parameters of such complex models and (b) their lack of numerical stability in process simulations, the different adsorption steps are usually summarized by an overall mass transfer resistance for semi-empirical models. Serna-Guerrero et al. showed that pseudo-first-order (PFO) and pseudo-second-order kinetic models (PSO) have some limitations describing the adsorption of CO_2 on amine-functionalized materials [31]. In comparison, Avrami's fractional-order kinetic model (AFO) [31] and the generalized fractional-order kinetic model (GFO) [32] are able to describe the CO_2 uptake of amine-functionalized solid sorbents accurately. However, for these two models the CO_2 uptake is a power function of the time and consequently the effective kinetic coefficient increases with adsorption time. Thus, these two models have the following physical limitations:

(i) In Avrami's model and the generalized fractional-order kinetic model (see Eqs. (2) and (3)), the effective adsorption kinetics are an exponential function of the adsorption time. Therefore, the effective adsorption coefficient becomes infinitely large at long adsorption times. Actually, it should remain within reasonable bounds.
(ii) The identified adsorption parameters for Avrami's model and the generalized fractional-order kinetic model depend on the CO_2 mole fraction of the gas phase and the sorption temperature applied. Mostly, a systematic relationship of these parameters cannot be observed [32] (see also Table 1). Thus, the kinetics can only be used for the specific parameters investigated during the experimental studies, i.e. a particular temperature and concentration.
(iii) Avrami's model and the generalized fractional-order kinetic model can be used to describe the initial loading of amine-functionalized materials. However, in cyclic adsorption processes adsorption and desorption takes place. Usually, the sorbent is not fully regenerated because this would result in long cycle times. If the adsorption time of Avrami's model and the generalized fractional-order kinetic model restarts, it is expected that the kinetic parameters identified for the initial loading do not allow to describe the CO_2-uptake of already (partially) loaded sorbent materials.

Additionally, the time-dependent definition of the adsorption kinetics makes the simulation of adsorption processes challenging:

(i) Kinetic adsorption studies use thermogravimetric methods at isotropic conditions due to small sample sizes. However, in adsorption beds axial (and radial) temperature and concentration gradients are present. Thus, the adsorption time in the uptake kinetics has to be defined separately for each location in the adsorption bed. For Avrami's model and the generalized fractional-order kinetic model there is no explicit criteria for the start of the local adsorption time, which makes the choice of a starting point rather arbitrary. In particular, this is relevant for cyclic adsorption processes with incomplete regeneration and thus different initial conditions as in simple kinetic experiments.
(ii) For Avrami's model, the desorption has been described as an exponential function of time. As for the adsorption step, the desorption time has to be defined separately for each location of the bed because high temperature and concentration gradients exist.
(iii) In comparison to thermogravimetric measurements the temperature in column adsorption beds increases and decreases slowly during heating and cooling, respectively. Often the heating and cooling time can be in the range of the desorption period [36,37]. Thus, the desorption function has to be defined individually for each location in the adsorption bed. This is not an intrinsic limitation of the adsorption model, but makes modeling very inconvenient, since an (arbitrarily) chosen desorption time has to be defined for each location.

Table 1
Values of the kinetic model parameters for CO_2 adsorption on triamine-bearing organic species grafted on a mesoporous pore expanded MCM-41 silica at 5 vol % CO_2 and the corresponding normalized standard deviation.

Model	Variable	25 °C	40 °C	55 °C	70 °C
Pseudo-first-order model	k [$10^{-2} \cdot \mathrm{sec}^{-1}$]	2.65	3.13	2.86	2.70
	NSD [%]	15	12	13	21
Avrami's model	k_A [$10^{-2} \cdot \mathrm{sec}^{-n_A}$]	6.81	6.34	5.35	7.62
	n_A [–]	1.5	1.38	1.30	1.53
	NSD [%]	3.0	3.1	2.3	8.8
Generalized fractional-order kinetic model	k_G [$10^{-2} \cdot \mathrm{sec}^{-m_G} \cdot \mathrm{mmol}^{1-n_G} \cdot \mathrm{g}^{n_G-1}$]	0.95	1.72	2.29	1.38
	m_G [–]	1.68	1.46	1.11	1.77
	n_G [–]	1.70	1.33	1.32	2.34
	NSD [%]	3.5	3.6	10.2	3.4
Dual kinetic model	k_{DKM} [$10^{-2} \cdot \mathrm{sec}^{-1} \cdot \mathrm{mmol}^{1-n_{DKM}} \cdot \mathrm{g}^{n_{DKM}-1}$]	0.67	0.96	1.10	1.53
	β_{DKM} [$\mathrm{g} \cdot \mathrm{mmol}^{-1}$]	9.32	6.13	5.41	5.00
	n_{DKM} [–]	2	2	2	2
	Err [%]	3.1	3.1	3.4	10.0

To overcome these limitations, we propose a new semi-empirical kinetic model for the CO_2 adsorption on solid amine sorbents, where the CO_2 uptake is a function of the current CO_2 loading. This model allows for detailed process analysis which is of utmost importance to increase the process efficiency, to reduce the required separation energy for carbon capture processes and to evaluate the potential of new adsorption materials.

2. Models for amine-functionalized sorbents

In this study, we compare our dual kinetic model with the most commonly used kinetic models for CO_2 adsorption processes: (a) the pseudo-first-order model, (b) Avrami's fractional-order kinetic model and (c) the generalized fractional-order kinetic model. The pseudo-second-order model was not considered because it was shown that it is not suitable to describe the adsorption kinetics for amine-functionalized materials [31]. For clarity reasons the models are summarized shortly:

- Pseudo-first-order kinetic model: This is the most simple and thus