



Research article

Readily regenerable amine-free CO₂ sorbent based on a solid-supported carboxylate ionic liquid

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ABSTRACT

Accumulation of anthropogenic CO₂ is undoubtedly the major cause of global warming. In addition to reducing emissions, minimising the threatening effects of climate change in the near future might also require the capture of enormous amounts of CO₂ from point sources or from the atmosphere. In this regard, the development of novel affordable and energetically attainable capture technologies is greatly needed. In this work, we report rapid and greatly facilitated CO₂ desorption for amine-free carboxylate ionic liquid hydrates as compared to a benchmark amine-based sorbent. Complete regeneration was achieved at moderate temperature (60 °C) over short capture-release cycles using model flue gas on a silica-supported tetrabutylphosphonium acetate ionic liquid hydrate (IL/SiO₂), whereas the polyethyleneimine counterpart (PEI/SiO₂) only recovered half its capacity after the first cycle in a rather sluggish release process under the same conditions. The IL/SiO₂ sorbent achieved a slightly superior working CO₂ capacity than PEI/SiO₂. The easier regeneration of carboxylate ionic liquid hydrates, which behave as chemical CO₂ sorbents leading to bicarbonate in a 1:1 stoichiometry, is due to their relatively low sorption enthalpies (≈ 40 kJ mol⁻¹). The faster and more efficient desorption from IL/SiO₂ fits a first-order kinetic model ($k = 0.73$ min⁻¹), whereas a more complex process was observed for PEI/SiO₂ (pseudo-first order initially, $k = 0.11$ min⁻¹, pseudo-zero order at later stages). The remarkably low regeneration temperature, the absence of amines and the non-volatility of the IL sorbent are favourable assets to minimise gaseous stream contamination. Importantly, regeneration heats—a crucial parameter for practical application—are advantageous for IL/SiO₂ (4.3 kJ g (CO₂)⁻¹) vs. PEI/SiO₂, and fall within the range of typical amine sorbents indicating a remarkable performance at this proof-of-concept stage. Further structural design will enhance the viability of amine-free ionic liquid hydrates for carbon capture technologies.

1. Introduction

As set forth by the Intergovernmental Panel on Climate Change (IPCC) in its Sixth Assessment Report, there is unquestionable scientific evidence that the increasing atmospheric CO₂ levels due to the widespread use of fossil carbon resources since the industrial revolution are the major driver of positive radiative forcing, and consequently, of global warming (Keeling, 2008; Arias, Bellouin et al. 2021). The human perturbation of atmospheric CO₂ concentrations, which have almost doubled in less than three centuries, and of the global carbon cycle, is arguably more marked than that of any natural event, including glaciation, for the last million years (Falkowski et al., 2000; Tomkins and Müller, 2019). During these relatively recent glacial-interglacial cycles,

temperatures and atmospheric CO₂ levels correlate remarkably (Jouzel, Masson-Delmotte et al. 2007; Lüthi et al., 2008), a fact that reinforces the aforementioned IPCC conclusions on the unprecedented warming we are witnessing due, mainly, to anthropogenic CO₂. The climate models analysed by the IPCC indicate that global temperatures will continue to increase even under the most ambitious emission-reduction scenarios (Arias, Bellouin et al. 2021). Therefore, determined efforts to slow down and ultimately reverse CO₂ accumulation in the atmosphere are required to minimise the daunting effects of climate change. In this context, carbon capture, storage and utilisation encompasses a set of diverse valuable technologies that must rapidly advance to become relevant on a global scale (Bui, Adjiman et al. 2018; Gao, Liang et al. 2020).

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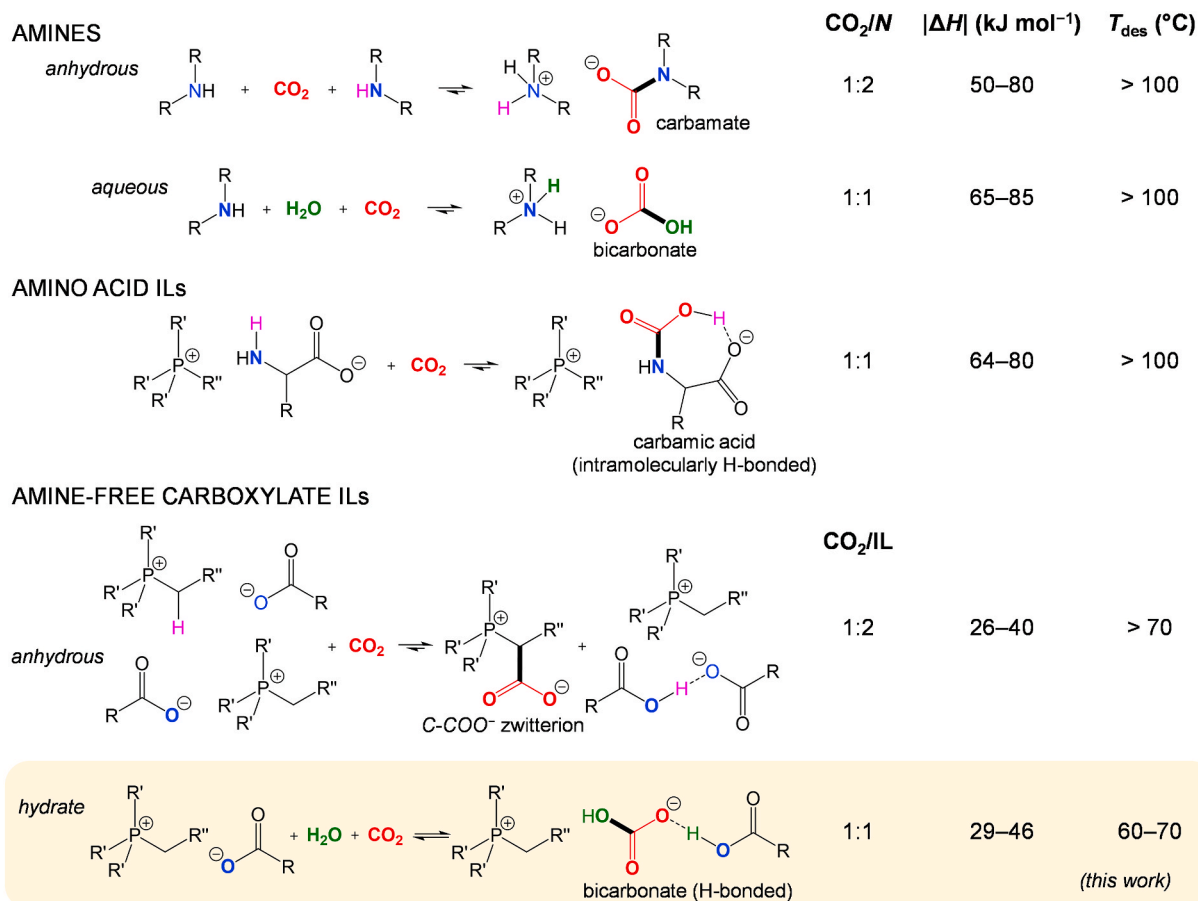
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The quest for novel efficient materials for CO₂ capture that can be readily regenerated with a low energy penalty still represents a major goal in the fields of flue gas treatment and direct air capture. Amine-based sorbents represent a mature technology since they offer remarkable CO₂ solubilities, albeit their regeneration poses serious issues related to volatility losses and degradability at the relatively high temperatures (>100 °C) required, resulting in the generation of gaseous contaminants (Bollini, Didas et al. 2011; Boot-Handford, Abanades et al. 2014; Sanz-Pérez, Murdock et al. 2016; Bui, Adjiman et al. 2018). Non-volatile liquid CO₂ sorbents, such as those based on ionic liquids (ILs) (Brennecke and Gurkan, 2010, Cui, Wang et al. 2016; Zeng, Zhang et al. 2017), are interesting for further development and eventual commercial implementation since they are not expected to pollute the recovered gas. Moreover, the variety of ILs is immense given the countless possible cation-anion combinations. By adjusting their basicity, chemical reactivity towards CO₂ capture can be achieved (Cui, Wang et al. 2016). A first class of ILs for CO₂ chemisorption was inspired by amine sorbents by incorporating amine groups onto their IL cations (Bates, Mayton et al. 2002), achieving a 1:2 CO₂/N capture capacity (anhydrous mechanism, Scheme 1). Conversely, if the amine functionality resides in the anion, capture enhancements up to a 1:1 CO₂/N stoichiometry have been reported (amino acid ILs, Scheme 1) (Zhang et al., 2006; Jiang, Wang et al. 2008; Zhang et al., 2009; Gurkan, de la Fuente et al. 2010; Goodrich, de la Fuente et al. 2011).

