Carbon Dioxide Capture with Amine-Grafted Activated Carbon

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Abstract There are several possible methods by which amine groups can be grafted on the surface of activated carbon (AC) to improve their capacity for CO_2 adsorption. Ethylenediamine and diethylenetriamine were selected as amino compounds for anchoring on the surface of an oxidized AC. Oxidation of AC was carried out by concentrated nitric acid. For each amino compound, two "in-solvent" and "solvent-free" methods with a number of grafting times were studied. Nitrogen adsorption–desorption at 77 K and proximate and ultimate analysis were used to determine physical and chemical characteristics of the samples. Temperature-programmed (TP) CO_2 adsorption test from 30°C to 120°C were performed to investigate the effect of modification on CO_2 capture. The modification clearly had a negative effect on the textural characteristics of the samples, so the samples showed a less CO_2 uptake at lower temperatures. However, the decrease of capture capacity with increasing temperature is to somewhat softer for amine-grafted samples, so that they have a capacity comparable to the parent sample or even more than that at elevated temperatures. This property may give the new adsorbents this opportunity to be used at flue gas temperature with a higher efficiency. CO_2 capture capacity per unit surface area of all the amine-modified samples, however, was significantly improved, compared to the parent sample presenting a great influence of amino groups on the CO_2 capture capacity. Moreover, the used amine compounds and grafting methods were compared in terms of adsorbent characteristics and CO_2 uptake curves. Cyclic adsorption–desorption tests showed a satisfactory regeneration for the modified samples.

Keywords Activated carbon · Surface modification · Amine grafting · Ethylenediamine · Diethylenetriamine

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1 Introduction

Energy consumption continues to grow worldwide in this century. Considering that fossil fuel is still the major source of energy, a great attention has been concentrated on developing solutions to mitigate anthropogenic CO_2 emission. Available methods

for capturing CO_2 include absorption, adsorption, cryogenic distillation, and membrane separation (Hiyoshi et al. 2004; Pevida et al. 2008; Plaza et al. 2009). Although, absorption with amine solutions is the most conventional, it is suffering from several disadvantages (Chaffee et al. 2007; Contarini et al. 2003; Drage et al. 2007; Gray et al. 2004; Plaza et al. 2007; Wang et al. 2007).

Adsorption has been appeared as one of the promising options for CO_2 capture. Its required energy is lower than amine scrubbing (Plaza et al. 2009). Development of solid adsorbents with higher adsorption rate, selectivity, and capture capacity, particularly in the temperature of flue gas, decreases the cost of CO_2 capture by adsorption and enhance competitiveness of this process (Plaza et al. 2008; Siriwardane et al. 2001).

Adsorption capacity of CO_2 depends on the adsorbent textural characteristics and surface chemistry, as well as temperature and partial pressure or concentration of CO_2. Both specific and nonspecific interactions are important (Arenillas et al. 2005; Guo et al. 2006; Maroto-Valer et al. 2005). As a truth of nonspecific adsorption, molecules of sizes less than 1 nm, especially from a gas phase, can be effectively adsorbed on microporous activated carbon (AC) (Arenillas et al. 2005; Drage et al. 2007; El-Sayed and Bandosz 2001; Gomes et al. 2008; Guo and Lua 2002; Kodama et al. 2002; Maroto-Valer et al. 2005; Plaza et al. 2007; Tamai et al. 2006). On the other hand, nitrogen functional groups in the structure of AC affect CO_2 adsorption positively (Arenillas et al. 2005; Drage et al. 2007; Maroto-Valer et al. 2005; Pevida et al. 2008; Shafeeyan et al. 2010). This may be attributed to the basicity contributed by nitrogen groups (Arenillas et al. 2005). Introduction of nitrogen surface groups has been done by ammonia treatment (Maroto-Valer et al. 2005; Pevida et al. 2008; Przepiorski et al. 2004; Shafeeyan et al. 2011), impregnation with amine-containing compounds (Maroto-Valer et al. 2005, 2008; Plaza et al. 2009) or grafting amino groups (Gray et al. 2004; Grondein and Bélanger 2011). It has been reported that amine functional groups have a high affinity for CO_2 through forming complex (Harlick and Sayari 2005; Hiyoshi et al. 2004, 2005; Knowles et al. 2005).

