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Article

Pentaethylenehexamine-C₆₀ for Temperature Consistent Carbon Capture

Thales Albuquerque Fabiano ^{1,2,†}, Vanessa Pavanelo Soares ^{1,3,†} and Enrico Andreoli ^{1,*}

¹ Energy Safety Research Institute, Swansea University, Bay Campus, Swansea SA1 8QQ, UK; E-Mails: thales_fabiano@hotmail.com (T.A.F.); vanessapavanelo@ufrj.br (V.P.S.)

² Department of Materials Engineering, Federal University of São Carlos, Washington Luís Km 235, Sao Carlos 13569-905, Brazil

³ Polytechnic College, The Federal University of Rio de Janeiro, Rio de Janeiro 21941-909, Brazil

† These authors contributed equally to this work.

* Author to whom correspondence should be addressed; E-Mail: e.andreoli@swansea.ac.uk; Tel.: +44-1792-602-524.

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Abstract: Fullerene C₆₀ is directly added to and reacted with plain pentaethylenehexamine (PEHA) to give PEHA-functionalized C₆₀ powders. The CO₂ capture performance of PEHA-C₆₀ appears to be consistent across a range of temperatures wider than that of polyethyleneimine (PEI)-modified C₆₀, whose high CO₂ capture performance drops rapidly with decreasing temperature. At about 30 °C, the CO₂ capture capacity of PEHA-C₆₀ is six times higher, 65 mg CO₂/g sorbent, than that of PEI-C₆₀, 10 mg/g. In contrast to PEI, PEHA reacts with C₆₀ to form products of greater porosity and smaller particles size that allow for a faster contact between CO₂ and amine functions. This in turns translates into a lower energy requirement for CO₂ sorption and desorption.

Keywords: CO₂ capture; fullerene C₆₀; pentaethylenehexamine

1. Introduction

The steady increase of global CO₂ emissions from fossil energy, cement and metal productions reached for a new record in 2013 with 35.3 billion tonnes (Gt) of CO₂ emitted in the atmosphere [1].

The three largest global CO₂ emitters were China (10.3 Gt), the United States (5.3 Gt), and the European Union (3.7 Gt), accounting for more than half of total global CO₂ emissions [1]. The concentration of CO₂ in the atmosphere has now reached values beyond 400 ppm, increasing from 280 ppm in pre-industrial times [2]. With a concerted political, financial, and technological response to global emissions, the CO₂ levels could be stabilized at 450 ppm, a value beyond which it is believed that the resulting temperature increase would further alter precipitation patterns, melt glaciers, rise sea levels, and intensify weather extremes as never experienced before [3].

Anthropogenic CO₂ emissions are mainly due to coal-, oil- or natural gas-fired power plants. A strong signal of the scale and severity of the problem comes with the new Clean Power Plan announced by US President Barack Obama to fight climate change, aiming to reduce the CO₂ emissions in the United States by 32% in 2030 from the 2005 baseline [4–6]. The new rule would be applied to the nation's power plants, the largest source of CO₂ pollution in the US. This new initiative could result in the decommissioning of large number of coal-fired power plants, encouraging the market to invest in low-carbon energy solutions.

Carbon capture and storage (CCS) technologies represent a concrete solution to CO₂ mitigation. In particular, in the United Kingdom these technologies are gathering momentum with large financial investments in the development of commercial scale CCS. In 2014, the White Rose CCS project was awarded a 300 million Euro funding from the European NER 300 programme, the largest in the world for innovative low-carbon energy demonstration projects [7,8]. Currently in a phase of consultation, the White Rose project plans to develop a state-of-the-art oxyfuel coal-fired power plant integrating full carbon capture and storage technology [9]. With about 450 MW electric gross output and 90% of CO₂ emissions captured, the plant would provide enough low-carbon electricity for over 630,000 households [9]. The captured CO₂ would be pipelined for permanent undersea storage in the North Sea [9]. The Peterhead CCS project is another approach for the production of low-carbon electricity in the UK. The post-combustion retrofit of CO₂ capture at one of the existing Peterhead Power Station combined gas cycle turbines, would allow to store more than 90% of emitted CO₂ in offshore Shell-operated depleted gas reservoirs [10].