Despite the remarkable CO₂ solubilities of amine-functionalised ILs, they are not devoid of the drawbacks of amine sorbents, such as high sorption enthalpies, hence requiring regeneration temperatures

generally above 100 °C and/or vacuum to induce CO₂ release (Zhang et al., 2006; Yu, Wu et al. 2009). In this regard, amine-free carboxylate ILs are particularly suitable, since they chemically capture CO₂, yet less tightly than amine-based sorbents (Shiflett, Kasprzak et al. 2008; Shiflett, Drew et al. 2010; Gurau, Rodríguez et al. 2011; Yasaka, Ueno et al. 2014; Moya, Alonso-Morales et al. 2016; Yasaka and Kimura, 2016, Simon, Zanatta et al. 2017; Santiago, Lemus et al. 2019; Avila, Lepre et al. 2021; Pena, Soto et al. 2021). This is somewhat surprising on the grounds of the relative acid-base strengths. For example, acetate ILs are good chemical absorbers of CO₂, whilst a solution of an acetate salt in water cannot absorb CO₂ to any significant extent, as expected by pK_a values in aqueous media, *i.e.* 4.76 and 6.35 for acetic and carbonic acids, respectively. Even more intriguing is the tendency of carboxylate ILs to undergo self-deprotonation of weakly acidic moieties, such as aromatic imidazolium C–H positions (Gurau, Rodríguez et al. 2011), quaternary alkylphosphonium (Yeadon, Jacquemin et al. 2020; Avila, Lepre et al. 2021; Pena, Soto et al. 2021) or carbonylic α-hydrogens (Avila, Lepre et al. 2021) (pK_a range: 20–30). The resulting C-nucleophile is able to strongly bind CO₂, although the maximum capacity is limited to a 1:2 CO₂/IL stoichiometry due to the formation of a hydrogen-bonded adduct between two carboxylate anions (C–COO[−] zwitterion formation, Scheme 1) (Gurau, Rodríguez et al. 2011; Yasaka and Kimura, 2016, Pena, Soto et al. 2021), and reversibility of CO₂ capture becomes hindered to some extent due to thermodynamic and kinetic constraints of cleaving the C–C bond formed.

In the presence of water, the chemisorption mode changes drastically (as in the case of amines) for amine-free carboxylate ILs, resulting in an



Scheme 1. Examples of CO₂ chemisorption modes by amines, amino acid ILs and amine-free carboxylate ILs. Molar ratios (CO₂/N or CO₂/IL) are enhanced from 1:2 to 1:1 in the presence of water for primary and secondary amines (tertiary amines only react via the hydrous route) and for amine-free carboxylate ILs. Newly formed chemical bonds upon CO₂ capture are marked as bold lines. Sorption/desorption enthalpy (ΔH) ranges and desorption temperatures (T_{des}) are based on a compilation of literature values (Yokozeki et al., 2008; D'Alessandro et al., 2010; Gurkan, de la Fuente et al. 2010; Ebner et al., 2011; Goodrich, de la Fuente et al. 2011; Gurkan, Gohndrone et al. 2013; Boot-Handford, Abanades et al. 2014; Goeppert et al., 2014; Anderson, Atkins et al. 2015; Yasaka and Kimura, 2016).

enhancement of capture capacity. The solubility of CO₂ is maximum at equimolar IL/H₂O ratios due to the formation of bicarbonate via a 1:1 CO₂/IL reaction, while avoiding C–C bond formation (Scheme 1) (Quinn, Appleby et al. 1995; Wang, Hou et al. 2011; Wang, Dai et al. 2012; Stevanovic, Podgorsek et al. 2013; Yasaka, Ueno et al. 2014; Anderson, Atkins et al. 2015; Yasaka and Kimura, 2016). Recyclability is greatly facilitated for the IL hydrates as compared to the corresponding dry ILs, and also to amine-based sorbents. This is related to the relatively low heat of (de)sorption of hydrated carboxylate ILs ($\approx 30\text{--}40\text{ kJ mol}^{-1}$, Scheme 1) (Wang, Hou et al. 2011; Yasaka and Kimura, 2016) and to the straightforward decomposition of bicarbonate in hydrated media, as proved in this work. Therefore, the presence of residual water, a common phenomenon in carboxylate ILs since exhaustively drying them is challenging, becomes an advantage for CO₂ capture rather than a drawback.

