SYNTHESIS OF HIGH SURFACE AREA ACTIVATED CARBON XEROGEL FROM RESORCINOL-FORMALDEHYDE RESIN FOR CO$_2$ ADSORPTION AND SEPARATION

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ABSTRACT

In this study, activated carbons xerogel were produced from a polycondensation reaction of resorcinol and formaldehyde in presence of monoethanolamine as a catalyst and under different CO$_2$ activation conditions. The effects of activation time and temperature were investigated. The increase in activation time results in a continuous steady rise of the mesopore area and volume, while the micropore and total pore area and volume tend to reach a maximum at approximately two hour. The application of this material for CO$_2$ capture and adsorption was studied using a perturbation gas chromatograph technique. The sample with the highest carbon dioxide adsorption capacity and CO$_2$/N$_2$ ratio (156.3 mg CO$_2$/g and 2.9), was that one activated at a temperature of 850^{0}C for three hour, its surface area and pore volume are 2398 m^2/g and 1.982 cm^3/g, respectively. The study also demonstrates the potential of the surface chemistry of RF-carbon xerogels for the generation of efficient CO$_2$ adsorbents, if their beneficial surface chemistry could be combined with advantageous pore structure.

KEYWORDS

Resorcinol-formaldehyde resin; Carbon xerogel; Activation; CO$_2$ adsorption; Pore structure and perturbation gas chromatograph

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NOMENCLUTER

m	molar flow rate of perturbation gas stream of general composition (mol s^{-1})
M	molar flow rate of the main gas stream of general composition (mol s^{-1})
Q	volumetric flow rate of the main gas stream (ml s^{-1})
y_A^O, y_B^O	gas-phase mol fraction of A and B in the main gas stream
y_A^P, y_B^P	gas-phase mol fraction of A and B in the perturbation gas stream
τ_n	retention time of the flow rate transient time (s)
τ_x	retention time of the composition transient time (s)
w	mass of adsorbent (g)
ε	defined geometrically in terms of superficial shape of the adsorbent particles
C	concentration in the gas (mol ml^{-1})
Q	concentration in the adsorbent (mol g^{-1})
v_c	sample column volume (ml)

1. INTRODUCTION

Due to the increased consumption of fossil fuels in power stations and use of automobiles world wide, the airborne carbon dioxide level has increased, which requires a continuous removal of carbon dioxide at the source of emission. Currently, carbon capture and carbon sequestration technologies are being developed to achieve zero emissions when using carbon based fuels [1].carbon dioxide capture and separation from the fuel gas is the first step towards carbon sequestration. Due to highly developed porous structures, porous materials include molecular sieve and zeolite, as well as activated carbons, are suitable candidates for carbon dioxide capture by physical adsorption [2]. However, due to the high cost of production and regeneration of zeolite, alternative adsorbents are highly desirable [3]. In addition to, zeolites are not suitable if the gas stream containing moisture [4]

Most commercial grade activated carbons are derived from naturally occurring carbonaceous materials such as palm-shell and coconut shell [6,7]. Activated carbons are synthesized through physical or chemical activation processes of these precursors [5]. The activation process, together with the intrinsic nature of the precursors, strongly determines the characteristics of the resulting activated carbons. Carbons prepared from resorcinol-formaldehyde have structure similar to those in coals but contain fewer mineral impurities. Recently, increasing attention has been focused on using resorcinol-formaldehyde resin as feedstock for activated carbons, due to their fine structure and relatively low price that make them excellent raw materials for the production of activated carbons with highly developed microporosity and surface area [8].

The objective of the current work to further develop and modify resorcinol formaldehyde sol-gel synthesis procedure to make high surface area RF carbon xerogels with a controlled pore structure and new surface functional groups, the

effect of varying activation temperature and time on the development of pore volume and surface area were investigated. The effect of the prepared activated carbon xerogels pore structure on the carbon dioxide adsorption and CO_2 / N_2 uptake ratio were measured from composition and flow rate transient times in chromatographic columns.