Solvents, solid sorbents, and membranes represent the three main types of CO₂ capture and separation materials available at present [11]. The CO₂ capture mechanism is dependent on the chemistry of the capture materials. For example, among well-established technologies, the monoethanolamine (MEA) scrubbing approach is based on the reaction of CO₂ with amines to form carbamates or bicarbonates with water. Aqueous solutions of alkali metal salts, sterically hindered amines, amino acids, or ionic liquid, are other patented solvent-based technologies [11]. Solid sorbents, such as alkali metal oxides, soda-lime, carbonates, zeolites, molecular sieve, silica gel, alumina, active carbon, amine solid sorbents, metal organic frameworks, are also all represented in the patented literature [11]. In contrast, a smaller number of materials have been considered as CO₂ capture membranes, such as polyimides, zeolites, and fluoropolymers [11].

Solid amine-based sorbents are being extensively investigated since they can combine the high selectivity and capture capacity of amines whilst overcoming the problems of corrosion, high regeneration energy, and environmental impact of liquid systems [12]. Within this research effort, our group has focused its attention on the development of new materials made from the immobilization of amine compounds on different types of carbon nanomaterials. Building upon the work of Barron *et al.*, on the

covalent functionalisation of nanocarbons with amines [12,13], we have developed fullerene-cross-linked polyethyleneimine (PEI)-based sorbents and characterized their CO₂ capture performance [14–18]. In particular, PEI-C₆₀ achieved very high CO₂ capture selectivity and a maximum sorption capacity of 200 mg/g (mg CO₂/g sorbent) [14]. We recently demonstrated that this high performance originates from a non-affinity hydrophobic-hydrophilic “repulsive” effect between C₆₀ and amino groups that forces them to be actively exposed to CO₂ [18]. On the other hand, PEI-C₆₀ is a compact material and the CO₂ capture rate at room temperature is slow because of diffusion limitations, for this reason the best CO₂ performance is achieved at higher temperatures, e.g., 90 °C [16]. In the attempt to overcome this limitation, we present herein the preparation and characterization of pentaethylenhexamine (PEHA)-C₆₀ sorbents with improved CO₂ capture performance at room temperature. We introduce PEHA-C₆₀ as a new temperature consistent CO₂ sorbent, since its CO₂ capture capacity is less affected (more consistent) by the temperature when compared to PEI-C₆₀, with corresponding reduced energy demand for CO₂ sorption/desorption process.

2. Results and Discussion

PEHA-C₆₀ was synthesized from the reactive dissolution of fullerene grains directly in pure amine in the absence of any solvent. In particular, C₆₀ was put to vigorously stir in plain PEHA for about 24 h at a temperature of 100–120 °C. A dark almost black liquid mixture was obtained. The PEHA-C₆₀ adduct was precipitated in toluene where the excess reactants were both soluble. The isolated dry product was a compact brown cake easily reduced to fine powder when rubbed between fingers. These product and synthetic procedure are notably different to those of PEI-C₆₀ [14], since the thick molasses-like consistence of PEI requires the use of solvents to allow for an intimate dispersion and contact of fullerene and amine, and the resulting PEI-C₆₀ has a characteristic rubber consistence not evident in the case of PEHA-C₆₀.

The CO₂ capture performance of the thus obtained PEHA-C₆₀ powder was characterized using a thermogravimetric analyser (TGA), the resulting CO₂ sorption curves are presented in Figure 1. In all cases, the sorbent material was preconditioned in Ar at about 90 °C for 60 min prior to the exposure to CO₂. It is immediately evident that the rate of CO₂ sorption and the resulting CO₂ capture capacity after about 5-h exposure are higher at increased temperature. This type of temperature dependence is common in sorbent materials where the kinetics of sorption is limited by slow CO₂ mass transport in the bulk of the absorbent, as previously seen and discussed for PEI-C₆₀ [14]. This result is somewhat surprising for PEHA-C₆₀ since linear PEHA is about one hundred times smaller than branched PEI (232.37 g/mol and 25,000 g/mol, respectively), and PEHA has only 2 ending primary amino groups per molecule compared to about 140 for PEI (assuming a primary:secondary:tertiary amino groups ratio of 1:2:1). It appears that two possible factors might be affecting the temperature dependence of CO₂ capture of polyaziridine materials like PEHA and PEI: (1) each terminal primary amino group of PEHA can react with a different C₆₀ molecule to form a bridge and then consequently a cross-linked network, as already found for PEI [14], and (2) there might be an activation energy barrier to the successful sorption of CO₂, a barrier that is easier to overcome at higher temperature, although purely speculative since we provide no direct evidence for this consideration. In any case, a CO₂ sorption plateau is achieved only for the sorption at 90.2 °C in about 5 h (Figure 1), at lower temperature more time is needed.

