Adsorption of carbon dioxide on naturally occurring solid amino acids

Sreedipta Chatterjee[a], Sadhana Rayalu[a], Spas D. Kolev[b], Reddithota J. Krupadam[a,*]

[a] National Environmental Engineering Research Institute, Jawaharlal Nehru Marg, Nagpur 440020, India
[b] School of Chemistry, The University of Melbourne, VIC 3010, Australia

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A B S T R A C T

Adsorption of CO_2 on solid natural amino acids (AAs) D-arginine, bis(2-hydroxypropyl)amine, cysteamine, L-leucine, D-serine, L-valine, sarcosine, and taurine has been studied in the temperature range of 303–423 K. In a temperature programmed thermal reactor, CO_2 adsorption was carried out in an isothermally controlled flow of CO_2 and the adsorbed CO_2 was desorbed by shifting temperature to 523 K. Based on the experimental results, the amino acid taurine (TAU) was found to adsorb the highest quantity of CO_2 (3.7 mmol g^{-1}) among the studied AAs which was two-fold higher than the quantity of CO_2 absorbed by activated carbon at 303 K. Theoretical calculations have agreed with the experimental results and have revealed that the interaction between the AAs and CO_2 is non-covalent in nature. The polar side chains of AAs are responsible for their high binding ability with CO_2. AAs with heteroatoms such as sulfur has great potential as ligands in developing selective adsorbents for CO_2 capture.

1. Introduction

The impact of increasing atmospheric CO_2 concentration on global warming is recognized as one of the key environmental issues facing human kind [1]. The concentration of CO_2 in the Earth's atmosphere is approximately 398 ppmv as of 2015 [2,13] and increased with the rate of 2.0 ppmv yr^{-1} during the 2000–2009 period [4]. Various CO_2 capture technologies including absorption, adsorption, cryogenics and membrane separation have been reported [7]. Among them, amine or ammonia-based absorption used in industrial separations and capture of CO_2, require relatively high energy for solvent regeneration, solvent evaporation losses are high and damage to the equipment due to corrosion the scope of application of method [3]. A special report of Intergovernmental Panel on Climate Change (IPCC) has pointed out that the development of new generation materials with high adsorption capacities will undoubtedly enhance the competitiveness of adsorptive separation in flue gas applications [6,8]. On the other, the success of this approach is dependent on the development of a low cost adsorbent with high CO_2 adsorption capacity and selectivity, even at moderate (30–50 °C) to high (100–200 °C) temperatures. Materials with large surface area, such as zeolites and activated carbon have been widely reported in the literature [12,15]. Recently, amine functionalized polymer adsorbents have attracted much attention because they are expected to offer benefits over liquid amines in a typical absorption process [17]. Some of the polymer adsorbents reported for their high adsorption capacity for CO_2 include (i) polyethylenimine (PEI) impregnated with MCM-41 adsorbent (2.55 mmol g^{-1}) [18], (ii) amine-modified SBA-15 with N-β-(amino ethyl)-y-aminopropyl dimethoxy methylsilane (AEAPMDS) (1.27 mmol g^{-1}) [19] and (iii) PEI-modified glass fiber adsorbent (4.12 mmol g^{-1}) [9]. These adsorbents have limitations of low CO_2 selectivity and high synthesis costs and difficulty in the production of large quantities required for industrial applications.

CO_2 capture applications of natural materials such as amino acids (AAs) have not been explored so far, and these materials could be attractive candidates for post-combustion CO_2 capture because of their low environmental impact, low volatility compared with conventional amines, low ecotoxicity, and high biodegradability [11]. Importantly, AAs can be used as ligands to functionalize materials/polymers to achieve higher selectivity of CO_2 adsorption from mixture of gases. The dual functionality of AAs due to their carboxylic acid and amino groups works effectively in binding CO_2 in gas phase.

This paper reports on a thermogravimetric study of the influence of temperature, pressure and flow rate on CO_2 adsorption by small AAs (i.e. D-arginine-ARG, bis(2-hdroxypropyl)amine-BHA, cysteamine – CYS, leucine – LEU, D-serine-SER, L-valine-VAL, sarcosine-SAR and taurine-TAU). These AAs can be used as ligands for functionalization of high surface area materials. The potential regeneration of AAs and their reusability for application in cyclic processes have been also evaluated. The nature of interactions

* Corresponding author.
  E-mail address: rj_krupadam@neeri.res.in (R.J. Krupadam).

between AAs and CO_2 has been investigated using computer simulation. The theoretical predictions based on computer simulations have provided information about nature of binding and CO_2 accommodation capacity.

2. Experimental section

2.1. Chemicals

All AAs (ARG, BHA, CYS, LEU, SER, VAL, SAR, and TAU) used in the study were purchased from Sigma-Aldrich (St. Louis, USA) and were of analytical grade. The gases used in this study, He, N_2 and CO_2 of purity higher than 99.999%, and were supplied by Nikita Enterprises (Nagpur, India).

2.2. Description of thermal reactor and CO_2 adsorption experiments

CO_2 adsorption experiments were carried out in a thermal analyzer (STA, Perkin-Elmer STA 6000) equipped with a SaTumA^{TM} sensor.