The authors have reviewed the potential methods for anchoring amino groups on the surface of activated carbon (Houshmand et al. 2011): There

are viable options to graft amine groups on the surface of AC, including silylation with aminosilanes, nitration followed by reduction, anchoring diamines/polyamines, anchoring halogenated amines, and surface-initiated polymerization of ethylene imine and its derivatives.

In the present work, one diamine and one polyamine, i.e., ethylenediamine (EDA) and diethylenetriamine (DETA) were selected for direct grafting on the surface of palm shell AC. Linearity and small size of EDA and DETA and microporosity of original AC were the reasons for selecting them from a collection of available amino compounds that may be employed for amine anchoring. Diamines and polyamines can be directly or indirectly anchored on the surface of AC. In the direct method, amine groups of these compounds condense with carboxyl groups on AC to generate surface amide groups. In the indirect method, they are anchored on the surface via a linking agent such as thionyl chloride ($SOCl_2$). In this case, first, the linking agent reacts with carboxylic groups of the surface to produce a chlorinated product; and in the next stage, the amine groups of diamines/polyamines condense with anchored chlorine atoms. The reaction of AC with thionyl chloride is usually carried out in an organic solvent such as toluene. As another modification option, the medium used for the condensation of diamines/polyamines with AC (or chlorinated AC, in the case of the indirect method) can be a solvent such as toluene or may be liquid/molten diamine/polyamine itself. In this paper, these two methods are denoted as "in-solvent" and "solvent-free", respectively.

2 Experimental

2.1 Materials

The original material for preparing developed adsorbent was a microporous palm shell AC produced by Bravo Green Sdn Bhd, Malaysia. As received, AC was sieved to the size range of 500–850 μm and washed with distilled water to remove fines. It was then dried in an oven at 110°C overnight and kept in closed bottles for experiment. Hereinafter, it is referred to as A1. Fisher Scientific, Malaysia supplied the chemicals including reagent-grade nitric acid, analytical-grade toluene, EDA, and DETA.

2.2 Modification of AC

AC samples were subjected to a two-stage modification. At the first stage, they were oxidized by nitric acid to increase the density of oxygen surface groups, and then, at the second stage, amine anchoring was performed.

For oxidation, a specified amount of AC was refluxed with concentrated nitric acid in a 250-ml round bottom flask, which was heated by a heating mantle, for a specified time. It was greatly rinsed with deionized water until pH of water reached at 5 and then dried in oven overnight. The oxidized sample was the starting material for amine grafting. At the second stage of modification, the oxidized AC was divided into equal parts to prepare four series of modified samples, each series including three samples: each part of the oxidized AC was refluxed with pure EDA (or DETA) or refluxed with a solution of EDA (or DETA) in toluene for times of 1, 2, or 4 h. The amine-grafted samples were washed with an amount of toluene and then were purified in a Soxhlet extraction unit for 24 h to make ensure to remove unbound diamine/polyamine molecules. In the halfway of extraction, the used solvent was replaced with the fresh one. The extracted samples were dried in oven overnight before use for analysis and CO_2 capture tests. The prepared samples are denoted as follows: P-EDA-1 is the sample modified with pure EDA for 1 h, T-DETA-4 is the one refluxed with DETA solution in toluene for 4 h and so on.

2.3 Characterization Methods

N_2 adsorption–desorption isotherms were measured at 77 K using ThermoFinngan Sorptomatic 1990 Series analyzer to determine textural characteristics of the samples. Prior to the measurements, the samples were outgassed at 120°C and under vacuum. BET surface area (S_{BET}) was calculated based on adsorption data at the relative pressure (P/P$_0$) less than 0.3. Total pore volume (V_t) was calculated based on the nitrogen adsorbed volume at relative pressure of 0.995.

2.4 CO_2 Capture Measurements

Temperature programmed (TP) CO_2 adsorption and cyclic adsorption–desorption operation were carried out with the aid of TGA/SDTA851 Ultramicro Balance, Mettler-Toledo by the method as follows: At the first step, the samples were first outgassed from pre-absorbed CO_2 and water at 120°C for 1 h in 50 ml/min nitrogen stream and were allowed to be cooled to 30°C. Then, the gas was switched to pure CO_2 of 50 ml/min for 1 h to achieve a complete saturation. The increase in sample weight was considered as CO_2 uptake capacity at the target temperature.