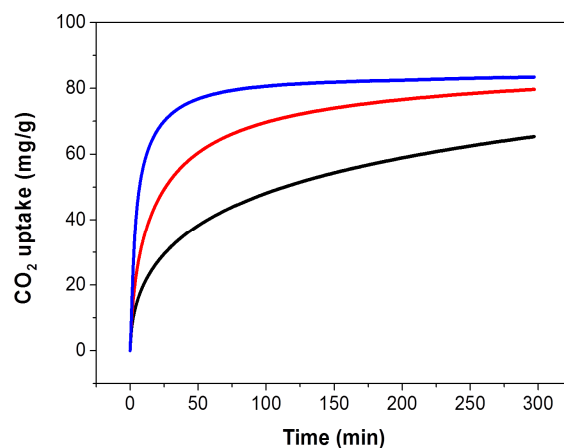


Figure 1. CO₂ uptake of PEHA-C₆₀ in single component CO₂ at atmospheric pressure and various temperatures: 29.3 °C (black curve), 49.6 °C (red curve), and 90.2 °C (blue curve).

It is relevant to comment shortly on the prevalence of chemical/physical adsorption (surface sorption) and absorption (bulk sorption) of CO₂ in PEHA-C₆₀. It is reasonable to say that PEHA-C₆₀ is both a surface and bulk CO₂ chemical sorbent. This statement is based on the well-known chemistry of fullerene C₆₀ and CO₂ with amines. C₆₀ can undergo multiple amine addition to its double bonds. It is then realistic that one C₆₀ molecule reacts with more than one PEHA molecule, especially because in the present reaction conditions the C₆₀:PEHA molar ratio is about 1:300 (0.05 g C₆₀ in 4.75 g of PEHA). Covalently PEHA-decorated C₆₀ molecules are then the molecular components of PEHA-C₆₀. These components form a solid either through amine-amine hydrogen bonding, or through the cross-linking of C₆₀ molecules each reacted with one of the terminal amino groups of PEHA. Based on this rationale, it is then reasonable to say that CO₂ can be adsorbed on the surface of the material, but also absorbed in its bulk since amine functionalities are entertained inside the bulk of PEHA-C₆₀. Additionally, CO₂ reacts chemically with amines to form carbamate and bicarbonate species, so PEHA-C₆₀ is certainly a chemical sorbent, as later elucidated in the infrared analysis of the sorbent materials conditioned in Ar and CO₂.

The CO₂ sorption capacities of PEHA-C₆₀ are 65.3, 79.7, and 83.4 mg/g (corresponding to 1.48, 1.81, and 1.90 mmol/g) at 29.3, 49.6, and 90.2 °C, respectively. However, as just noticed, it is important to underline that these are kinetically limited CO₂ sorption capacities, meaning that equilibrium conditions are only attained at 90.2 °C within the timeframe of sorption, hence larger equilibrium capacities are expected for longer CO₂ exposure times. In comparison, PEI-C₆₀ can achieve a much higher CO₂ sorption capacity of 180 mg/g at 90.3 °C, but this high capacity rapidly plunges to just 40 and 10 mg/g at 49.8 and 29.5 °C, respectively [16]. These drops are equivalent to CO₂ uptake performance losses of up to 95% when the sorption temperature is reduced from 90 °C to room temperature. This is clearly not the case for PEHA-C₆₀. In fact, PEHA-C₆₀ maintains more than 78% of its CO₂ capture performance in going from a sorption temperature of 90 to 30 °C. For this reason, C₆₀-PEHA has a temperature consistent carbon capture performance, *i.e.*, the CO₂ uptake is reliable over a wider range of temperatures opposite to what seen for PEI-C₆₀. PEHA-C₆₀ represents a good trade in CO₂ capture properties where in exchange of a decrease in sorption capacity one gets a more robust performance across a significant range of temperatures. Furthermore, the CO₂ uptake capacity of C₆₀-PEHA is in the range of PEHA-impregnated mesoporous silica sorbents such as