2. EXPERiMeNTAL

2.1 Preparation of activated carbons xerogel from resorcinol formaldehyde resins.

Activated carbons xerogel prepared from resorcinol formaldehyde resins according to the schematic diagram shown in figure1. RF resins were firstly synthesized by the polycondensation reaction of resorcinol (R) (1, 3-dihydroxybenzene $C_6H_4(OH)_2$) (reagent-grade 98%, Aldrich) and formaldehyde(F) (HCHO)(37% in water, stabilized by 10-15% wt. methanol, Aldrich) using an initial R/F molar ratio of 1:2. Deionised water (W) was used as the diluent. Monoethanolamine (MEA), (research grade, Aldrich) was used as the catalyst with different resorcinol to catalyst (R/C) molar ratios. The vials were sealed and gelation was performed at 85^{0}C in an oven for three days.

The solvent was then removed from the pores of the gel slowly, first by evaporating at 60^{0}C for two hours, and then further by exposing it to a vacuum at 120^{0}C for 12 hours. The resins were then placed in a ceramic boat, pyrolized at 850^{0}C under Argon flow (100 ml/min) in a tubular oven for three hours. The pyrolysis conditions were determined by the thermogravimetric analysis. After pyrolysis all samples are activated with carbon dioxide 100 ml/min. The activation temperature was varied between 850 and 980^{0}C with heating rate 30 ^{0}C/min. for a period of one to three hours. Argon flow was used during heating and cooling steps. The resultant activated samples were labelled as RF - a,b,c where a is the catalyst ratio, b and c denote the activation temperature and activation time, respectively.

2.2 Carbon characterization.

The porous structures of the activated carbons xerogel samples were determined by nitrogen adsorption-desorption techniques at 77 K using a Micromeritics ASAP 2000. The sample was first degassed at 110^{0}C for 12 hours under vacuum, and then the isotherm was measured in the relative pressure range 0.01 and 0.99. The Brunauer-Emmett-Teller (BET) analysis was performed for relative pressures between 0.06 and 0.2. The total pore volume was calculated from the amount of vapor adsorbed at a relative pressure of 0.975. The micropore volume was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.2, and the mesopore volume was calculated by subtracts the amount adsorbed at a relative pressure of 0.2 from that adsorbed at a relative pressure of 0.99. The average pore diameter was calculated from (4V/A by BET) equation.

2.3 CO$_2$ capture and separation measurements by perturbation gas chromatograph

Gas chromatographic (GC) methods provide an alternative to conventional gravimetric or volumetric methods in the determination of adsorption isotherms. In general, Gas chromatographic methods are low cost and are characterised by short experiment time. The theory and experimental process are covered in detail by Masson and Buffham [9]. The technique differ from the conventional gas chromatographic in that the variation of flow rate with time is monitored, this leads to the definition of a new retention time defined as flow rate retention time (τ_n).

The method involves adding a small perturbation flow to a main gas mixture passing through a chromatographic column. The two principal measurement used to identify the amount of each component adsorbed are the variation of column effluent flow and composition, which are measured using differential pressure transducer (DPT) and thermal conductivity detector (TCD) respectively. Figure 1 shows the basic experimental arrangement required to determine the composition and flow rate transient times. The adsorption column is packed with mass w of adsorbent, the carrier gas has composition (y_A^O, y_B^O), volumetric flow rate Q and molar flow rate M. At time zero a pulse (small perturbation) of one of the pure components is added to the carrier gas with molar flow rate m and mole fraction y_A^P (the p stands for perturbation). The whole process was repeated for main gas mixtures with approximate carbon dioxide mole fractions of 0, 0.25, 0.5, 0.75 and 1.0. Data acquisition and processing was used to record the response of DPT and TCD. The total amount of species i in the system both adsorbed and free in any void space, is the hodup, H$_i$, which could be calculated from both transient times as indicated in Eq.(1).

