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Phenomenological analyses of carbon dioxide adsorption kinetics on supported zinc-functionalized ionic liquid hybrid sorbents

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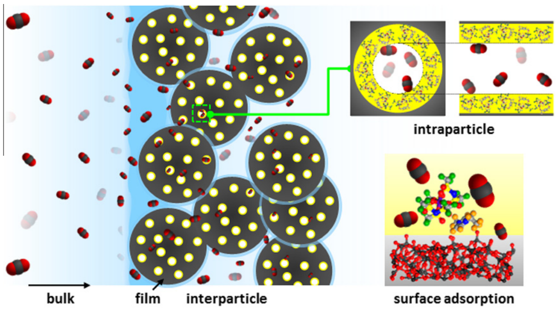
HIGHLIGHTS

- Operational description of the CO_2 sorption kinetics by zinc-functionalized SILP hybrid sorbents.
- Apparent kinetics models reveal the nature of adsorbate–adsorbent interaction.
- Overall sorption kinetics controlled by film diffusion resistance.
- Promoted intraparticle diffusion by the highly accessible pore network.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption kinetics is an important parameter often overlooked in the evaluation of CO_2 sorbent materials performance. In this contribution, we established an operational description of the CO_2 adsorption kinetics by our recently reported family of novel hybrid sorbents (HS) based on supported zinc-functionalized ionic liquid (IL), across a wide range of IL loading and a morphologically diverse set of porous supports. Phenomenological analyses of apparent and diffusion kinetics models elucidated the nature of adsorbate–adsorbent interactions and the determination of the rate-limiting mechanistic step, respectively. Correlation of the calculated rate constants from Lagergren's pseudo-first order model, and Ho and McKay's pseudo-second order model with IL loading and textural properties of the sorbents strongly suggests that the IL remained the active component of the sorbent, and overall adsorption occurs via a combination of physical and chemical interactions. Insights into the rate-limiting mechanism derived from selected diffusion kinetics models revealed film diffusion resistance controlled overall adsorption, with intraparticle diffusion promoted by greater accessibility to the IL within the pore networks of these HS systems.

1. Introduction

There is no longer any contention that the average global temperature has increased in the last five decades [1], prompting widespread efforts to curtail one of the primary contributors, CO_2 emissions from large point sources. Carbon capture and storage [2] and utilization [3] are two large-scale efforts deemed as near-term solutions to effectively lower CO_2 atmospheric emissions. The effectiveness of these strategies relies on the selection of highly efficient and sustainable CO_2 capture media generally classified as solvents [2,4], solid sorbents [5,6], membranes [7,8] and their hybrids [9–11]. Contributing to these efforts, our group recently reported a family of high capacity novel hybrid sorbents (HS) based on zinc-functionalized ionic liquid (IL) impregnated into porous supports [12–14].

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High capacity and selectivity, fast sorption kinetics and recyclability are among the important and desirable properties of a CO_2 capture medium. Remarkably, novel material analyses rarely include CO_2 adsorption kinetics details [15–19]. In contrast, evaluation of capacity, selectivity and recyclability are usually present in every report on new CO_2 capture media [9,20–29]. A detailed analysis of the adsorption kinetics would provide improved fundamental understanding of the sorption process, with implications towards industrial applicability. A complete description of the adsorption kinetics would typically involve a thorough understanding of the mass transport processes to and from the adsorbent, and account for the physical and chemical properties of the gas and the sorbent. The complex nature of adsorption processes of gases by porous sorbents challenges a lucid analysis of the overall kinetics process. To reduce the complexity, it is possible to deduce kinetics parameters by fitting experimental data to a series of well-established, relatively simple, theoretical kinetics models [18]. Such phenomenological analyses enabled efforts to rationalize simple kinetics models, clarifying sorbate–sorbent interactions [30–34].