MCM-41-PEHA-50 (50 wt% PEHA) with a capacity of 59 mg/g at 25 °C in modeled flue gas (20% CO₂ in N₂) [19], and SBA-15-PEHA-50 (50 wt% PEHA) with a capacity of 104.4 mg/g at 25 °C in simulated flue gas (12% CO₂ in N₂) [20] or of PEHA-impregnated metal-organic framework PEHA-MIL-101 with a capacity of 57.2 mg/g at about 25 °C in single component CO₂ at 10 bar [21].

The scanning electron microscopy (SEM) images of PEHA-C₆₀ are given in Figure 2. The sorbent material appears to be made of short fibrous particles gathered to form porous chunks. In comparison, PEI-C₆₀ consists of large coalesced lumps with a broad diameter distribution, some of them approximately 2 to 10 μm in size [14]. Evidently, PEHA-C₆₀ consists of much smaller particles in agreement with the limited ability of small and linear PEHA to react with C₆₀ to generate fewer cross-linking points compared to the larger and much primary amine richer branched PEI. Hence, the particle size in PEHA-C₆₀ is smaller than in PEI-C₆₀, and consequently the void volume in PEHA-C₆₀ is greater than in PEI-C₆₀. The greater porosity and smaller particle size of PEHA-C₆₀ is reasonably one of the key reason of the better CO₂ capture performance of PEHA-C₆₀ at ambient temperature.

Fourier transform infrared spectroscopy (FTIR) was employed to identify the functional groups of PEHA-C₆₀, ensuring that C₆₀ was functionalized with the amine, and to establish the formation of carbamates and bicarbonates, groups related to the sorption of CO₂. The FTIR spectra of PEHA-C₆₀ conditioned in Ar and CO₂ are compared to the spectrum of as-received PEHA in Figure 3. Preconditioning in Ar at 90 °C was carried out to remove unbounded H₂O and other adsorbed gases (including CO₂) that could be present in the material. PEHA-C₆₀ was analyzed immediately after Ar preconditioning, and also after additional CO₂ sorption at 90 °C for at least 1 h. A direct comparison of spectra (a) and (b) in Figure 3, confirms the presence of the characteristic amine groups of PEHA in PEHA-C₆₀. In the fingerprint region, five bands can be assigned to the out of plane deformation of N-H at 764 cm⁻¹, C-N stretching at 1009 and 1114 cm⁻¹, C-H scissoring at 1449 cm⁻¹, and the in plane deformation of N-H responsible for the peak at 1589 cm⁻¹ [22,23]. At high wavenumber values, three distinctive bands are assigned to the C-H stretching of the methylene groups of PEHA at 2818 and 2931 cm⁻¹ (symmetric and asymmetric stretching, respectively), and to the N-H stretching at 3274 cm⁻¹ [22,23]. There is also one new peak at 1650 cm⁻¹ that could be related to N-H deformation. Tentatively, this might be related to changes in the IR activity of the amines functions of PEHA caused by the presence of C₆₀, similarly to what observed previously with polypropylenimine dendrimers [18].