The motivation of this work is to demonstrate a fast and readily reversible CO₂ capture-release operation based on the favourable chemistry of hydrated amine-free carboxylate ILs. Efforts have concentrated on proving that regeneration energies, arguably the most critical parameter to assess the viability of CO₂ capture materials, are competitive with commercial amine sorbents. This aspect is of utmost importance in the context of enriching the portfolio of carbon capture technologies with novel and feasible alternatives. The validation of ionic liquids as energy-efficient CO₂ sorbents also requires circumventing their typically high viscosities. This is herein ameliorated by adjusted hydration. Moreover, the use of solid-supported materials is adopted in order to maximise contact area with the sorbent and minimise mass transfer limitations. This was inspired by the work on hybrid and supported amines as a realistic technological solution (Choi, Drese et al. 2009; Bollini, Didas et al. 2011). A tetraalkylphosphonium acetate IL hydrate supported on silica is herein chosen as a representative example to prove the concept. It exhibited slightly superior CO₂ capture capacity, significantly faster desorption at moderate temperature, and lower regeneration heat, as compared to the commercial amine counterpart.

2. Materials and Methods

Tetrabutylphosphonium hydroxide solution (40% by mass, in water), polyethyleneimine (PEI, branched, average molecular mass $\approx 800\text{ g mol}^{-1}$), tetrabutylammonium acetate (97%) and methanol (EMSURE® ACS reagent) were purchased from Sigma-Aldrich. Acetic acid (CH₃COOH, glacial, extra pure) was obtained from Scharlau. A model flue gas mixture (CO₂, 15.012%; O₂, 5%; N₂, 80%) and dinitrogen (99.999%) were obtained from Carburos Metálicos. Fumed silica powder (SiO₂, AEROSIL® R816) was obtained from Evonik. All chemicals were used as received unless otherwise stated.

2.1. Ionic liquid synthesis

Tetrabutylphosphonium acetate ([P_{4 4 4 4}][AcO]) was synthesized by acid-base neutralization. Tetrabutylphosphonium hydroxide (40 mL, 40% in water, $\approx 58\text{ mmol}$) was added drop-wise to an equimolar amount of CH₃COOH ($\approx 3.5\text{ g}$, $\approx 58\text{ mmol}$) in distilled water, up to a total volume of 200 mL, in a round bottom flask. The addition was carefully performed until the calculated final molar equivalence point at pH = 8.98 (Ferguson, Holbrey et al. 2011), as measured using a Metrohm pH meter. Subsequently, water was removed at 60 °C under reduced pressure (reaching *ca.* 15 mbar in latter stages) in a rotary evaporator until constant weight. The resulting liquid was characterized by NMR (see Supplementary Data) confirming the expected structure and composition, and its water content was determined by Karl Fisher titration as 4.508% (weight fraction), equivalent to [P_{4 4 4 4}][AcO]·0.834H₂O. Before further experiments, water was added up to the optimal 1 mol (H₂O)/mol (IL) ratio and the resulting mixture was homogenised, resulting in [P_{4 4 4 4}][AcO]·H₂O as a colourless viscous liquid, which was then stored under N₂ atmosphere.

2.2. Preparation of silica-supported IL or amine CO₂ sorbents

The silica-supported CO₂ sorbents were prepared by impregnation. PEI was selected as an example of commercial non-volatile amine sorbent, for comparison purposes. The fumed silica powder was compacted by means of a hydraulic press into cakes, and then crushed and sieved. The fraction composed of pellets between 0.25 and 0.50 mm in size were separated and employed as solid support. The desired amount of liquid sorbent ([P_{4 4 4 4}][AcO]·H₂O or PEI) was dissolved in methanol ($\approx 5\text{ mL}$) in a Schlenk flask and then the SiO₂ pellets (3.00 g) were added. The amount of liquid sorbent was adjusted to attain the same theoretical (stoichiometric) maximum sorption capacity, around 1.6 mmol (CO₂)/g_{sorbent}, where sorbent accounts for the total amount of impregnated solid (see Table S1). This equates to *ca.* 100 and 21% by weight for [P_{4 4 4 4}][AcO]·H₂O or PEI, respectively, relative to the amount of SiO₂ support. The mixture was gently shaken and dried off under a gentle N₂ flow at 50 °C until constant weight, resulting in free-flowing granular solids, designated as IL/SiO₂ and PEI/SiO₂, respectively. Fig. 1 illustrates the preparation procedure for the sorbent materials. The solid-supported sorbents were stored under N₂ atmosphere until used for CO₂ capture experiments.

2.3. CO₂ sorption-desorption experiments

Calibration. The concentration of CO₂ was measured using a non-dispersive infrared gas analyser (HORIBA VA-5001, measurement steps: 1 s). Initially, a first calibration was performed under N₂ flow (300 mL min⁻¹) to set the 0% CO₂ baseline. A second calibration was then performed after flowing CO₂ gas mixture (300 mL min⁻¹, model flue gas, 15.012% CO₂).

Capture. In typical sorption experiment, a custom-designed glass U-tube with an inner diameter of 8 mm was loaded with the desired pelletised solid (equivalent to 3.0 g blank SiO₂, total bed volume *ca.* 11 cm³) and secured on both sides by means of glass wool plugs. After purging with N₂ to ensure the absence of CO₂, the model flue gas containing 15.012% CO₂ (in addition to *ca.* 5% O₂ and 80% N₂) was flowed (300 mL min⁻¹, 1 atm) and 25.0 ± 0.5 °C through the solid in the U-tube glass container, in a fixed-bed-type operation. The concentration of CO₂ in the gas effluent was monitored in real time by using the infrared gas analyser described above. The CO₂ sorption was considered to be completed when the CO₂ concentration of the outlet stream was equal to the inlet one. For cycling tests, capture time was set to 10 min, which was shown to be sufficient for equilibrium to be reached. Afterwards, the glass U-tube was immersed in an ice/salt cooling bath at approximately -15 °C and N₂ flowed (300 mL min⁻¹), in order to remove any CO₂ in the gas phase remaining in the system, while avoiding any possible reversal of the CO₂ sorption reaction.

Regeneration. Desorption was carried out by monitoring the CO₂ concentration in the same way as described for the sorption method by heating at moderate temperature in an oil bath while flowing N₂ (60 °C, 300 mL min⁻¹, 1 atm) through the CO₂-saturated sorbents. In this stage, CO₂ was released and increases in CO₂ concentration were observed. Desorption was considered to be completed when the CO₂ concentration reading returned down to 0% concentration. For cycling tests, release time was set to 10 min, which was shown to be sufficient for essentially complete regeneration of IL/SiO₂, while not for PEI/SiO₂ (see below).

