

Modification of Activated Carbon Using Nitration Followed by Reduction for Carbon Dioxide Capture

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Activated carbon (AC) samples were modified using nitration followed by reduction to enhance their CO₂ adsorption capacities. Besides characterization of the samples, investigation of CO₂ capture performance was conducted by CO₂ isothermal adsorption, temperature-programmed (TP) CO₂ adsorption, cyclic CO₂ adsorption–desorption, and dynamic CO₂ adsorption tests. Almost all modified samples showed a rise in the amount of CO₂ adsorbed when the comparison is made in unit surface area. On the other hand, some of the samples displayed a capacity superior to that of the parent material when compared in mass unit, especially at elevated temperatures. Despite ~65% decrease in the surface area, TP-CO₂ adsorption of the best samples exhibited increases of ~10 and 70% in CO₂ capture capacity at 30 and 100 °C, respectively.

Keywords: Activated carbon, Surface modification, Anchoring, Amino groups, Nitration

Introduction

Carbon dioxide is the most significant greenhouse gas that contributes to global warming. This is due to its high emission rate.¹ CO₂ capture and sequestration (CCS) is one of the possible strategies for mitigating the amount of emitted CO₂. However, these approaches are considered as short-term solutions.² Adsorption is the viable method among the various methods currently in use or undergoing investigation for the initial stage of CCS (*i.e.*, CO₂ capture). Adsorption does not have the drawbacks of amine scrubbing as with most conventional technique for CO₂ capture and has lower energy requirement.^{3–12} Adsorption capacity of an adsorbate such as CO₂ is determined by the surface area, pore size, adsorbent's surface chemistry, temperature, and partial pressure/concentration of the adsorbate.^{12,13} In this regard, surface functional groups may strongly increase the adsorption capacity via the creation of specific interactions between the adsorbent and the adsorbate. However, it is worth noting that textural characteristics have a governing effect on the capacity, whereas surface chemistry has an influencing effect.¹⁴

Activated carbon (AC) is a suitable adsorbent that has a number of advantages over other porous materials.^{10,12,15–18} Modification of AC in terms of surface chemistry has received great attention in producing adsorbents with high capture capacity. It is widely accepted that nitrogen functionalities, in the form of amino or other nitrogen groups, enhance CO₂ adsorption capacity on the AC surface.^{4,12,13,19–28} There are a number of methods that can be used to modify the AC surface with nitrogen functionalities (amino groups, in particular), including impregnation with amine-containing compounds,^{12,13,22} amination,^{13,19–21} silylation with aminosilanes, nitration followed by reduction, anchoring diamines/

polyamines, anchoring halogenated amines, surface-initiated polymerization of ethyleneimine and its derivatives, and plasma treatment. The possible techniques for modifying AC with amino groups have been reviewed.²⁹

Nitration followed by reduction as one of these potential methods has been studied in this work. Nitration of AC with the mixture of nitric acid and sulfuric acid (the so-called nitrating mixture³⁰ or mixed acid³¹) creates –NO₂ groups directly attached to the benzene ring of the AC surface.^{30–32} Electrophilic aromatic substitution is believed to be the mechanism of nitration^{31,33,34}: sulfuric acid is stronger than nitric acid and can protonate the latter with the following reaction:



Nitronium ion (NO₂⁺), which is an electrophile center for nitration, is produced by the above reaction.^{30,31,34} This ion is highly reactive and can attach to the aromatic rings with activating or deactivating groups.³⁵ Theoretically, nitric acid alone is not able to nitrate the benzene ring.³⁰ However, some studies show that it can produce a small amount of NO₂⁺ by electrophilic aromatic substitution.^{31,34–36} Reduction of nitro groups to amino groups may be carried out via a variety of methods. Na₂S₂O₄^{33,34} or iron powder³⁷ has been employed for reduction of nitrated AC.

Experimental

Materials. The starting material for experimental study was a commercial AC produced from palm shell by Bravo Green Sdn Bhd, Malaysia. After sieving to the size range of 500–850 μm, it was washed with distilled water to remove

finer, and dried in an oven at 110 °C overnight. In the following, it is referred to as sample A1. Fisher Scientific, Malaysia, supplied the chemicals including reagent-grade nitric acid, sulfuric acid, and sodium dithionite.