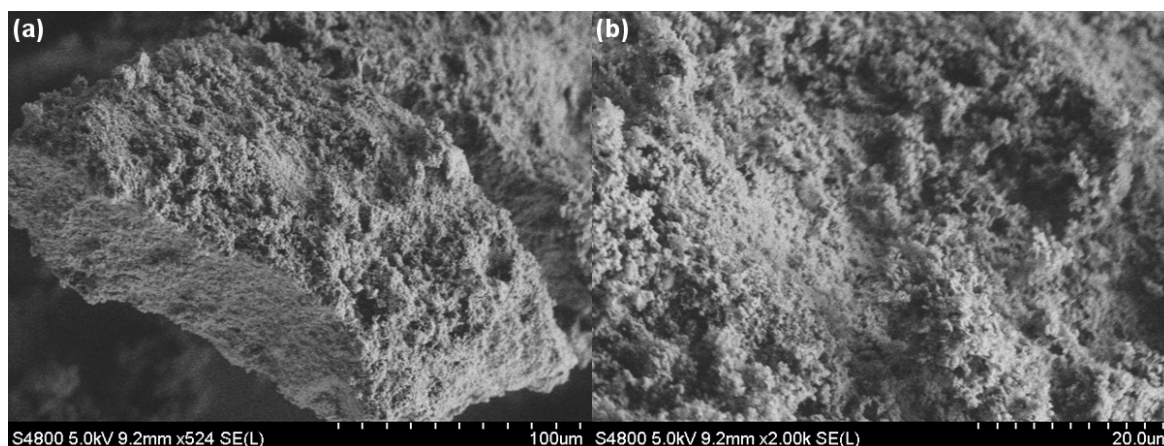


Figure 2. SEM images of PEHA-C₆₀ at different magnifications (a) ×524; and (b) ×2000 showing the porous morphology of the sorbent material.

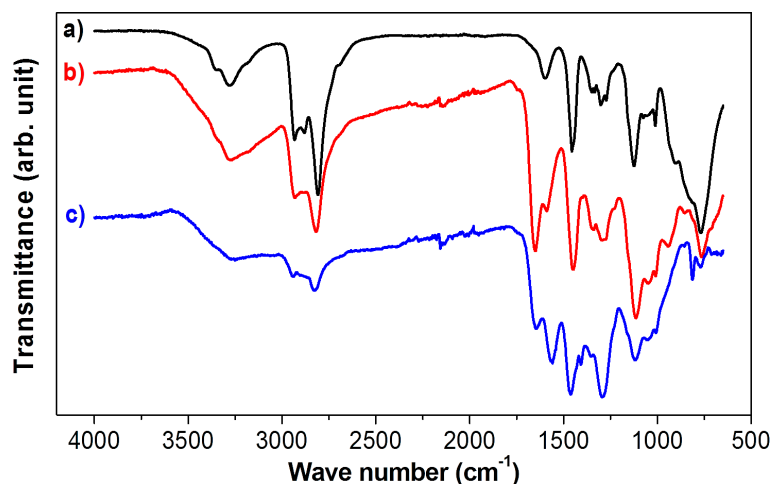


Figure 3. IR spectra of (a) PEHA; and (b) PEHA-C₆₀ conditioned in Ar; and of (c) PEHA-C₆₀ conditioned in CO₂. The spectra have been scaled for ease of comparison.

PEHA-C₆₀ was also conditioned in CO₂ and the corresponding FTIR spectrum (c) is given in Figure 3. Upon CO₂ sorption, no notable changes were recorded in the high frequency section of the spectrum. On the other hand, new peaks appeared in the fingerprint region. The peak at 1559 cm⁻¹ might be associated to the asymmetric stretch of the carboxylic portion of carbamate, although it could be also related to ammonium carbonate species [24]. The peak at 1293 cm⁻¹ could be due to the formation of bicarbonate or to the symmetric stretching of carbamate [24]. Ammonium carbamate, bicarbonate and carbonate species have often overlapping vibrational bands [24]. For this reason, PEHA-C₆₀ can capture CO₂ with the likely formation of two main chemical species (1) ammonium carbamates (-NH-COO⁻ +H₂N<) which are formed when pure CO₂ is absorbed, like in the present case; and (2) ammonium bicarbonates (>NH₂⁺ -HCO₃⁻), which are formed in the presence of water, in this case there could be some residual water molecules bounded to PEHA-C₆₀ that cannot be removed during Ar condition [14,18].