2.4. Characterisation

The as-synthesized IL was characterized by NMR spectroscopy on a Varian Gemini 400 spectrometer (400 MHz), either dissolved in dimethyl sulfoxide-d₆ (dms_o-d₆; ¹H NMR) or as neat liquid using dms_o-d₆ in a sealed capillary tube as an external standard (¹³C and ³¹P NMR). Thermal behaviour and stability studies were performed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) on DSC 3+ STAR^e System and TGA 2 STAR^e System, respectively, Mettler

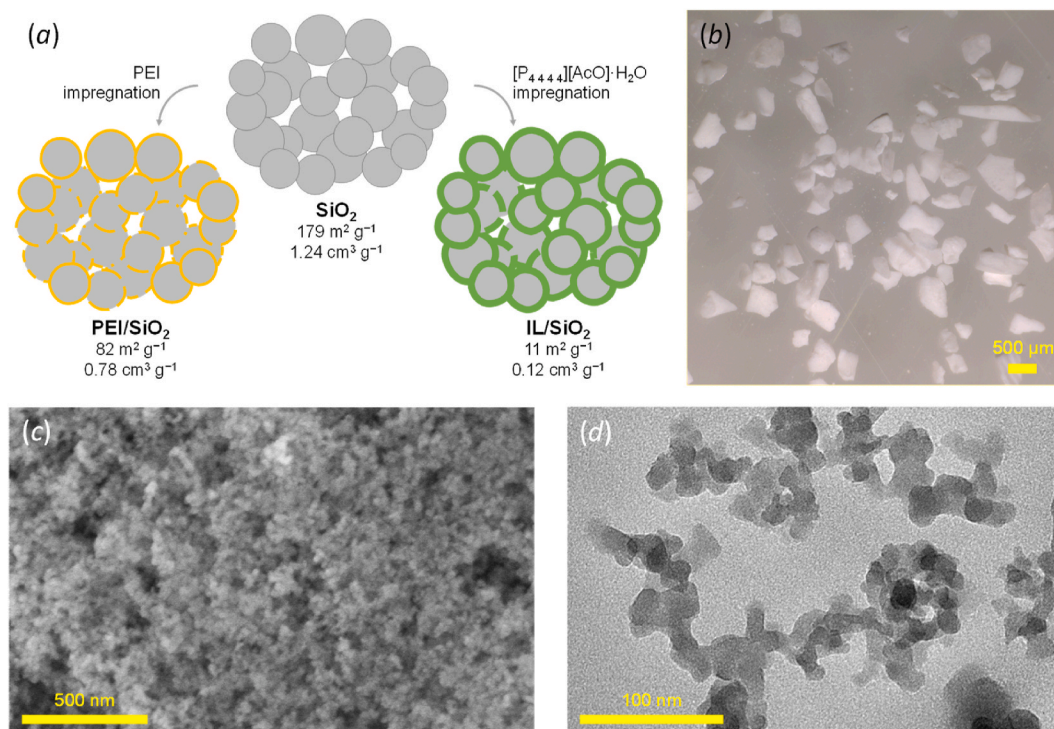


Fig. 1. (a) Scheme representing the impregnation model for PEI/SiO₂ and IL/SiO₂, consisting of aggregated SiO₂ nanoparticles and an interstitial porous network. Specific surface areas and pore volumes, as determined from N₂ physisorption data, are indicated below each material code. (b) Optical microscopy images of IL/SiO₂ pellets. (c) FESEM images of crushed IL/SiO₂ pellets, and (d) TEM images of dispersed primary IL/SiO₂ nanoparticles.

Toledo instruments. The DSC analyses were performed from 50 to -80 °C, and then from -80 to 50 °C, cooling and heating cycles, respectively, at 5 °C min⁻¹, under N₂ (50 mL min⁻¹). The TGA profiles were recorded from 30 to 600 °C, at 10 °C min⁻¹, under air atmosphere (50 mL min⁻¹). Specific surface areas and pore volumes were measured by N₂ physisorption at -196 °C using a Quantachrome Autosorb instrument, after a degassing pre-treatment at 60 °C for 5 h, and determined by Brunauer–Emmet–Teller (BET) and Barrett–Joyner–Halenda (BJH) analyses, respectively. Viscosities were measured on an IKA ROTAVISC lo-vi viscometer and a VOL-SP-6.7 spindle, using ca. 10 mL samples immersed in a thermostatic bath at the desired temperature with ± 0.5 °C accuracy. Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra were recorded on a Jasco FT/IR instrument and processed using the Spectra Manager™ Suite Spectroscopy Software by Jasco Corporation. Optical microscopy images were taken using a Leica DMS 1000 digital microscope. The morphology of solid materials was studied by field-emission scanning electron microscopy (FESEM) on a Scios2 instrument from ThermoFisher Scientific at an accelerating voltage of 5 kV. Energy dispersive X-ray spectroscopy coupled to scanning electron microscopy (EDX-SEM) analyses were performed on a FEI Quanta 600 ESEM equipped with an Oxford Instruments EDS Detector. Transmission electron microscopy (TEM) images were recorded using a JEOL 1011 instrument at an accelerating voltage of 80 kV.

3. Results and discussion

3.1. Preparation and characterisation of sorbents

The synthesis of [P_{4 4 4 4}][AcO], as the reference IL sorbent, was performed by acid-base neutralization of tetrabutylphosphonium hydroxide with acetic acid in aqueous medium (see Section 2.1 and characterisation by multinuclear NMR in Fig. S1). One of the reasons to select a phosphonium-based IL is the remarkably high thermal degradation resistance of this class of salts as compared to ammonium

counterparts (Wang, Hou et al. 2011; Pena, Soto et al. 2019). This was confirmed by TGA for the IL under study herein (Fig. S2). In order to maximise CO₂ sorption capacity, the water content was adjusted to an equimolar IL/H₂O ratio (see Section 2.1). The resulting [P_{4 4 4 4}][AcO]·H₂O exhibited a wide liquidus range, showing no crystallisation events by DSC down to -80 °C (Fig. S3). These properties, *i.e.*, thermal stability and low propensity towards crystallisation, are favourable for the use of this hydrated IL for multicycle CO₂ capture-release under a temperature-swing operation mode.