Modification of AC. AC samples were subjected to a two-stage modification, namely nitration and reduction. Nitration of the AC samples was carried out by refluxing a specified amount of A1 with mixed acid in a round-bottomed flask placed on a heating mantle and connected to a condenser. Four series of nitrated samples were prepared by using mixtures of concentrated sulfuric acid/nitric acid (v/v) with ratios of 2, 3, 4, and 5. Based on the following observations, three steps were distinguished in nitration experiment and three different nitration durations were selected accordingly. When an AC sample is refluxed with concentrated mixed acid of a specified ratio, a brownish gas starts to evolve (step 1). After the specified time of t_1 min, which is different from a mixed acid ratio to another one, evolution of the aforementioned brownish gas is stopped and evolution of a white color gas starts (step 2). Evolution of the latter lasts for a time of t_2 min and then it is stopped (start of step 3). In the light of above, for each ratio of sulfuric acid to nitric acid, three treatment times of t_1 , $t_1 + t_2$, and $t_1 + t_2 + 40$ min were considered. A good repeatability was found for t_1 and t_2 for each ratio. Table 1 shows the conditions of nitration experiments along with their designated names. It should be mentioned that sample R2-100 was not considered for the characterization and adsorption tests because it was found by visual check that the sample was mostly converted to powder and almost completely destroyed by concentrated acid. For the second stage of modification, *i.e.*, reduction, the same conditions were considered for all the nitrated samples: they were reduced by a solution of sodium dithionite of a specified concentration in a shaker for 24 h.

Characterization Methods. N₂ adsorption–desorption isotherms were measured using a ThermoFinnigan Sorptomatic 1990 Series analyzer (Thermo Electron Co., USA) to determine textural characteristics of the samples. Prior to the measurements, the samples were outgassed at 120 °C and under vacuum. Adsorption data of the relative pressure (P/P_0) less

than 0.3 was used to calculate BET surface area (S_{BET}). The total pore volume (V_t) was calculated on the basis of the nitrogen adsorbed volume at relative pressure of 0.995. Proximate analysis was carried out with the aid of thermogravimetry (TGA) to determine the amount of ash and volatile matter. Ultimate analysis was performed using a 2400 Series II CHNS/O elemental analyzer, (Perkin Elmer, USA), to evaluate the nitrogen content.

CO₂ Capture Measurements. The modified samples were subjected to CO₂ capture measurements including isothermal CO₂ uptake, temperature-programmed (TP) CO₂ adsorption, and cyclic operation tests with the aid of TGA/SDTA851 Ultramicro Balance (Mettler-Toledo GmdH Analytical, Switzerland). Moreover, dynamic CO₂ adsorption test was also carried out. For isothermal uptake experiments, the samples were first outgassed from preabsorbed CO₂ and water at 120 °C for 1 h in 50 mL/min nitrogen stream and allowed to cool to 30 °C, the desired temperature for the test. Thereafter, the gas was switched to pure CO₂ of 50 mL/min for 1 h to achieve complete saturation. The increase in sample weight was considered as the CO₂ uptake capacity at the target temperature. Afterward, the temperature was increased with a ramp rate of 1 °C/min to obtain CO₂ adsorption capacity of the samples at a range of temperature. For dynamic CO₂ adsorption test, around 1 g of the modified AC was placed in a tube of 8 mm inside diameter as adsorption media and supported by quartz wool. It was heated by a flow of nitrogen at 120 °C for 1 h to remove water and CO₂ adsorbed from atmosphere. Afterward, the sample was cooled to 100 °C, the adsorption temperature of breakthrough tests. Then, the gas was switched to a 30 mL/min flow of 10% CO₂ balanced nitrogen, while the concentration of CO₂ in the effluent was detected and recorded by a CO₂ analyzer.

Results and Discussion

Characteristics of the Modified Samples. Table 2 shows textural and chemical characteristics of the modified samples along with their CO₂ capture capacity at 30 °C from isothermal CO₂ uptake experiments. Data for the untreated sample A1 is also incorporated into the table. It can be seen that all the modified samples have higher nitrogen content and volatile matter, compared to A1. Moreover, nitration followed by reduction causes a drastic decrease in surface area and pore volume, as can be seen from Table 2. From the data presented in the table, incorporation of nitrogen functional groups into the structure of AC is inferred for all the modified samples, but with different degrees depending on the conditions of nitration stage.