In this contribution, phenomenological analyses of CO_2 adsorption kinetics for our novel HS were performed by deducing the nature of adsorbate–adsorbent interaction using two of the most widely used kinetics models: Lagergren's pseudo-first order (PFO) model [35] and Ho and McKay's pseudo-second order (PSO) model [36]. Additionally, to gain insights into any rate-limiting steps for CO_2 adsorption kinetics, we considered individual mechanistic steps of mass transport (Fig. 1). These included: (1) bulk diffusion: molecular or self-diffusion of CO_2 molecules from the bulk phase to a film layer surrounding the HS; (2) film diffusion: diffusion of CO_2 across the film to the surface of the sorbent; (3) interparticle diffusion; (4) intraparticle diffusion exploiting available porosity; and (5) surface adsorption. Since bulk diffusion and surface adsorption are relatively fast processes [16–18], the rate-limiting step analyses were confined to the film, interparticle, and intraparticle diffusion steps. These analyses extend beyond our previous contributions [12–14], which utilized a linearized Weber–Morris intraparticle diffusion model to describe the CO_2 adsorption kinetics by our SILP hybrid sorbents. Our results provided crucial information and understanding to establish an operational description of the CO_2 adsorption kinetics across a wide range of IL loading and a morphologically diverse set of porous supports.

2. Adsorption kinetics model

The published literature contains a large number of kinetics models, enabling the calculation of characteristic kinetics parameters and thus providing insights into the mechanism of CO_2 adsorption by sorbents. The simplicity and efficacy of Lagergren's PFO model [35] and Ho and McKay's PSO model [36] are well reflected by the number of systems to which models appear to apply, describing the corresponding sorption processes. These models provide apparent rate parameters, representing the entire adsorption process [17]. To gain further insight into the adsorption mechanism, rate-limiting kinetics models such as film diffusion [37], interparticle diffusion [18] and intraparticle diffusion [38] have also been explored.

2.1. Apparent kinetics models

2.1.1. PFO kinetics model

If one assumes that the adsorption rate were proportional to the number of effective adsorption sites, then the adsorption rate would be

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \tag{1}$$

where q_e (mmol g^{-1}) and q_t (mmol g^{-1}) are the adsorption capacities at equilibrium and at time t, respectively, and k_f (s^{-1}) is an equivalent first order rate constant. The integrated form of Eq. (1) with the boundary conditions, $t = 0$, $q_t = 0$ and $t = \infty$, $q_t = q_e$ becomes

$$q_t = q_e(1 - e^{-k_f t}) \tag{2}$$

The k_f obtained from Eq. (2) represents the reversible interaction between adsorbate and adsorbent [16], suitably predicting physisorption of CO_2 on the HS systems.

2.1.2. PSO kinetics model

If one assumes that the adsorption rate were proportional to the square of the number of effective adsorption sites, then the adsorption rate would become

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \tag{3}$$

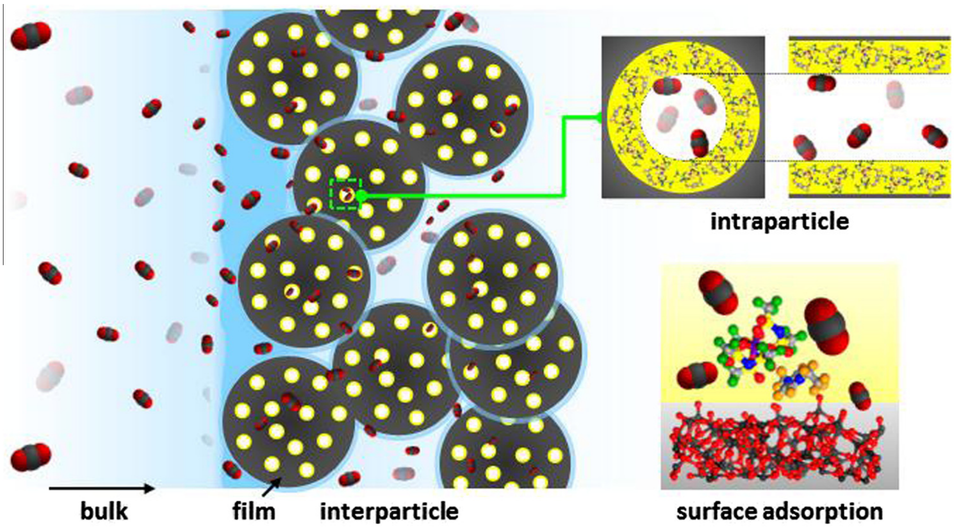

Fig. 1. Schematic representation of CO_2 diffusion mechanisms in EZT3-functionalized, porous hybrid sorbents.