Comparison to commercial amines is key to evaluate the prospects of this class of IL sorbents for the competitive separation of CO₂ in strategically relevant processes such as flue gas treatment or direct air capture. Therefore, two silica-impregnated materials, one IL-based and one based on polyethyleneimine (PEI), were prepared. The loadings of [P_{4 4 4 4}][AcO]·H₂O and PEI were adjusted to achieve essentially equal maximum CO₂ sorption capacity (see Section 2.2 and Table S1), based on the expected stoichiometries, as indicated in Scheme 1 (Hicks et al., 2008; Wang, Hou et al. 2011; Anderson, Atkins et al. 2015). The resulting IL/SiO₂ and PEI/SiO₂ were obtained as free-flowing granulated solid materials (Fig. 1b and Fig. S4). The hierarchical porous system consisting of macro-channels around pellets, and interparticle porosity in their interior, as suggested by FESEM (Fig. 1c, Fig. S4 and Fig. S5), is expected to favour gas diffusion. Primary nanoparticle sizes were determined by TEM ($\phi = 19 \pm 7$ nm, Fig. 1d and Fig. S4). These observations indicate that there is little or no noticeable differences in morphology between IL/SiO₂ and PEI/SiO₂.

The loading of either IL or PEI on the silica support was confirmed by ATR-FTIR spectroscopy. Bands due to the IL, chiefly C–H stretching of cation alkyl chains and acetate methyl group, and COO⁻ stretching of the acetate carboxylate moiety (Yeadon, Jacquemin et al. 2020), are clearly visible in the IL/SiO₂ spectrum, and distinguishable from the typical Si–O–Si stretching bands of SiO₂ (Fig. S6). The presence of PEI is also confirmed by the observation of N–H and C–H stretching, and N–H bending signals (Fig. S7) (Choi, Drese et al. 2009).

Specific surface areas, as measured by N₂ physisorption, were 11 and

82 m² g⁻¹ for IL/SiO₂ and PEI/SiO₂, respectively. The significantly smaller surface area as compared to the pristine SiO₂ pellets (179 m² g⁻¹) indicates that the liquid sorbents effectively fill large fractions of the porous network of the pellets. As illustrated in Fig. 1a, the liquid coating layer is thicker and covers more extensively the silica surfaces in IL/SiO₂, given the higher loading as compared to PEI/SiO₂. Pore volume is, as expected, smaller for the IL-based material than for the PEI counterpart (0.12 and 0.78 cm³ g⁻¹, respectively, see Fig. 1a and Table S1), and hence, somewhat limited transport of CO₂ into and through the IL coating, which is partly more occluded and thus less accessible, could be a possibility. However, the propensity of [P₄ 4 4 4] [AcO]-H₂O for chemical CO₂ sorption and its lower viscosity as compared to PEI (129 and > 1600 mPa s at 25 °C, respectively, see Table S2) are sufficient to counterbalance this fact and to promote fast and efficient capture and release, as detailed below.

The distribution of the sorbents (IL or PEI) on the silica support was also investigated by EDX-SEM. Individual pellets and powdered samples were analysed to investigate on any possible preferential loading on the surface relative to the bulk (Table S3). The P/Si ratios, and hence the IL loadings, were close to the expected values both on the external surface and in the interior of IL/SiO₂ pellets. This indicates effective and uniform distribution of the IL sorbent well within the interparticle porous network inside the pellets, as illustrated in Fig. 1a. This is confirmed by elemental mapping, showing even distribution of IL on the pellet exterior and interior (Fig. S8). Loading of PEI was also uniform at the micrometre range both outside and inside the pellets (Fig. S9), yet somewhat preferential distribution on the surfaces is hinted by elemental analysis (Table S3), probably due to the bulkiness of the branched polyamine which may restrict its diffusion throughout the interparticle porous network. From a broad perspective, both materials are structured as matrixes of SiO₂ nanoparticles effectively coated with IL or PEI (Fig. 1), maintaining free-flowing appearances and porous networks for gas diffusion within the pellets.

3.2. CO₂ capture-release experiments

The CO₂ capture was studied at 25 °C in a fixed-bed setup whereby a model flue gas containing ca. 15% CO₂ by volume was flowed through the pelletised solids (see Materials and Methods for details). The concentration of CO₂ downstream the sorption unit was monitored by means of an infrared gas analyser. Resulting breakthrough curves showed delayed increase in carbon dioxide concentration in the effluent gas streams for both PEI/SiO₂ and IL/SiO₂ relative to blank SiO₂, thus indicating effective CO₂ sorption in both cases (Figs. S10–S11). Regeneration of the sorbents were carried out under a N₂ stream by firstly purging the gas phase at low temperature, and then, recording the desorption of CO₂ from the material under moderate heating at 60 °C.

The behaviour over several consecutive capture-release cycles exhibited clear differences (sorption and desorption capacities, determined as shown in Figs. S11–S12, are summarised in Tables S4–S5, and graphically compared in Fig. 2). During the first capture stage, the sorbent based on the amine-free IL hydrate captures less carbon dioxide in absolute terms than PEI (1.7 and 2.8% by mass, respectively) as expected due to the stronger CO₂ affinity of the latter, albeit this is counterbalanced by rapid and essentially complete desorption at 60 °C for the former. Consequently, the IL/SiO₂ sorbent recovered its full sorption capacity during regeneration, thus capturing essentially the same amount of CO₂ in all cycles (working capacities around 16 mg g_{sorbent}⁻¹, see Fig. 2). By contrast, regeneration of PEI/SiO₂ was inefficient, resulting in the release of only half the amount of captured carbon dioxide, and in a consequently reduced working capacity for the subsequent cycles (ca. 14 mg g_{sorbent}⁻¹, see Fig. 2). This is consistent with a much easier desorption for the IL hydrate material than for the amine counterpart at moderate temperature. The latter is capable of absorbing more CO₂ when fresh, but more resistant to release it, in accord with the stronger basicity and higher sorption enthalpies of amines (see Scheme