As can be perceived from the data in Table 2, for each ratio, the sample nitrated for t_1 has the highest nitrogen content. In other words, these experiments show that the first step of treatment of the AC samples with mixed acid is the most effective one for nitration purpose and continuing the treatment into the second and third steps reverses nitration. These observations are somewhat in agreement with those of Zhang *et al.*,³⁸ according to whom nitration of AC with mixed acid is a

Table 1. Conditions of the nitration experiments.

Sample ID	Sulfuric acid/nitric acid ratio	Nitration time (min)
R2-100	2	100
R2-60	2	60
R2-30	2	30
R3-90	3	90
R3-50	3	50
R3-20	3	20
R4-85	4	85
R4-45	4	45
R4-15	4	15
R5-80	5	80
R5-40	5	40
R5-10	5	10

Table 2. Characteristics of the samples modified by nitration/reduction treatment.

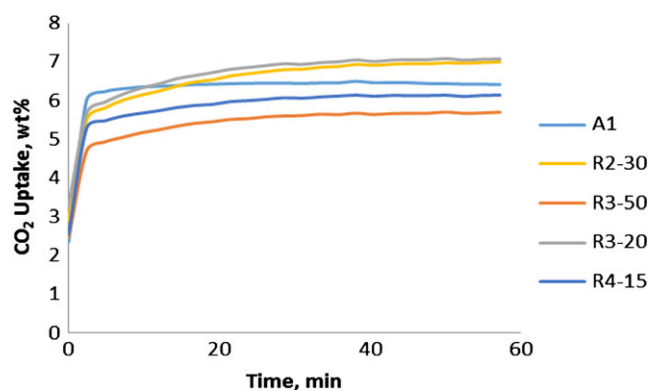
Sample ID	Proximate analysis (wt%) ^a			Ultimate analysis (wt%)				<i>S</i> _{BET} (m ² /g)	<i>V</i> _t (cm ³ /g)	CO ₂ capture capacity at 30 °C (wt%)
	VM ^b	FC ^c	Ash	C	H	N	O ^d			
A1	17.64	75.70	6.66	85.26	1.51	0.31	6.26	846.3	0.434	6.41
R2-60	42.97	51.86	5.17	62.42	2.26	5.00	30.32	328.87	0.219	5.43
R2-30	40.15	54.45	5.40	65.27	2.61	7.57	24.55	298.32	0.166	7.00
R3-90	42.70	52.25	5.05	64.16	2.23	4.92	28.69	342.91	0.248	4.97
R3-50	40.69	53.42	5.89	67.33	2.28	5.27	25.12	300.34	0.186	5.70
R3-20	38.53	55.80	5.67	67.20	2.63	7.85	22.32	278.77	0.158	7.08
R4-85	37.63	57.14	5.23	65.56	2.19	4.03	28.22	405.67	0.230	4.66
R4-45	34.42	60.12	5.46	68.03	2.26	4.74	24.97	397.28	0.228	5.11
R4-15	31.83	62.14	6.03	70.26	2.30	5.38	22.06	394.53	0.232	6.14
R5-80	36.09	58.23	5.68	66.95	2.24	4.82	25.99	372.55	0.240	5.02
R5-40	35.13	59.35	5.52	67.18	2.21	5.05	25.56	369.98	0.275	5.25
R5-10	34.96	58.94	6.10	70.10	2.15	5.11	22.64	368.67	0.282	5.19

^a Dry basis.^b Volatile matter.^c Fixed carbon.^d Calculated by difference.

transient step that gets oxidized over a prolonged period rather than nitrated. Although in the current study, the density of nitro groups decreased with increased time, the groups were not completely eliminated for the maximum time considered. The results show that the AC samples still have considerable amount of nitrogen groups even after the second or third step of treatment. The results also showed the interaction between the two independent variables: time has a smaller effect on nitration when ratio increases from 3 to 4 or 5. For the ratio 5, increase in time causes just a slight change in surface area and nitrogen content. On the other hand, mixed acid ratio shows a significant effect on the nitration efficiency. Of the prepared samples, R3-20, followed by R2-30, has the highest nitrogen content. It is apparent from Table 2 that increase in the ratio from 2 to 3 has a small positive effect on the nitrogen content, whereas its increase from 3 to 4 and 5 causes a large negative effect.