$$\frac{\Delta H_i}{\Delta C_i} = Q_c \left[\tau_x + \frac{y_i^0}{y_i^p - y_i^0} \tau_n \right] \tag{1}$$

Where τ$_x$ is the retention time of the composition transient time, τ$_n$ is the retention time of the flow-rate transient time, y_i^0 the composition of the component i in the main flow and y_i^p the composition of the component i in the perturbation flow. A change ΔC_i in the composition of the stream causes a change Δq_i in the concentration of species i in the adsorbent. The quantity $\Delta q_i / \Delta C_i$ which represents a gradient of the equilibrium hypersurface can be calculated from Eq.(2).

$$\frac{\Delta q_i}{\Delta C_i} = \frac{\Delta H_i / \Delta C_i - \varepsilon V_C}{W} \tag{2}$$

Where ε is defined geometrically in terms of the superficial shape of the adsorbent particles, C is the concentration in the gas and q the concentration in the adsorbent, V_c is the sample column volume and W is the amount of the adsorbent. A full binary isotherm for carbon dioxide and nitrogen adsorbed could be then calculated by integration of the straight lines fitted to the gradients $\Delta q_i / \Delta C_i$.

3. RESULTS AND DISSCUSSION

3.1. Ultimate and proximate analysis

The proximate and ultimate analyses of the pyrolyzed and activated samples were measured using a Thermogravimetric Analyzer (Perkin Elmer TGA 7) and elemental analyzer (Heraeus, CHN-O-RAPID), respectively. Table 1 shows that as the activation time increased from one to three hours the volatile content and the percent oxygen decreased while the fixed carbon increased. However, it is worth to notice that, the nitrogen percent does not affected by the activation, this may be due the strong C-N bond which is could withstand high heat treatments.

3.2 Effect of resorcinol to catalyst ratio on the porous structure of the activated carbon xerogel.

The influence of the resorcinol to catalyst ratio (R/C) on the texture properties of the prepared activated carbon xerogel was investigated. All samples were prepared under the same conditions with varying (R/C) molar ratios followed by activation with carbon dioxide at 850^{0}C for one hour. Figure 2 shows the plot of nitrogen adsorbed (77K) against the relative pressure while the R/C ratio is a parameter. The samples vary from a micro-mesoporous solid (R/C = 50 and 100) which is combination of types I and IV isotherm to an approximately microporous material (R/C = 200 and 300) type I isotherm. The main feature of such an isotherm is the long plateau which is indicative of a relatively small amount of multilayer adsorption on the open surface [13]. For the samples prepared at the lower R/C ratio, the N_2 adsorption isotherms are different: they exhibit a significant increase in adsorption at higher relative pressures. The knee comes to be more open and rounder and the slope of the plateau increases. Also, the nitrogen uptake occurs mostly at relative pressure (P/P$_0$>0.9). This indicates that the meso- or macropore structure in these samples is significantly developed. Table 2 shows the characteristic pore properties of the samples prepared with variety of R/C molar ratios and activated at a temperature of 850^{0}C for one hour. The influence of the R/C ratio is obviously marked: as the R/C ratio is increased from 50 to 300, the total pore volume decreases from 1.358 cm^3/g to 0.460 cm^3/g. In general, the basic catalyst ratio affects the mechanisms and kinetics of addition, as well as condensation reactions and thus the composition of the reaction medium and the final resin structure. Moreover, RF-resins have a highly cross-linked structure that is mainly of an interconnected spherical particle structure with particle size ranges from 3 to 20 nm. The particle size increases with R/C ratio lead to decrease the surface area. On the other hand, in the case where the particle size is small, the surface area of the gel is large .

3.3 Effect of activation time and temperature on the porous structure of the activated carbon xerogel.

It is well known that the activation conditions, time and temperature, as well as the properties and structure of the precursor, affect the porous structure of the resultant activated carbon [10]. Accordingly, this study was conducted to ascertain the effect of time and temperature on the porous structure of activated carbons xerogel produced from resorcinol-formaldehyde resins.