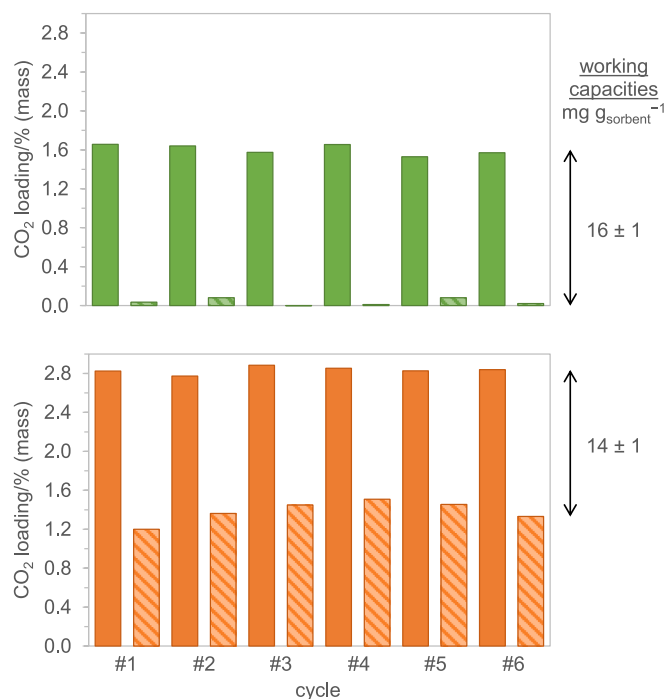


Fig. 2. Cycling CO₂ capture-release performance of IL/SiO₂ (top, green) and PEI/SiO₂ (bottom, orange). For each cycle, solid and striped bars represent the cumulative CO₂ loading after capture and after release at moderate temperature, respectively. The IL/SiO₂ sorbent is essentially regenerated to completeness after each release cycle, whereas approximately half of the trapped CO₂ remains in PEI/SiO₂. Experimental capture conditions: model flue gas (15% CO₂, 300 mL min⁻¹, 1 atm, 25 °C, 10 min). Experimental release conditions: pure N₂ (300 mL min⁻¹, 1 atm, 60 °C, 10 min). See Materials and Methods, Figs. S11–S12 and Tables S4–S5 for more details.

1).

On a stoichiometric basis, an average of 0.23 mol (CO₂) per mole of IL was captured by IL/SiO₂ upon each cycle (hence, 23% of theoretical maximum capacity, see Table S4). For comparison, the practical working capacity of PEI/SiO₂ was around 0.11 mol (CO₂) per mole of active amine group (primary plus secondary) (Hicks et al., 2008), which equates to ca. 22% of theoretical maximum capacity assuming a 1:2 CO₂/N stoichiometry (see Scheme 1 and Table S5). Overall, the working CO₂ capture capacity under these conditions is slightly more favourable for IL/SiO₂ than for PEI/SiO₂ (see Fig. 2).

Considering the low partial pressure of carbon dioxide in the model flue gas used (0.15 atm), the CO₂ capture ability of IL/SiO₂ is remarkable, and consistent with chemisorption through the acid-base reaction mechanism involving both water and an acetate anion detailed in Scheme 1 (Quinn, Appleby et al. 1995; Anderson, Atkins et al. 2015; Yasaka and Kimura, 2016, Atkins, Kuah et al. 2021). Infrared spectroscopy (ATR-FTIR) was used to find evidence of this. The formation of bicarbonate as the trapped carbon dioxide species is strongly supported by the emergence of a weak, yet clearly observable, signal at ca. 1640 cm⁻¹ due to its asymmetric COO⁻ stretching, for a IL/SiO₂ sample after a CO₂ capture cycle (Fig. 3); the symmetric stretching is probably masked by the IL signals below 1400 cm⁻¹ (Quinn, Appleby et al. 1995). A very weak shoulder at ca. 1700 cm⁻¹ might be due to the contribution of the carboxylic C=O bond stretching of acetic acid, although the strongly H-bonded environment, whereby tightly-bound adducts with bicarbonate (or acetate) are the expected major species instead of free acetic acid (see Scheme 1) (Yasaka, Ueno et al. 2014; Yasaka and Kimura, 2016), would result in band broadening, thus preventing unambiguous assignment. The reversibility of the process was also proven by recording an ATR-FTIR spectrum of the same material after a

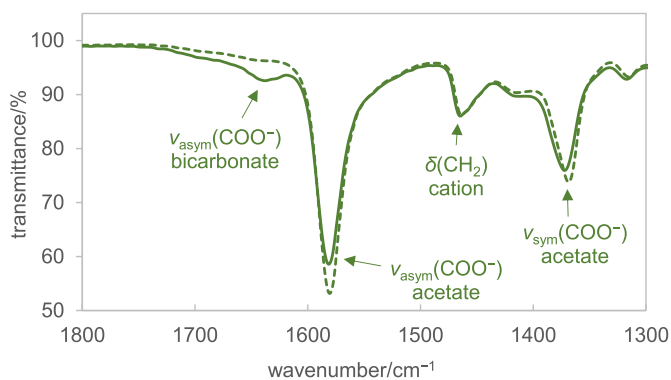


Fig. 3. ATR-FTIR spectra of IL/SiO₂ after a CO₂ capture (solid green trace) and after a CO₂ release (dashed green trace) cycle. The nascent signal observed at 1640 cm⁻¹ upon capture is attributed to the asymmetric stretching of the COO⁻ moiety of the bicarbonate anion formed by chemical sorption of CO₂ by the hydrated acetate ionic liquid, as shown in Scheme 1. The carboxylate stretching signals of the acetate anion are observed on both cases at ca. 1580 cm⁻¹ and 1370 cm⁻¹, whereas the methylene bending signal of the alkyl chains in the cation experiences little change.

regeneration cycle. The disappearance of the bicarbonate signal at 1640 cm⁻¹ confirms that the release of CO₂ is efficient and essentially complete at the moderate regeneration temperature employed (60 °C). Moreover, the acetate COO⁻ stretching signals are less intense and slightly shifted after capture (Fig. 3), most likely reflecting the progressive transformation of the anions into H-bonded adducts upon CO₂ capture. No significant change is observed for the bending signals of the alkyl methylene moieties of the cation, in accord with its role as a stable spectator species in the acid-base CO₂ capture process. It is important to note, however, that the flexibility and size of the cation are important to weaken interionic forces and ensure a wide liquid temperature range for the IL.

3.3. Desorption kinetics

One of the key advantages of IL/SiO₂ as a CO₂ sorbent is its fast desorption. As commented in Section 3.2 above and shown in the release profile plots (Fig. S12), a remarkably short regeneration time at moderate temperature is sufficient to attain an essentially total reversal of the reaction, whereas strongly bound CO₂ is noticeably slower to desorb from PEI/SiO₂ under the same conditions (Fig. 4a). Relevant data have been processed into cumulative plots to track the evolution of key species in the corresponding chemical desorption mechanism, namely released CO₂, and in turn, the related trapped species (e.g. bicarbonate, carbamates), relative to the total mass of the sorbent materials (Fig. S13).