CO₂ Capture Performance. CO₂ capture capacities of the prepared samples at 30 °C (collected from isothermal uptake test) are listed in the last column of Table 2. It is interesting to note that samples R2-30 and R3-20 have a capture capacity higher than that of A1, while their surface area and pore volume are much lower compared with A1. Moreover, the capacities of the other samples are considerable when their surface areas are compared with that of A1. It may be observed that the capacities of the modified samples show the same trend as their nitrogen content despite the different surface area of the samples. However, the parent sample does not follow this trend because of the large difference between its surface area and that of the modified samples. The values of CO₂ capture capacities presented in Table 2 express only the maximum capture capacity of the samples under the test condition, but they do not reveal dynamics of CO₂ capture. Figure 1 shows

the typical isothermal CO₂ uptake profile for some selected modified samples. The profile is expressed as the percentage of weight rise vs. time at 30 °C when the sample has been placed in a pure CO₂ atmosphere. Inspection of Figure 1 shows that the parent A1 is completely saturated with CO₂ in a few minutes, whereas for the modified samples it took a longer time to achieve equilibrium. As a consequence, it can be said that the adsorption rate is retarded by modification. Moreover, the slopes of the capture curve are almost alike. TP CO₂ adsorption tests of the samples can be employed to reveal the effect of temperature on CO₂ adsorption capacity of the modified samples. The TP CO₂ curves for some selected samples are shown in Figure 2. It is observed from the figure that the capture capacities of all the samples including the parent and modified ones decline with increasing temperature. This observation is easily attributed to the fact that physical adsorption is the prevailing mechanism in adsorption. Samples R3-20 and R2-30 present remarkable capture capacities over A1

**Figure 1.** Typical isothermal CO₂ uptake profile of the selected modified samples.

throughout the full range of temperature of Figure 2. The fact that their surface area and pore volume are much less than those of A1 may present these modified ACs as superior CO₂ adsorbents and can introduce nitration/reduction as a valuable modification method for CO₂ capture purpose. A closer look at Figure 2 demonstrates that the slope of the TP CO₂ curve of all the modified samples is less than that of A1, so that the excess capacity of R3-20 (and R2-30) over A1 increases on going from 30 to 100 °C. Capacities of other samples, which are less than that of A1 at lower temperatures, exceed it at elevated temperatures. Lower dependence of CO₂ capture capacity on temperature for the modified samples is justified by presence of a significant amount of nitrogen functional groups attached on the surface, which creates or strengthens the role of chemisorption of CO₂ species by the amino groups. In other words, for the samples modified with amino groups, chemisorption plays a major role in the adsorption of CO₂. The CO₂ capture capacity is due to two simultaneous mechanisms of physisorption and chemisorptions: the former depends on porous structure, and the latter is affected by nitrogen content (amino groups for our purpose). These two mechanisms are acting inversely, as the modification decreases surface area and increases the amine contents. In order to evaluate the role of chemisorption itself, TP CO₂ capture curves have been normalized by the BET surface area and shown in Figure 3. The effect of the amino groups on the capacity of AC is obviously seen from the figure. This is due to chemisorptions effect; all the modified samples present considerable capacities over A1 when compared at unit surface area. R3-20 presents threefold and fivefold capacity over A1 at 30 and 100 °C, respectively. These observations agree quite well with nitrogen content in Table 2.

Cyclic Tests. One of the requirements for using adsorbents in industry is their long-term stability. Cyclic tests are helpful in providing information about stability of the modified AC samples in practical applications. Figure 4 presents the results of cyclic tests for selected samples, where the capacities for first saturation and after three consecutive regenerations are shown. The figure indicates that, on going from the first saturation to the second one (occurring after the first regeneration), the capture capacities decrease slightly, whereas they remain

essentially unchanged after the next regenerations. The decrease in capacity after first regeneration can be mainly attributed to the unreleased CO₂ resulting from the first saturation. A higher regeneration temperature may retain the former capacities more or less. The regeneration temperature employed for this study was same as the initial outgassing temperature (120 °C). However, it may be concluded from the figure that there is no considerable accumulation of CO₂ in the samples during each step of adsorption after the first regeneration. In other words, a satisfactory and established regeneration can be reached. This may be interpreted as a promising indication for stable performance in practical cyclic operations.