The kinetics of CO₂ capture of PEHA-C₆₀ is also presented. The kinetic analyses were performed using previously reported models and selection criteria [16]. It is found that among the different kinetic models the CO₂ capture data of PEHA-C₆₀ are better described by three models: pseudo-1st-order, pseudo-2nd-order, and modified Avrami. A detailed description of these three kinetic models, with their respective meaning, is reported elsewhere [16]. Shortly, the pseudo-1st-order and pseudo-2nd-order models are referred as “pseudo” because the driving force of reaction is expressed in terms of sorption capacity of the solid, herein represented with w_{∞} (Table 1), instead of the concentration of the species (CO₂ and amine). The difference between pseudo-1st-order and pseudo-2nd-order is that the time needed to reach half of the maximum absorption, τ for which $w(\tau) = w_{\infty}/2$, is $\tau = 0.693/k_1$ for a pseudo-1st-order kinetics and $\tau = 1/(k_2 w_{\infty})$ for the pseudo-2nd-order model. This means that the time required for the reaction to proceed is dependent on sorption capacity w_{∞} , only in the pseudo-2nd-order model. This implies that only sorbents with pseudo-2nd-order kinetics have faster CO₂ sorption rates (shorter τ) at improved CO₂ capture capacity (higher w_{∞}). Hence, a pseudo-2nd-order could be associated to a more effective CO₂ sorbent material. With regard to the modified Avrami model, we found in our previous work that the introduction of the factor mt^{m-1} (Table 1) might allow correcting for mass transport limitation due to the diffusion of CO₂ in the bulk of the sorbent [16].

Table 1. Kinetics fitting results of CO₂ sorption of PEHA-C₆₀.

Kinetic Models *	Parameters	Temperature of CO ₂ Capture		
		29.3 °C	49.6 °C	90.2 °C
Pseudo-1st-order $\frac{dw(t)}{dt} = k_1[w_\infty - w(t)]$	k_1	0.01868	0.03755	0.10578
	w_∞	0.06080	0.07541	0.08123
	R^2	0.921	0.915	0.921
Pseudo-2nd-order $\frac{dw(t)}{dt} = k_2[w_\infty - w(t)]^2$	k_2	0.32882	0.70773	2.33693
	w_∞	0.07149	0.08280	0.08466
	R^2	0.971	0.990	0.999
Modified Avrami $\frac{dw(t)}{dt} = k_a^m m t^{m-1} [w_\infty - w(t)]$	k_a	0.00571	0.03400	0.11425
	w_∞	0.08994	0.08131	0.08257
	m	0.47768	0.55216	0.58556
	R^2	1.000	0.999	0.990

* The weight of the sorbent at time t is $Q(t)$, while $Q(t = 0) = Q(0)$ is the weight at the moment of first exposure to CO₂. The amount of CO₂ absorbed at the time t is $q(t) = Q(t) - Q(0)$, and its corresponding normalized weight is $w(t) = q(t)/Q(0)$. The amount of CO₂ absorbed at equilibrium is $q(t = \infty) = q_\infty$ and its normalized value is w_∞ [16].

Among the three models, the best overall fittings were obtained using the pseudo-2nd-order kinetic model, as summarized in Table 1 and Figure 4. The pseudo-2nd-order model gives the best combination in terms of coefficient of correlation (R^2) for the fittings of the CO₂ sorption data (Table 1) and the corresponding Arrhenius plot (Figure 4). According to the description of the pseudo-2nd-order model given before, it appears that C₆₀ can convert PEHA in an improved CO₂ sorbent because of the hydrophobic-hydrophilic incompatibility of the two molecules, an effect that we have previously observed and described [17].