After an initial period ($t < 3$ min) required for the desorbed gas front to fully flow through the analyser, time ranges were identified for adequate fitting to different kinetic models (Fig. 4b). Desorption profiles reasonably fit a first order kinetic model for the amine-free IL material until complete depletion of trapped bicarbonate within 10 min. The amine counterpart behaves in a more complex fashion, apparently following a pseudo-first order trend at initial stages yet later slowing down and turning into lower order kinetics. By comparing the first-order regions for both sorbents, the faster desorption kinetics for IL/SiO₂ is evidenced by a significantly higher rate constant than that of PEI/SiO₂ (0.73 vs. 0.11 min⁻¹, respectively). Release for the latter follows a nearly linear trend after ca. 5 min, and hence can be described as a pseudo-zero-order desorption process, though at a sluggish rate. The simpler and faster CO₂ desorption from the carboxylate IL hydrate sorbent can be ascribed to a straightforward mechanism whereby bicarbonate readily decomposes back to carbon dioxide and water, regenerating the phosphonium-acetate ionic pair, and to the low enthalpy of (de)sorption

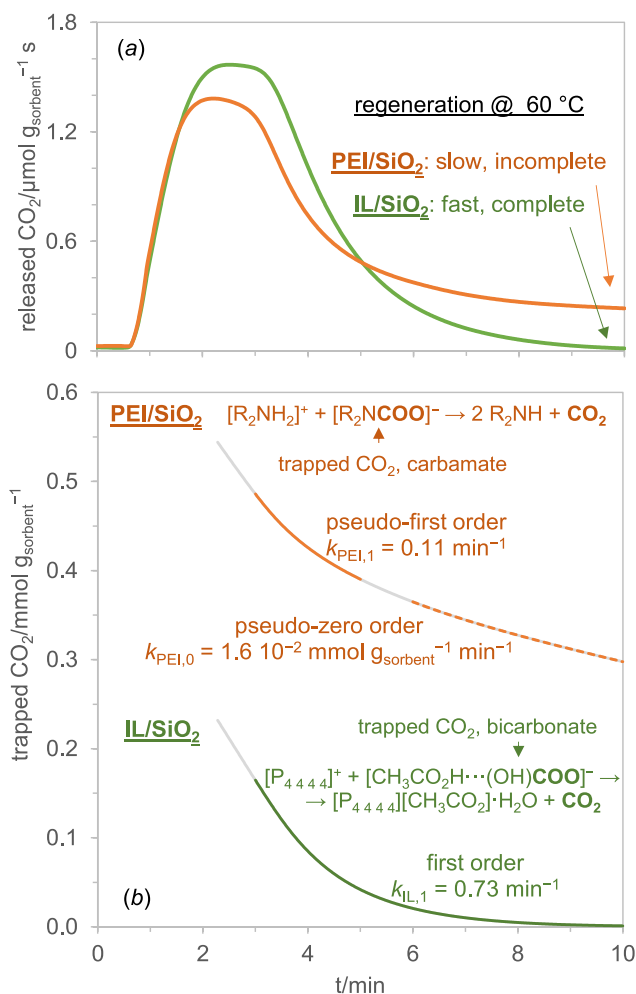


Fig. 4. (a) Regeneration plots and (b) kinetic curves representing the depletion of trapped carbon dioxide species (e.g. bicarbonate, carbamates) for IL/SiO₂ (green) or PEI/SiO₂ (orange). Fitting to first-order kinetics is satisfactory for IL/SiO₂ after $t = 3$ min (solid green line, $k_{IL,1}$, $R^2 = 0.9991$). The desorption profile is more complex for PEI/SiO₂; first order is barely suitable initially (solid orange line, $k_{PEI,1}$, $R^2 = 0.990$), whereas zero order provides a better fit at longer times (> 5 min, dashed orange line, $k_{PEI,0}$, $R^2 = 0.996$). Experimental conditions as described in Fig. 2.

(see Scheme 1). In other words, the hydroxyl moiety in bicarbonate is a better leaving group than the amide analogue in carbamate (IL and PEI sorbents, respectively, see Fig. 4).

Regeneration under moderate temperatures for short cycles can be suitable for designing separation units with low energy requirements operating under high gas flows, as for example point emission sources. In this regard, the possibility of employing amine-free carboxylate IL hydrates must be assessed by analysing energy balances, as discussed below.

3.4. Regeneration energies

Given that the recovery of CO₂ is the most prominent energy-intensive step in carbon capture processes, the determination of regeneration energies is of utmost importance to assess the feasibility of novel sorbent materials. The noticeably lower desorption enthalpies for carboxylate ionic liquid hydrates as compared to amines are a limitation to the capture capacities of the former, but at the same time, their positive effect on the ease of regeneration compensates from an energetic point of view. In fact, the experimental regeneration heat for IL/

SiO₂, determined based on the heat required to achieve 60 °C for the entire system including the sweep gas, is 4.77 kJ g (CO₂)⁻¹, around the upper end of the range for typical aqueous amines (Fig. 5 and Table S6), which have been intensely developed and optimised for almost a century (Bui, Adjiman et al. 2018). This is remarkable for this IL-based material at this proof-of-concept stage and encouraging to pursue further improvement by structural design. Moreover, a less conservative estimation considering the enthalpy of desorption and the sensible heat needed to take the sorbent from capture to regeneration temperature (Goepfert et al., 2014; Zhang, Liu et al. 2014) results in a slightly lower regeneration heat of 4.31 kJ g (CO₂)⁻¹ (see Table S6). This implies an outstanding efficiency (90.3%, see Fig. 5) for the laboratory-scale fixed bed stripping method employed in this work, indicating that even at the moderate regeneration temperature chosen, this IL-based process may be a feasible option.