For cyclic operation, the abovementioned procedure was repeated three times as first, second, and third regenerations, and the capacities of the samples were compared with the first saturation.

To carry out TP CO_2 adsorption tests after the first saturation, the temperature was increased with a ramp rate of 1°C/min from 30°C to 120°C to obtain CO_2 temperature dependence of CO_2 adsorption capacity.

3 Results and Discussion

3.1 Grafting Amino Groups

Table 1 presents the results of proximate and ultimate analysis along with the textural characteristics of the samples. It is observed from the table that amine grafting decreases surface area and pore volume of the samples, as widely reported by others (Gorgulho et al. 2008; Marcoux et al. 2007; Pittman et al. 1997a, b, c; Torres et al. 2006). This can be interpreted in terms of pore blockage by functional groups attached on the surface. The degree of amine anchoring can be quantified from the raise in nitrogen content and also volatiles. All these measures agree pretty well with each other to indicate amine grafting qualitatively and quantitatively.

To interpret the results in a more exact manner, the trends of changes in nitrogen content and surface area vs. time of amine grafting have been shown in Fig. 1 for different series of the samples. In each series, increased treatment time leads to higher nitrogen content and lower surface area. However, as time increases, the slope of increase in nitrogen content and of decrease in surface area is becoming softer, indicating reaching at a saturation state for each case. With the maximum time used in the experiments, a saturation state is about to be reached, although it is not completely achieved. So we may consider amine grafting at 4 h as the saturation state in our future discussion.

Table 1 Textural characteristics and results of proximate and ultimate analysis for amine-modified samples

Sample name	Proximate analysis (wt%)[a]			Ultimate analysis (wt.%)				S_{BET}	V_t
	VM	FC	Ash	C	H	N	O[b]	(m²/g)	(cm³/g)
A1	17.64	75.7	6.66	85.26	1.51	0.31	6.26	846.3	0.434
P-EDA-1	38.2	57.35	4.45	67.21	2.04	3.75	22.55	287.7	0.187
P-EDA-2	42.12	53.72	4.16	64.78	2.21	4.89	23.96	190.4	0.135
P-EDA-4	42.67	53.12	4.21	65.43	2.25	5.23	22.88	147.1	0.106
T-EDA-1	42.82	52.95	4.23	67.56	2.2	5.32	20.69	195.35	0.138
T-EDA-2	47.03	49.72	3.25	64.81	2.58	7.68	21.68	111.3	0.081
T-EDA-4	48.44	48.27	3.29	65.93	2.67	8.25	19.86	80.4	0.052
P-DETA-1	34.75	61.65	3.6	67.45	1.94	3.04	23.97	358.2	0.212
P-DETA-2	41.09	55.3	3.61	66.29	2.04	3.86	24.2	239.7	0.171
P-DETA-4	42.56	53.98	3.46	65.38	2.11	4.15	24.9	208.6	0.154
T-DETA-1	39.88	55.97	4.15	69.04	2.21	4.43	20.17	240.64	0.16
T-DETA-2	43.88	52.38	3.74	67.22	2.46	6.37	20.21	148.12	0.113
T-DETA-4	44.37	51.85	3.78	66.45	2.53	6.94	20.3	98.67	0.072

[a] Dry basis

[b] Calculated by difference

It is interesting to notice the effect of amine compound type. An increase in the nitrogen content is observed in going from DETA to EDA, either in solvent-free or in-solvent method. The smaller size of EDA gives it a higher diffusion rate, compared with DETA. However, this fact seems not to be crucial to