Figures 3 and 4 show the variation of total, micro- and mesopores volume and surface area for a series of resin samples activated with carbon dioxide at a temperature of 900^0C for various times, respectively. It can be observed that increasing the activation time at this temperature results in a continuous steady rise of the mesopores area and volume, while the micropore and total pore area and volume reached a maximum and then decreased. The increase in the micropore volume could be due to a pore-creating mechanism that occurs through selective activation, in which sequential burning of a carbon crystal that is based on its sensitivity to be burnt out, the first crystals to be burned are the single layer crystals, followed by disordered crystals and finally parallel group crystals. In the latter phase, excessive activation reaction lead to knocking down of the pore walls by the activating agent, and this result in an increase in transitional pores and macropores. The volume of the micropores decreases and there is no significant increase in adsorption capacity or internal surface area

A series of samples were activated at a temperature of 850, 900 and 980^0C for time periods of one to three hours. The variation of total pore volume and surface area with activation temperature and activation time are shown in figures 5 and 6, respectively. The BET surface area and pore volume increased progressively with increasing activation temperature. This was attributed to the strong dependency of the carbon-CO_2 reaction on the reaction temperature. For a fixed activation time, both the pore volume and surface area increase with increasing activation temperature. However, for a fixed activation temperature, the surface area and pore volume do not rise continuously with increasing activation time. For example, for the activation studies conducted at 900 and 980^0C, the surface area and pore volume decrease when the activation time is extended over two hour. For the sample activated at a temperature of 850^0C, the surface area and pore volume do not decrease till the activation time is extended over three hour.

3.4 CO_2 adsorption and separation of the activated carbon xerogel. Effect of pore structure and activation condition on carbon dioxide adsorption and separation.

Figure 7 shows the binary adsorption isotherm for the carbon dioxide and nitrogen system at 25^0C and 1.05 bar, which was obtained from the experimental setup described in section 2.5. The isotherm is for the sample prepared with R/C ratio of 50 and activated at a temperature of 850^0C for one hour. The upper limit of each

isotherm was used to calculate the adsorption capacity of the activated carbon. The isotherm shows that, the CO_2 adsorption increased rapidly with increase CO_2 mole fraction in the main gas flow. The uptake of CO_2 was higher than that of nitrogen; this may be due to presence of the basic sites on the carbon surface resulting from the nitrogen functional groups introduced by the usage of monoethanolamine as a catalyst. This preferential uptake of CO_2 indicates that this sorbent may be suitable for the separation of CO_2 from gaseous mixtures.

Table 4 shows the carbon dioxide capacity and CO_2/N_2 uptake ratio at 25^0C and 1.05 bar for activated carbon prepared at different initial R/C ratios and different activation conditions. The carbon dioxide adsorption capacity increases with a decreasing R/C ratios and its significantly affected by the extent of activation. This could be attributed to the decrease of the micropore volume of the resulting carbon due to change of the R/C during the polycondensation reaction as described before. However, it should be notes that the CO_2/N_2 uptake ratio is approximately constant, this because both of CO_2 and N_2 are physically adsorbed at that adsorption condition. In general, the adsorption capacity of an activated carbon highly depends on the presence of micropores. So, with regard to activated carbon adsorption capacity, it is of interest to investigate how it depends on the microporosity.

Figure 8 shows the relationship between carbon dioxide adsorption capacity and the micropore volume of the activated carbon xerogel. It seems like the samples with the highest micropore volume have the highest carbon dioxide adsorption capacity and of course CO_2/N_2 uptake ratio. Previous studies have shown that only pore sizes less than 5 times that of the molecular size of the adsorbate are effective for gas adsorption at atmospheric pressure. Since the molecular size of carbon dioxide is 0.209 nm, only pores less than 1.0 nm are effective towards carbon dioxide adsorption at atmospheric pressure. Therefore, it is desirable to increase the micropore volume and to tailor the pore size distribution of the activated carbons, especially in order to maximize the pores less than 1.0 nm, to optimize the physical adsorption of carbon dioxide onto the carbon surface. The surface functional groups on the surface of activated carbons play an important role in carbon dioxide capture and selectivity. Since carbon dioxide is an acid gas, alkaline surface functional groups will favor chemisorptions of carbon dioxide. Among the surface functional groups studied on the activated carbon surface, only some nitrogen groups are alkaline [3]. This is why this material shows higher affinity to adsorb CO_2 more than N_2 due the effect of its surface chemistry. In addition to, increasing the activation temperature sometimes leads to a reduction in the intensity of the surface functional groups and consequently the amount of carbon dioxide adsorbed.