Under the same working conditions, the PEI/SiO₂ counterpart studied herein is more energy-intensive (6.74 kJ g (CO₂)⁻¹) and less efficient than IL/SiO₂. Other amine-based solid sorbents operating at higher temperatures, widely investigated and improved in recent years, exhibit experimental regeneration heats well below 4 kJ g (CO₂)⁻¹ (Goepfert et al., 2014; Qi, Fu et al. 2014; Zhang, Liu et al. 2014), in addition to remarkably high CO₂ capacities more than one order of magnitude superior to the materials studied here, as illustrated in Fig. 5. Nevertheless, regeneration heats are within comparable magnitudes, above 3 kJ g (CO₂)⁻¹ (Table S6). Efficiency of desorption units can be enhanced using fluidised bed as compared to fixed beds, up to almost 99% (3.32 kJ g (CO₂)⁻¹) for a PEI/SiO₂ material on a pilot plant scale (Zhang, Liu et al. 2014). This is an encouraging performance for solid based CO₂ sorbent materials. Some promising state-of-the-art materials, such as metal organic frameworks functionalised with diamines, have shown the possibility to bind CO₂ selectively and reversibly by a peculiar chain mechanism, leading to energy-efficient regeneration (2.2–2.3 kJ g

(CO₂)⁻¹), albeit at a noticeably high temperature of 150 °C (McDonald, Mason et al. 2015), which might result in thermal degradation, and consequent emission of contaminants, upon long-term operation. Greatly optimised aqueous amine processes also operate with similarly outstanding energetic balance (see shaded purple area in Fig. 5 and data examples in Table S6), in part owing to heat recovery from the absorbent solution coming out of the stripper unit using exchangers in pilot or industrial-scale plants (Bui, Adjiman et al. 2018). It should be noted that further optimisation for amine sorbents might be restricted by their desorption enthalpy, setting a lower bound in regeneration energy (see dashed orange line in Fig. 5). Interestingly, this issue is much less critical for carboxylate ionic liquids given their lower desorption enthalpies (ca. 0.84 kJ g (CO₂)⁻¹, dashed green line in Fig. 5, and Table S6), leaving ample room for improvements, for example by reducing cation sizes while maintaining favourable liquid properties, and hence, minimising sensible heat duties required to elevate temperatures for regeneration. Work is underway in our laboratories to move forward along this pathway.

The regeneration procedure using N₂ as sweep gas employed herein is ineffective to separate carbon dioxide into concentrated streams, as required for an eventual process, but has proven useful to validate the appropriateness of this class of ILs as an alternative to amine sorbents. Other options such as steam-based regeneration are also considered as necessary next steps to progress on the development of amine-free CO₂ sorbent materials.

4. Conclusions

Determined action is required to decelerate, and ideally revert, the accumulation of atmospheric CO₂, and hence avoid disastrous effects of climate change, especially global warming. In addition to reducing emissions, large-scale CO₂ capture might be necessary to avoid the worst near-future scenarios, as concluded by the IPCC in its most recent Assessment Report. Advances in novel, energy-efficient materials and technologies are intensely sought to consolidate the viability of carbon capture. In this work, effective, rapid, and low-energy regeneration of solid-supported CO₂ sorbents based on non-volatile and thermally stable carboxylate ionic liquids, as alternatives to classic amine materials, has been proven by cyclic capture-release performance in a fixed-bed configuration. Capture is enabled in the ionic liquid material, *i.e.* SiO₂-impregnated with tetraalkylphosphonium acetate hydrate (IL/SiO₂), by means of a 1:1 CO₂/IL stoichiometry leading to trapped bicarbonate, as proven by FTIR spectroscopy, confirming the beneficial effect of water on the chemical sorption mechanism. The sorption process is as fast as that of a benchmark analogous material with polyethyleneimine as the sorbent component (PEI/SiO₂), and slightly superior in terms of working capacity (16 and 14 mg (CO₂) g_{sorbent}⁻¹, respectively). Furthermore, desorption of carbon dioxide was essentially complete within 10 min from IL/SiO₂ at a remarkably moderate temperature (60 °C), thus showing the straightforward regenerability of the amine-free ionic liquid material, owing to its relatively low heat of desorption (<40 kJ mol⁻¹). This is a clear advantage over the amine counterpart, which only recovered approximately half of its total CO₂ capture capacity under the same conditions. Based on a first-order desorption kinetics model, CO₂ release was 6–7 times faster for IL/SiO₂. Probably the most relevant aspect of the amine-free carboxylate ionic liquid materials is their remarkably competitive regeneration energies (as low as 4.3 kJ g (CO₂)⁻¹), which fall within the range of amine sorbents (2.3–4.5 kJ g (CO₂)⁻¹) that have been optimised and used in industry for almost a century. The possibility to design CO₂ capture processes using non-volatile amine-free sorbents operating at moderate temperature regimes (well below 100 °C), thus limiting degradation issues, minimising the emission of gaseous contaminants, and reducing costs, might represent a new paradigm in carbon capture technologies.

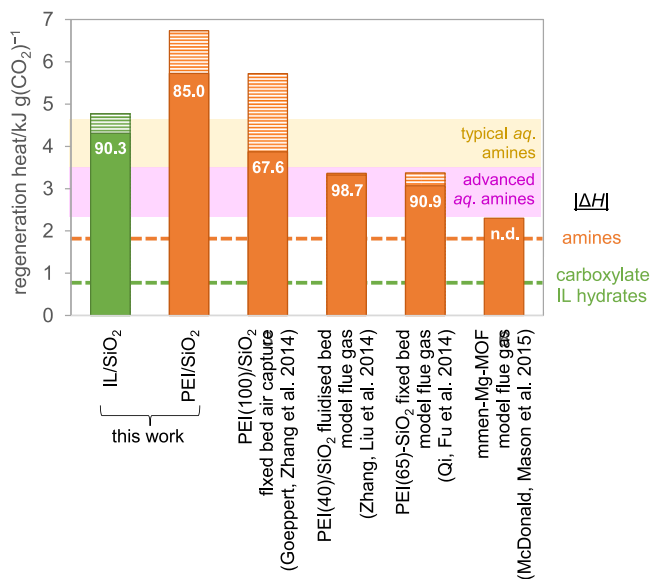


Fig. 5. Comparison between regeneration heats for IL/SiO₂ and PEI/SiO₂ studied in this work and related literature materials (mass ratios, as percentages, in round brackets for other PEI/SiO₂ counterparts; references in round brackets below). Striped and solid bars represent values determined, either experimentally by computing all heat duties involved based on heat capacities, or estimated from desorption heats, respectively (see Table S6 for details). Efficiencies (figures in white, percentages) are defined as the ratio between estimated and experimental regeneration heats. Literature ranges for typical and advanced aqueous amine sorbent processes, mostly taken from Bui, Adjiman et al. (2018), are indicated as pale yellow and purple shaded areas. Average desorption enthalpies are marked by green and orange dashed lines for amine-free carboxylate ionic liquid hydrates and amines, respectively.

Credit author statement

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Alberto Puga reports financial support was provided by State Agency of Research.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2023.117469>.

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