Fig. 1 Effect of anchoring time on the nitrogen content (**a**) and surface area (**b**) for different series of modified samples
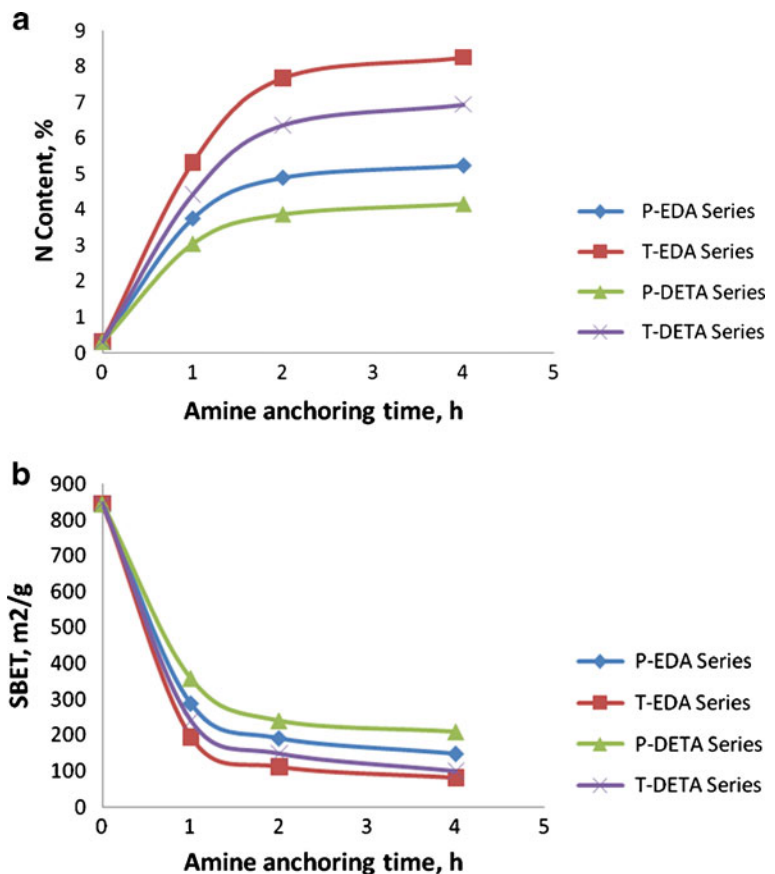
the differences in the results. It is evident from Fig. 1a that after 4 h, the samples are very near to the complete saturation, so P-DETA (or T-DETA) series will not achieve P-EDA (or T-EDA) series in terms of nitrogen content by giving more time. The lower size of EDA has two determining effects by its inherent nature: It allows EDA molecules to access a higher number of active sites for bonding. Moreover, bound DETA molecules offer a larger steric hindrance and may prevent other DETA molecules from bonding to the neighbor active sites. Thus, it may be inferred that active sites available for DETA anchoring are more limited, compared to EDA.

On the other hand, improvement in the performance of amine anchoring is achieved by adding toluene as solvent to the system. Figure 1a shows that for both amine compounds, if anchoring is performed in a solvent like toluene, instead of liquid diamine/polyamine itself, an increased content of nitrogen is resulted. In going from solvent-free to in-solvent method, increases of 57.7% and 67.2% in the nitrogen content are observed in the cases EDA and DETA, respectively. So DETA anchoring is more influenced by solvent, compared with EDA. In total, of all the samples, EDA-anchored AC in toluene medium presents the highest nitrogen content.

As it can be perceived from Fig. 1b, going from EDA to DETA and from solvent-free to in-solvent method, lead to more decreases in surface area. Comparing Fig. 1a and b confirms the rationalization that higher nitrogen content leads to a higher degree of pore blockage.

3.2 CO_2 Capture Performance

TP CO_2 adsorption test is a suitable technique to estimate CO_2 adsorption capacities of the adsorbent samples at different temperatures and so examine the effect of temperature. Figure 2 compares CO_2 uptake capacity, expressed as the percentage of weight increase during test, of the samples modified at the maximum anchoring time with that of the parent sample.

It is observed from the figure that the uptake capacities of the samples, either treated or untreated, reduce as temperature increases. The reason can be easily attributed to the nature of physical adsorption as the prevailing mechanism, which is negatively affected by temperature. All the treated samples have a surface area lower than the parent sample, so their

CO_2 adsorption profiles are located under that of the parent. However, the slope of decrease in capacity of the modified samples is softer than A1, so the difference between the capacities of the treated samples and the parent is vanished as temperature increases. It may be seen from Fig. 2 that at the elevated temperature (near 115°C), uptake capacity of T-EDA-4 exceeds A1. All these observations may be justified by considering the presence of a significant amount of nitrogen functional groups attached on the surface, which create or strengthen the role of chemisorption of CO_2 species by amino groups. Figure 3 shows TP CO2 adsorption curves for one of the modified series, T-EDA, as the representative of all the series.