4. CONCLUSIONS

High surface area (up to 2500 m^2/g) activated carbon xerogel were prepared from resorcinol formaldehyde resin activated by carbon dioxide. Nitrogen (77K) adsorption studies show that activated carbon with a high % of micropore could be prepared from resorcinol-formaldehyde resin prepared with R/C ratio of 300.   From activation studies we could conclude that, the initial increase in surface area is probably due to opening of porosity and formation of micropores, while the decrease in surface area

at higher activation time is probably due to the enlargement of micropores and pore wall removal.

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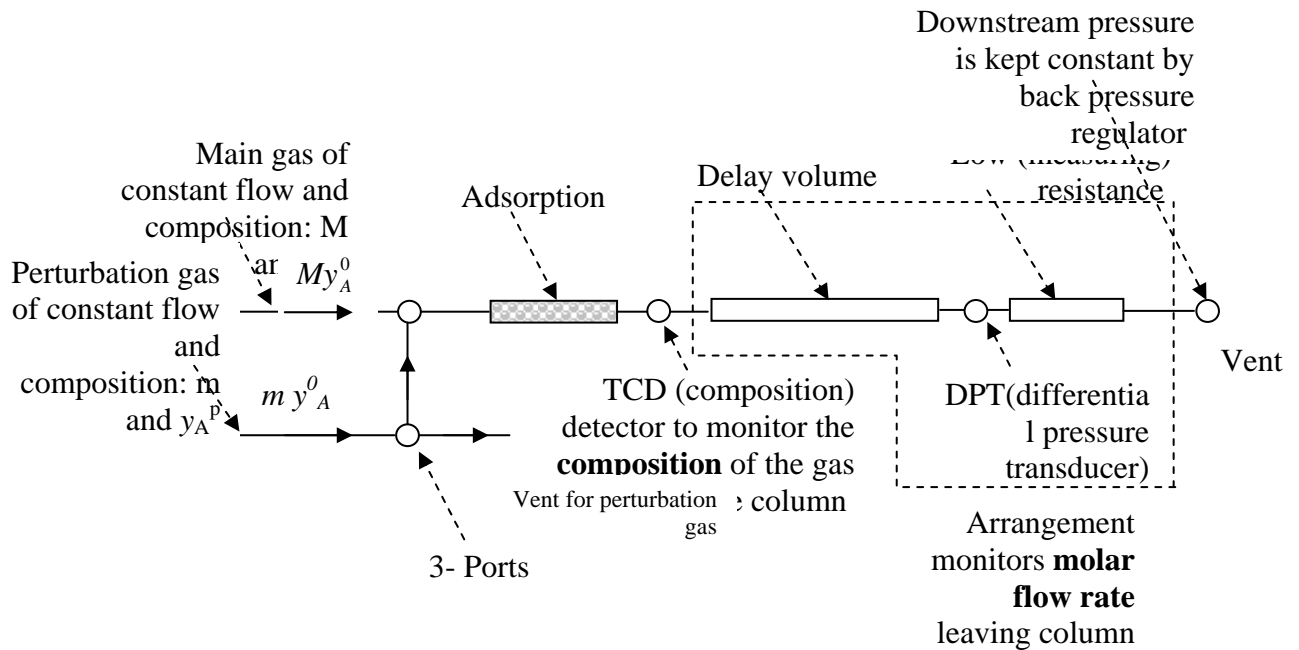
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Main gas of constant flow and composition: M

ar My_A^0

Perturbation gas of constant flow and composition: ṁ and y_A^p

$m y_A^0$

Adsorption

Delay volume

Downstream pressure is kept constant by back pressure regulator

resistance

Vent

3- Ports

Vent for perturbation gas

TCD (composition) detector to monitor the **composition** of the gas column

DPT(differential pressure transducer)