Dynamic CO₂ Adsorption Tests. The complete breakthrough curves of CO₂, plotting the relative concentration of CO₂ as a function of time at the test temperature of 100 °C, have been shown in Figure 5 for the selected samples. It is worth noting that the breakthrough curves have been normalized for the weight unit of AC by dividing the time by the exact weight of the sample. Relative concentration is defined as the ratio of the outlet CO₂ concentration to the inlet CO₂ concentration. The saturation adsorption capacities (*i.e.*, total adsorbed CO₂ by the weight unit of the sample in the column), q_{total} (mg/g), and breakthrough capacity (*i.e.*, CO₂ adsorbed

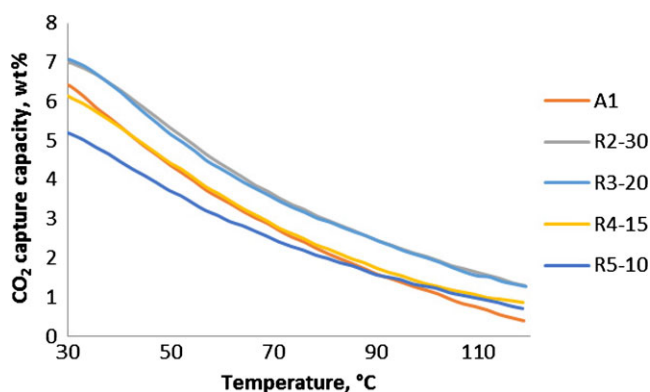


Figure 2. Typical TP CO₂ adsorption curves.

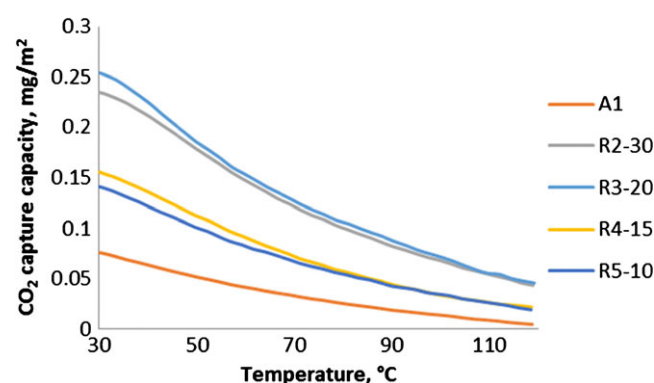


Figure 3. TP CO₂ adsorption test, normalized by surface area.

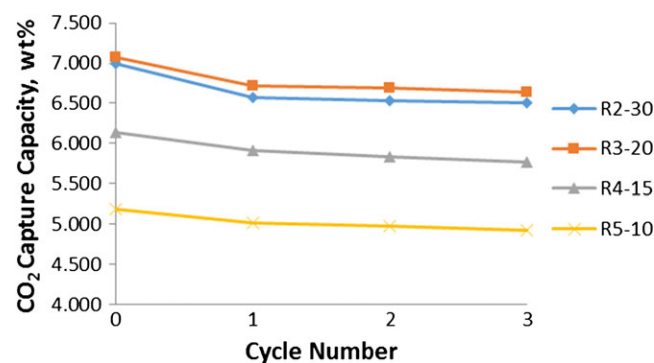


Figure 4. Cyclic adsorption-desorption tests: adsorption capacities were measured at 30 °C; regeneration was performed at 120 °C. Cycle number of 0 indicates first saturation and other cycle numbers show the corresponding regenerations.

amount by the weight unit of the sample in the column at breakthrough point), q_b (mg/g), may be calculated from Eqs. (1) and (2), respectively.

$$q_{\text{total}} = Q \int_{t=0}^{t=t_{\text{total}}} (C_{\text{in}} - C_{\text{out}}) dt \quad (1)$$

$$q_b = Q \int_{t=0}^{t=t_b} (C_{\text{in}} - C_{\text{out}}) dt \quad (2)$$

where C_{in} and C_{out} are molar concentration of CO₂ at the inlet and outlet, respectively, and Q is volumetric flow rate (mL/min). t_{total} and t_b are total flow time and breakthrough time, respectively. Breakthrough time is defined here arbitrarily as the time when the relative concentration reaches 0.01. Moreover, Table 3 compares the saturation adsorption capacity, breakthrough capacity, and pure CO₂ adsorption capacity (extracted from TP CO₂ adsorption tests) at 100 °C for the samples.