The figure indicates that increasing time leads to a decrease in CO_2 uptake capacity in lower temperatures, despite the increase in the nitrogen content. This is ascribed to physisorption contribution to total uptake capacity. However, the softer slope of the curves with increasing time is observed for most cases and confirms the role of chemisorption as described beforehand.

As pointed out previously, CO_2 capture capacity is contributed by two mechanisms of physisorption and chemisorption taking place simultaneously. The former depends on the porous structure, whereas the latter is affected by amino (or nitrogen) content (Arenillas et al. 2005; Drage et al. 2007; Maroto-Valer et al. 2005; Pevida et al. 2008). As amine anchoring decreases surface area and increase the amine content, these two mechanisms are acting inversely. This is the reason that the order of the modified samples in terms of CO_2 uptake capacity does not follow their order in terms of surface area or nitrogen content exactly. In order to separate the role of chemisorption, TP CO_2 capture curves can be normalized by the BET surface area, as shown in Fig. 4. In other words, we compare CO_2 capture capacity of the samples at the same surface area to detect the influence of grafted amino groups. It is observed from the figure that all the modified samples have a higher capacity than A1 due to the effect of chemisorption. The order of the samples in terms of capture capacity per unit surface area agrees quite well with nitrogen content in Table 1. All the samples, especially the modified by EDA in toluene present a significant increase in CO_2 capacity. Compared to A1, T-EDA-4 shows a seven- and ten-fold increase in

Fig. 2 TP CO_2 adsorption of the selected modified samples
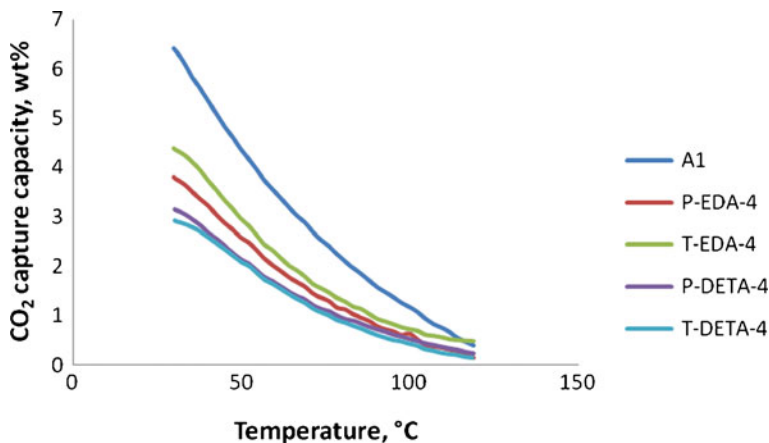
capacity at 30°C and 115°C, respectively. From the results, it is inferred that amino groups have an outstanding effect on the CO_2 adsorption.

3.3 Cyclic Operation

Stable performance of an adsorbent for long term is a pre-requisite for its use in industries. In order to have an insight into stability of performance of the amine-grafted ACs in practical applications, cyclic tests were carried out. Figure 5 illustrates the capacities of the selected samples for four consecutive adsorption–desorption tests, i.e., capacities in their first saturation (no regeneration) and after three subsequent regenerations. It may be observed from the figure that the adsorption capacities show slight decreases after first regeneration, compared with first saturation, whereas the decrease in capacity after next regenerations are almost negligible, i.e., the capacities remain essentially

unchanged. The decrease in capacity after first regeneration can be mainly attributed to the unreleased CO_2 resulted from the first saturation. This suggests that a higher regeneration temperature may be helpful. However, in this study, the regeneration temperature was assumed as same as initial outgassing temperature (120°C). On the other hand, it is concluded from the figure that there is no significant accumulation of CO_2 in the samples during each step of adsorption after first regeneration. The capability of the modified ACs for a satisfactory regeneration, as it is concluded from the figure, may be considered as a promising indication for stable performance in practical cyclic operations such as pressure swing adsorption.