Arrangement monitors **molar flow rate** leaving column

Figure 1. The basic experimental arrangement required to determine binary adsorption isotherm from flow rate and composition transient time .The diagram show only one side system. In reality, there is also a control or reference side of the system, this lead to two channels in the DPT and TCD devices.
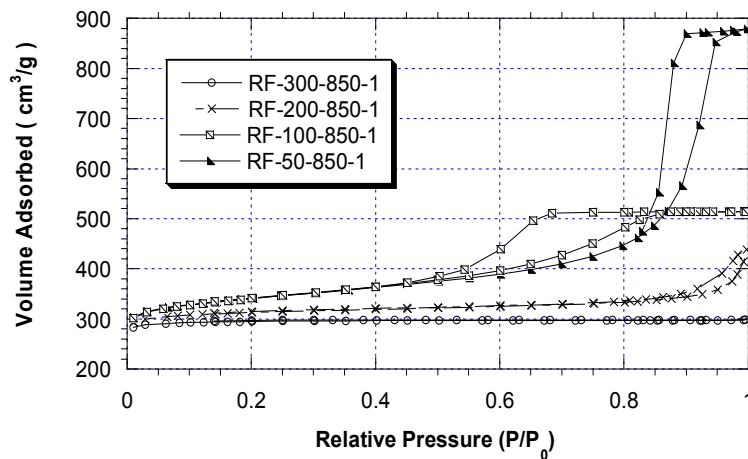

Figure 2. Adsorption profiles of N_2 (77K) on the activated carbon xerogel prepared with different R/C ratios and activated with CO_2 at a temperature of 850^0C for one hour.
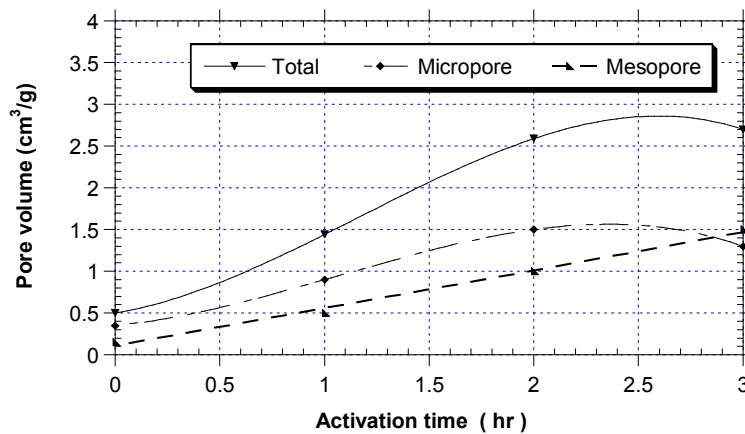
Figure 3. Variation of the pore volume with activation time for the sample prepared with an R/C ratio of 100 and activated at a temperature of 900^{0}C.
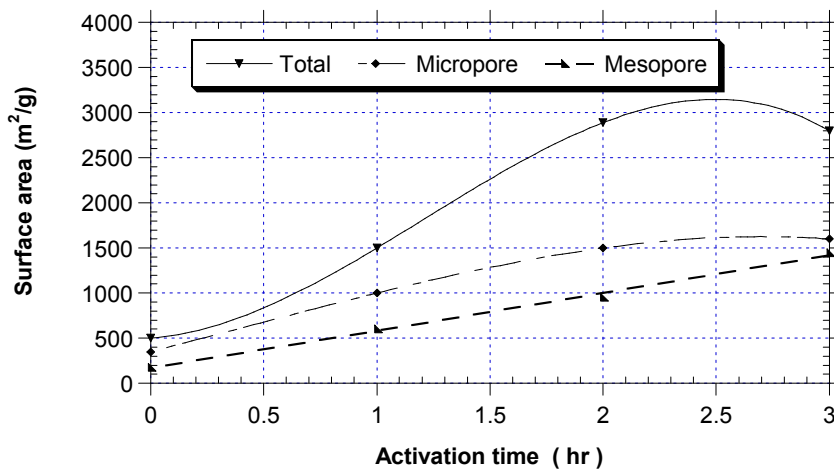