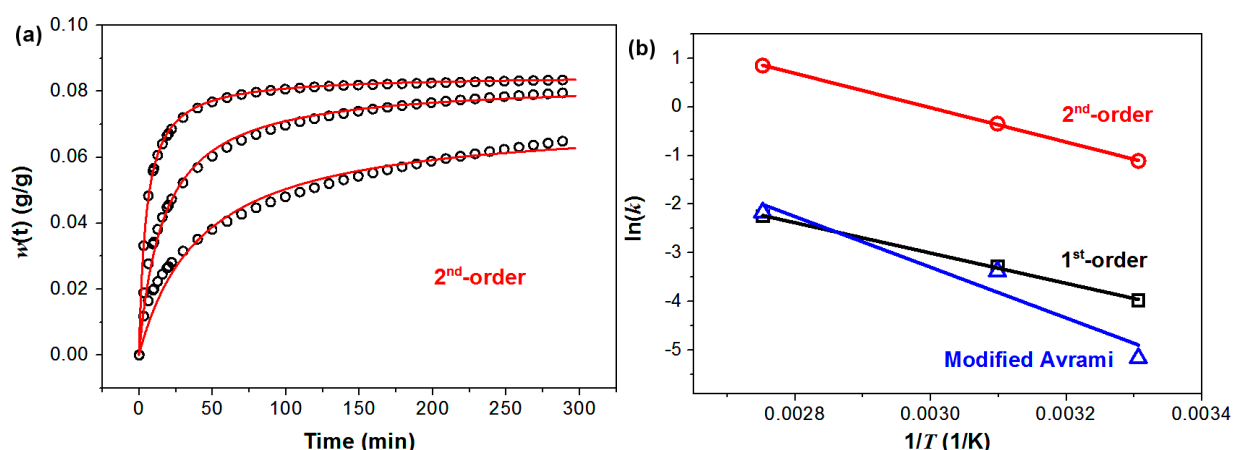


Figure 4. Kinetics of CO₂ capture of PEHA-C₆₀. (a) CO₂ capture data (open black circles) and corresponding pseudo-2nd-order fitting curves (red line); (b) Arrhenius plots for the temperature dependence of the kinetic constants obtained from the fitting of the CO₂ capture data using models pseudo-1st-order (in black, $R^2 = 0.999$), pseudo-2nd-order (in red, $R^2 = 1.000$), and modified Avrami (in blue, 0.937).

The activation energy of CO₂ sorption of PEHA-C₆₀ can be calculated from the slope of the Arrhenius plot ($\ln(k) = -E_a/R \times 1/T + \ln(A)$) to give $E_a = 29.3$ kJ/mol. This value of activation energy is higher than those previously reported for PEI-modified single-walled carbon nanotubes (13.3 kJ/mol) and graphite oxide (22.6 kJ/mol) [16]. It appears then that the energy barrier for CO₂ sorption is dependent on both the carbon substrate and type of amine. In fact, we previously showed that using nanocarbons of higher curvature should lower the energy barrier of CO₂ capture, but this observation does not hold between different amines since the activation energy of the curved PEHA-modified C₆₀ is higher than that of the flatter PEI-modified graphite oxide.

The CO₂ sorption/desorption cycling performance of PEHA-C₆₀ is shown in Figure 5. PEHA-C₆₀ was first conditioned in Ar at 90 °C for 1 h, the temperature was then decreased to 50 °C and the material cycled in CO₂ (for 45 min) and Ar (for 135 min) for twenty times at constant temperature. The resulting CO₂ working capacity decreases slightly after each cycle going from 55 to 50 mg/g (1.25 and 1.13 mmol/g, respectively). This decrease in sorption capacity is not caused by a deterioration of the CO₂ capture performance of the material, but to a progressive increase of the residual amount of CO₂ stored in the sorbent after each cycle, as shown in Figure 5b. PEHA-C₆₀ is then affected by a slow CO₂ desorption rate, however this limitation can be easily overcome at higher desorption temperatures.