3.4 Comparison of CO_2 Capture Capacities

As mentioned earlier, modification of AC with nitrogen groups for CO_2 capture purpose has been

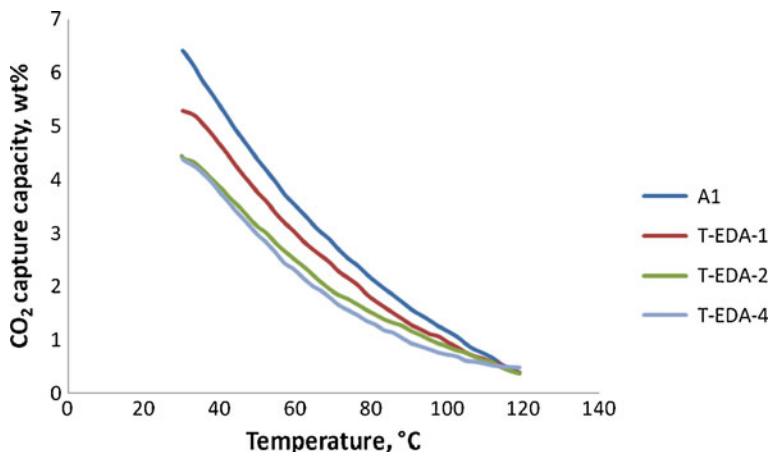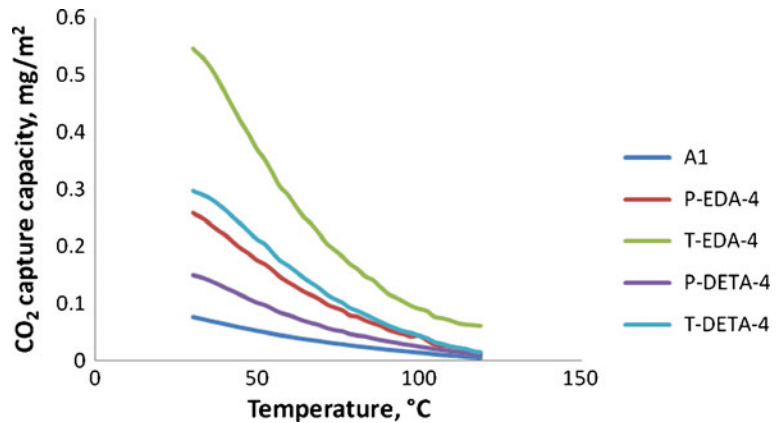Fig. 3 TP CO_2 adsorption of the samples of T-EDA series

**Fig. 4** TP CO2 adsorption curves, normalized by surface area

studied by several researchers. Due to different characteristics of virgin ACs used for modification and also different measurement methods and instruments, it is very difficult to compare the modified adsorbents with each others. However, the relative success achieved in modification may be compared, as carried out here for several available studies:

Bezerra et al. (2011) impregnated AC with concentrated triethanolamine (TEA, 98%) and dilute monoethanolamine (MEA, 0.2%), as a part of their study. They reported CO_2 capture capacities of 83 and 31 mg/g for original AC at 25°C and 75°C (1 bar), respectively. Both modified AC-MEA and AC-TEA showed lower capacities at 25°C (45 and 14 mg/g, respectively), indicating decreases of 45% and 83%, compared with AC. However, capacity of AC-MEA exceeded AC at 75°C (75 mg/g, an increase of 142%), whereas AC-TEA still had a very low capacity of 12 mg/g (a decrease of 61%) due to detrimental effect of impregnation of concentrated

TEA on AC texture. In the context of impregnation, Maroto-Valer et al. (2008) impregnated an activated fly ash with MEA, diethanolamine (DEA), methyldiethanolamine (MDEA), and MEA/MDEA. At 30°C, only AC-MEA presented a capacity more than virgin AC (68.6 vs. 41.8 mg/g). This was attributed to a chemical reaction of MEA and CO_2 at 30°C. Increase in temperature, reduced the capacity of the non-impregnated activated fly ash, whereas capacities of the impregnated carbons reached a maximum at a temperature of 75°C or 100°C, indicating the role of chemisorption. However, at 120°C, AC-MDEA and AC-MEA/MDEA still had capacities higher than non-impregnated carbon (16.1 and 23.7 mg/g, respectively vs. 7.7 mg/g) despite the considerable reduction in surface area due to impregnation. The authors believe that some of the results are similar to what is occurred in amine scrubbing processes. Plaza et al. (2007) impregnated a commercial AC with different polyamines, including DETA, pentaethylenehexamine and