Figure 4. Variation of the surface area with activation time for the sample prepared with an R/C ratio of 100 and activated at a temperature of 900^{0}C.
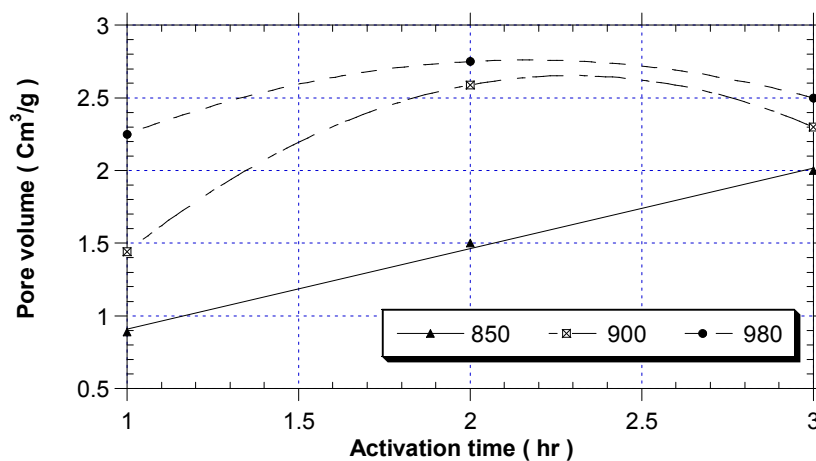

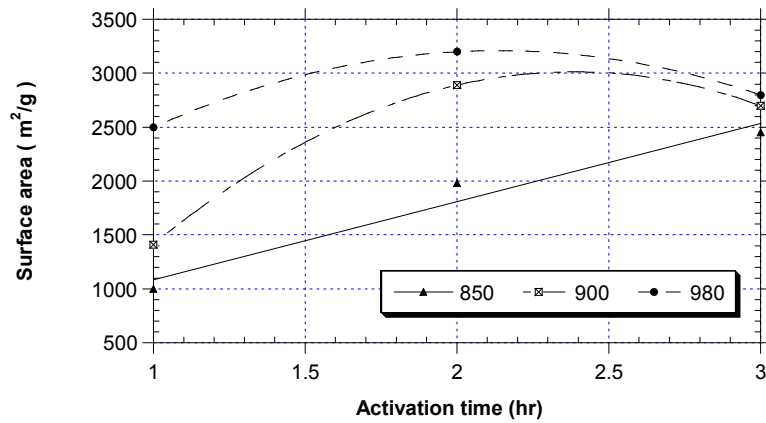Figure 5. Variation of the pore volume with activation time at different activation temperatures.

Figure 6. Variation of the surface area with activation time at different activation temperatures.
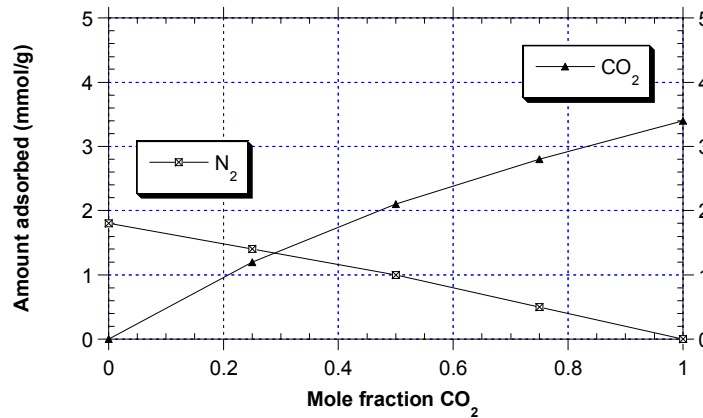