It may be observed from Figure 5 that, in the breakthrough curve related to the parent sample, the relative concentration reaches unity (the outlet concentration reaches the inlet one) after a short time of its function as a result of its lower CO₂ adsorption capacity. However, the breakthrough curves of the modified samples shift to the right, indicating that the modified samples adsorbed considerable amounts of CO₂ and have higher saturation and breakthrough capacities, compared with those of A1. If we neglect small differences between R2-30 and R3-20 specifications, Table 3 shows that all breakthrough, saturation, and pure CO₂ adsorption capacities follow the same trends. In other words, a sample with higher pure CO₂

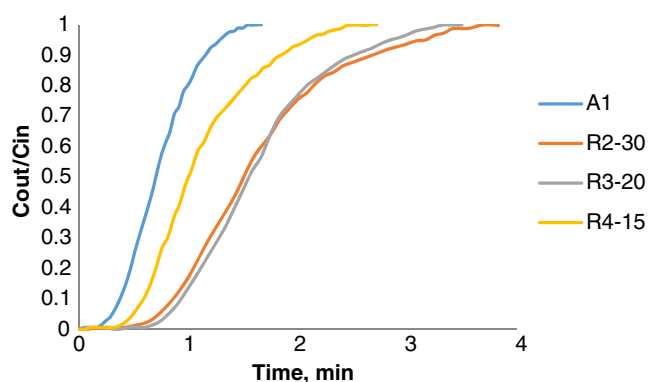


Figure 5. Breakthrough curves of the parent and modified samples.

Table 3. Comparison between the experimental CO₂ saturation and breakthrough capacities and pure CO₂ adsorption capacities (mg/g).

Sample ID	A1	R2-30	R3-20	R4-15
Breakthrough capacity	1.21	2.92	3.41	2.23
Saturation capacity	4.32	9.58	9.59	6.52
Pure adsorption capacity	11.7	20.3	19.9	13.4

adsorption capacity has higher saturation and breakthrough capacities. Therefore, it is inferred that the results of dynamic tests are in good consistency with those of the TP CO₂ adsorption tests. Table 3 also illustrates that the saturation capacity lies between breakthrough and pure CO₂ capacities for all cases. According to Table 3, going from A1 to R3-20 or R2-30 results in a 120% increase in saturation capacity and 140–180% increase in breakthrough capacity. On the other hand, comparison of the breakthrough curves in Figure 5 demonstrates that the breakthrough front of the amine-modified ACs is more spread than that of A1. This can be attributed to the lower CO₂ adsorption rate in the modified samples. It agrees quite well with isothermal CO₂ uptake profile (Figure 1), where the saturation of modified AC samples in pure CO₂ takes longer times. Lower adsorption rates lead to higher mass transfer resistances, which negatively affect the breakthrough capacity.

Conclusion

A series of modified AC samples were obtained by nitration followed by reduction. The effects of mixed acid ratio and nitration time were studied. Some of the modified samples presented CO₂ capture capacities higher than that of the virgin sample particularly at elevated temperature despite their lower surface area. Based on the TP CO₂ adsorption tests, samples R3-20 and R2-30 displayed increases of ~10 and 70% in CO₂ capture capacity at 30 and 100 °C, respectively. However, their surface area decreased by ~65% in comparison with the parent sample. The results were confirmed by dynamic CO₂ adsorption tests. The effect of the amino groups on the capture capacity is significant when the capacity of modified samples is compared with that of the virgin AC in terms of the surface area. Cyclic operation tests gave indications of good performance stability of the amine-modified samples. The results from the nitration/reduction study highlight the method as a promising one for generating superior CO₂ adsorbents.

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