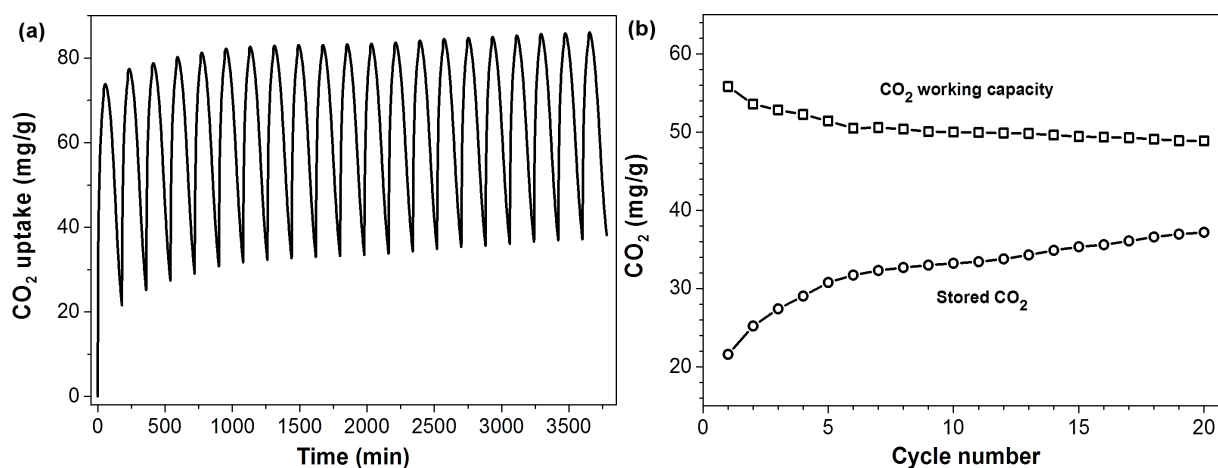


Figure 5. CO₂ sorption/desorption cycles of PEHA-C₆₀. (a) CO₂ capture and release cycles in single component CO₂ and Ar, respectively, at 50 °C and ambient pressure; (b) CO₂ working capacity and amount of stored CO₂ for each cycle.

3. Experimental Section

Fullerene C₆₀ (99.5%), pentaethylenehexamine (PEHA, technical grade), toluene (99.9%) were all purchased from Sigma-Aldrich and used as received. Pure Ar and CO₂ gasses were purchased from BOC UK.

PEHA-C₆₀ was prepared as follows. Fifty milligrams of C₆₀ were added to 5 mL of PEHA in a clean glass vial which was then put to stir at temperature 100–120 °C in a silicon oil bath. After 24 h of vigorous stirring a very dark solution was formed. The solution was then allowed to cool at room temperature, and added to 100 mL of toluene to immediately precipitate the product PEHA-C₆₀. The precipitate was left in toluene overnight. The next day the precipitate was collected on a Teflon membrane using a Millipore vacuum filtering system. The product was then washed with fresh toluene

to remove any residual unreacted PEHA and C₆₀ (both soluble in toluene). The resulting PEHA-C₆₀ was left to fully dry in air to give a brown powdered product.

The thermogravimetric CO₂ sorption/desorption performance of PEHA-C₆₀ was characterized with a TA Instruments SDT-Q600 TGA/DSC. All sorbent materials were preconditioned in Ar at 90 °C prior to any CO₂ measurement. All TGA measurements were performed at ambient pressure. The morphology of PEHA-C₆₀ was examined with an ultra-high resolution field emission scanning electron microscope Hitachi FE-SEM S-4800. The infrared spectroscopy characterisation of the sample was performed with a FTIR Thermo Scientific i510 equipped with a diamond ATR unit.

4. Conclusions

A major limitation in the CO₂ capture performance of polyamine-modified fullerene C₆₀ is the formation of products with limited porosity and correspondingly high CO₂ mass transport limitations at ambient temperature. This is especially true when bulky amine-rich macromolecules like branched polyethyleneimines are used as active CO₂ sorbent components. In order to investigate whether the use of much smaller polyaziridines can improve the CO₂ sorption performance of polyamine-C₆₀, we have modified C₆₀ with pentaethylenhexamine (a very short linear polyamine consisting of just five opened aziridine units plus an extra terminal primary amine) to prepare PEHA-C₆₀, which proved to have much better CO₂ capture performance than PEI-C₆₀ at ambient temperature. This finding is important because it shows how the CO₂ capture performance of polyamine-C₆₀ could be improved through the introduction of smaller amine-rich molecules in the amine/C₆₀ reaction mixture. In terms of bulk scale production, PEHA is used as intermediate of synthesis and as such it should be used in combination with other cheaper polyamines like PEIs that are available at a lower cost and in larger scale. This approach could result in the synthesis of new sorbent materials with improved mass transport properties and better CO₂ capture rates at lower temperature.

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Author Contributions

Thales Albuquerque Fabiano, Vanessa Pavanelo Soares and Enrico Andreoli performed the experiments, analyzed the data, created the Figures, and wrote the manuscript. Enrico Andreoli supervised the project.

Conflicts of Interest

The authors declare no conflict of interest.

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