The analyzer contains a microbalance (0.1 µg maximum sensitivity) in a stainless steel high-pressure housing (210 bar pressure), and feed and exit pumps (ISCO 500D). The balance and housing were positioned on an active air vibration isolation surface, and the whole system was placed inside a temperature-controlled chamber. Pressure in the chamber was measured by a digital pressure gauge (±0.035%) attached to the microbalance housing. An inbuilt data-acquisition board was used to continuously monitor the pressure, the temperature and the microbalance output. The chamber allowed fast cool down (<10 min) of the sample from 1273 to 303 K. The cooling system was integrated with a mass flow gas controller to pump accurately CO_2 into the chamber, which was sealed and purged with a steady flow of He gas. The programmable temperature of the chamber was ramped from room temperature to 373 K at a heating rate of 276 K min^{-1}, to degas and dehydrate the sample.

After the mass of the AA sample reached a constant value in He environment, and was shifted to CO_2 and CO_2 flow was maintain rate 20 mL min^{-1}. An increase in the sample mass was observed indicating that the AAs were adsorbing CO_2. The CO_2 flow was continued until constant mass was attained. The CO_2 gas was in the chamber at a given temperature to adsorption capacities. By varying the holding times the CO_2 adsorption capacities were determined. Data acquisition, storage, and numerical treatment of the CO_2 adsorption were carried out with the software Pyris^{TM} (Ver. 11, Perkin-Elmer).

2.3. FTIR analysis of AAs

Fourier Transform Infra Red (FTIR) was used to verify the formation of bonds between AAs and CO_2. AAs were treated with potassium bromide (Merck, Kenilworth, USA) approximately 1–3 wt % and the resulting powder was pressed into a transparent pellet using a hydraulic press. The pelleted sample was used to record IR spectra. The EZOMNIC software (Ver.7.3, Thermo Electron Corp. Madison MI, USA) was used to collect the peak intensities of the IR absorption bands.

2.4. Computational studies

Density Functional Theory (DFT) approach was used to study the interactions between CO_2 and AAs in gaseous phase. Initially, geometrically optimized CO_2 and AAs were built and configured. DFT computations applied to calculate the interaction energies between the AAs and CO_2 in vacuum. All the AAs and CO_2 were parameterized using the procedure described by [16] involving

quantum chemistry calculations, where bonding force parameters were estimated from analysis of Hessian Force Matrix (HFM) and atomic electric charges were determined from an Electrostatic Potential (ESP) fit. The bond lengths between AAs and CO_2 of linear structures were calculated by using a Linear Constraint Solver (LINCS) algorithm. During formation of a complex between an AA and CO_2, it was hypothesized that each site interacts with all sites of different molecules via Lennard-Jones (LJ) and columbic interactions. The cut-off distances of columbic and van der Waals forces used to describe the interactions mentioned above were 0.9 nm and 1.0 nm, respectively. The LJ parameters used in the calculations were σ = 3.40 Å and ε = 0.086 kcal/mol for carbon and σ = 2.60 Å and ε = 0.015 kcal mol^{-1} for hydrogen corresponding to values from the standard General AMBER Force Field (GAFF). Simulations were conducted with a time step of 0.5 fs for 2000 ps trajectories. The Particle Mesh Ewald (PME) summation method was used to calculate the electronic interactions between AA and CO_2 complex. The analysis of the energy and trajectory of the simulated system carried out with Gaussian 9.0 software (Gaussian Inc. Wallingford, USA). The methodology followed for the activation energy, reaction energy, and binding energy between AAs and CO_2, computed by DFT/ab-initio/6-31G*.

DELL Precision T7500 with Windows XP operating system, CPU − Intel (R) Xeon (R) 2.80 GHz/2.79 GHz Dual Processors, and 24 GB of RAM (memory), and 4 TB hard disk was used to run Gaussian 9.0 software.

3. Results and discussion

3.1. CO_2 adsorption onto AAs

The adsorption isotherms of CO_2 at 303 K up to 15 bar were constructed by monitoring the increase in mass of the AA sample exposed to a constant flow of CO_2. The isotherms in Fig. 1 show saturation at 12 bar and the increasing order of the adsorption capacity at 12 bar follows the order: ARG < BHA < CYS < LEU < SER < VAL < SAR < TAU. The amino acids TAU and SAR showed the highest adsorption capacity, and this could be due to the strong
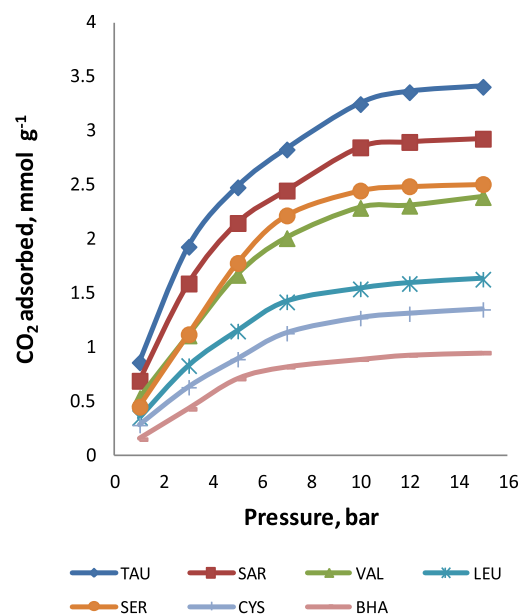
Fig. 1. Adsorption isotherms of CO_2 in the pressure range 0–15 bar. The quantity of each amino acid used was 50 mg in each experimental run and the temperature of the adsorption was 303 K.