Fig. 5 Cyclic adsorption–desorption tests: adsorption capacities were measured at 30°C, regeneration was performed at 120°C, cycle number of 0 indicates first saturation, and other cycle numbers show the corresponding regenerations
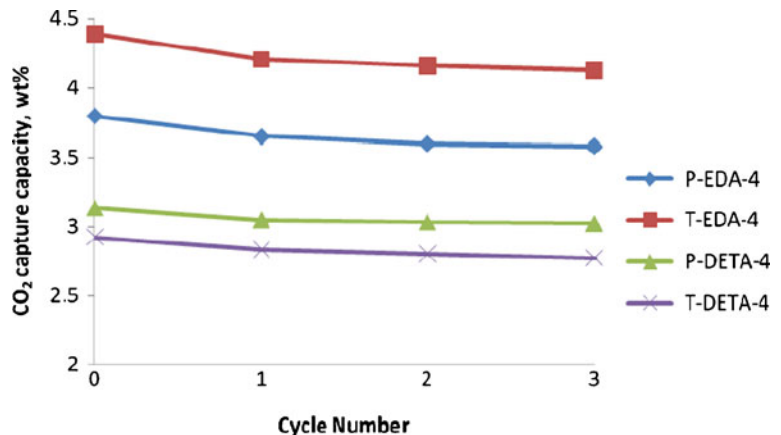
polyethyleneimine (PEI). In spite of a drastic decrease in surface area (a decrease of 90–95%), CO_2 capture capacities of the modified samples decreased only 32–45% at 25°C (based on TP CO_2 adsorption tests). Moreover, AC-DETA presented higher capacities at elevated temperatures (60–100°C) compared to original AC. Maroto-Valer et al. (2005) achieved an increase in CO_2 capture capacity by ammonia treatment at 800°C (21.55 vs. 23.69 mg/g). It should be mentioned that BET surface area was also increased from 925 to 952 m^2/g for this modification. For the same original AC, impregnation with PEI increased capacity to 26.30 mg/g, while BET surface area decreased to less than 1 m^2/g. Pevida et al. (2008) modified AC with ammonia treatment at different temperatures. They achieved increases of 20% and 35% in capacity for one of the ammonia-treated samples at 25°C and 75°C, respectively, in the expense of 28% decrease in surface area. Shafeeyan et al. (2011) prepared different modified samples by ammonia treatment following a preliminary heat treatment or oxidation. Some of the samples presented an improvement in CO_2 capture capacity in a range of temperature, particularly at elevated temperatures. Their best result at 105°C indicated an increase from 19 for the parent to 30.1 mg/g for the pre-oxidized sample which has been modified with ammonia at 800°C. Grondein and Bélanger (2011) selected three non-linear diamines including paraphenylenediamine, 4-aminobenzylamine, and 4-aminoethylaniline to graft on the surface of carbon using reduction of diazonium cations in situ generated from the diamine. They reported a decrease in capture capacity from 0.34 mmol/g for virgin AC to 0.24, 0.16, and 0.16 mmol/g (equal to 29%, 53%, and 53% decrease) for the abovementioned diamines at 40°C, respectively. They attributed the results to loss of microporosity and concluded that physisorption is the predominant mechanism for adsorption. Gray et al. (2004) grafted a halogenated amine (3-chloropropylamine-hydrochloride) on the surface of a fly ash and increased its CO_2 desorption capacity at 120°C from 72.9 to 174.6 μmol/g.

4 Conclusion

We prepared four series of modified AC samples by anchoring EDA and DETA on the surface of a microporous palm shell AC via two methods, i.e.,

with or without toluene as solvent. It was shown that a saturation state in terms of surface area, pore volume, and nitrogen content can be achieved in each series of the samples by increasing time. Although amine grafting resulted in a negative effect in the texture of all the samples, TP CO_2 test indicated that amino groups can enhance CO_2 capture capacity per unit surface area significantly. In addition, a lower temperature dependency was seen for capture capacity of the samples, compared to the parent. However, the capacity of the modified samples per unit weight is not larger than the parent in most cases, due to microporosity of the starting material, which results in a higher pore blockage by the oxidation and amine grafting. It seems that with a mesopore AC, this modification may lead to superior results. As one the best results, the sample modified with EDA in toluene revealed a capture capacity greater than the origin sample at elevated temperatures. Moreover, the experiments indicated that EDA and in-solvent method are more efficient than DETA and solvent-free method, respectively. Moreover, it was shown that adsorption capacities of the modified samples remain essentially unchanged during cyclic operation that is a promising indication for practical applications.

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