Figure 7 Experimental binary isotherm for CO_2-N_2 gas mixture at 25 ^{0}C and 1.05 bar for activated carbon xerogel prepared under R/C = 50 and activated at 850 ^{0}C for 1 h.
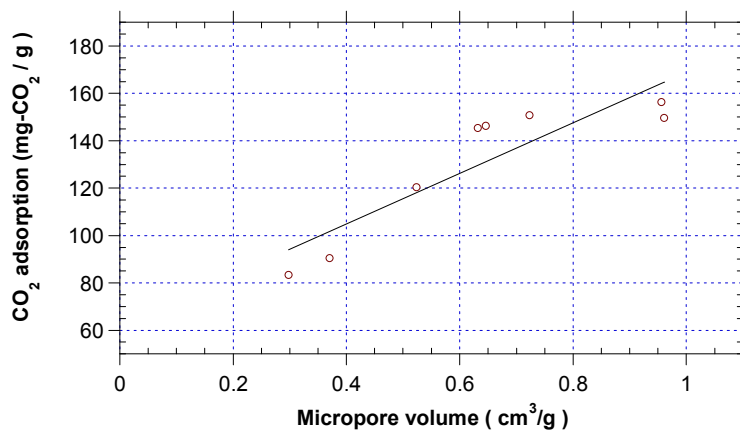

Figure 8 Variation of CO_2 adsorption capacities and microporosity of the activated carbon xerogel.

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Table 1 Analysis of samples prepared with R/C ratio of 100 before and after activation at a temperature of 850^{0}C for a period of one to three hours.

Nomenclature	Ultimate (wt% dry-ash-free basis)				Proximate (wt%)			
	C	H	N	O	Moisture	Volatile	Fixed carbon	Ash
RF-resin	62.98	5.45	0.42	31.15	4.664	61.796	33.293	0
RF-100-850-1	85.98	3.99	0.40	10.08	0.172	13.21	86.62	0
RF-100-850-2	86.78	3.35	0.40	9.47	0.102	8.936	90.964	0
RF-100-850-3	86.23	4.39	0.39	8.99	0.103	7.807	92.090	0

Table 2: Characteristic pore properties of activated carbon xerogels

Nomenclature	R/C	S_{BET}[a] (m^2/g)	V_t[b] (cm^3/g)	V_{mic}[c] (cm^3/g)	V_{mes}[d] (cm^3/g)	D_p[e] (nm)
RF-50-850-1	50	1148	1.358	0.604	0.754	6.914
RF-100-850-1	100	1096	0.794	0.524	0.270	3.452
RF-200-850-1	200	1042	0.677	0.480	0.197	3.265
RF-300-850-1	300	980	0.460	0.453	0.007	1.899

[a] Specific surface area determined from the BET equation.
[b] Total pore volume.
[c] Micropore volume determine by Horvath-Kawazoe equation.
[d] Mesopore volume.
[e] Mean pore diameter.

Table 3 CO_2 adsorption capacity and CO_2/N_2 uptake ratio for the activated carbon xerogel prepared at different conditions

Sample name	Adsorption capacity (mg /g adsorbent) at 25 ^{0}C and 1.05 bar		CO_2/N_2 ratio
	CO_2	N_2	
RF-50-850-1	149.6	53.2	2.8
RF-100-850-1	120.4	57.0	2.1
RF-200-850-1	90.5	47.6	1.9
RF-300-850-1	83.4	43.8	1.9
RF-100-850-2	145.3	60.5	2.4
RF-100-850-3	156.3	53.8	2.9
RF-100-900-1	146.4	58.56	2.5
RF-100-980-1	150.7	57.9	2.6