ELSEVIER

Chemical Engineering Journal 142 (2008) 1–13

Chemical Engineering Journal

www.elsevier.com/locate/cej

Influence of preparation conditions on the characteristics of activated carbons produced in laboratory and pilot scale systems

Emad N. El Qada, Stephen J. Allen, Gavin M. Walker*

School of Chemistry and Chemical Engineering, Queen's University of Belfast, Belfast BT9 5AG, UK

Received 22 June 2007; received in revised form 15 October 2007; accepted 4 November 2007

Abstract

The central theme of this investigation is to evaluate the feasibility of using bituminous coal as a precursor material for the production of chars and activated carbons using physical and chemical activation processes. The chemical activation process was accomplished by impregnating the raw materials with different dehydrating agents in different ratios and concentrations, prior to heat treatment ($ZnCl_2$, KCl, KOH, NaOH and $Fe_2(SO_4)_3 \cdot xH_2O$). Steam activation of the precursor material was adopted for the preparation of activated carbon using physical activation technology. Different types of bituminous coal; namely, contaminated Columbian (contaminated with pet. coke), pure Columbian, Venezuelan and New Zealand bituminous coal were used in the production processes. BET surface area, micropore area, pore size distribution and total pore volume of the chars and activated carbons were determined from N_2 adsorption/desorption isotherm, measured at 77 K. Charring conditions, charring temperature of 800 °C and charring time of 4 h, proved to be the optimum conditions for preparing chars. Contaminated Columbian were found to be the best precursor material for the production of char with reasonable physical characteristics (surface area = $138.1\ m^2\ g^{-1}$ and total pore volume of $8.656 \times 10^{-0.2}\ cm^3\ g^{-1}$). An improvement in the physical characteristics of the activated carbons was obtained upon the treatment of coal with dehydrating agents. Contaminated Columbian treated with 10 wt% $ZnCl_2$ displayed the highest surface area and total pore volume (surface area = $231.5\ m^2\ g^{-1}$ and total pore volume = $0.1227\ cm^3\ g^{-1}$) with well-developed microporisity (micropore area = $92.3\ m^2\ g^{-1}$). Venezuelan bituminous coal using the steam activation process was successful in producing activated carbon with superior physical characteristics (surface area = $863.50\ m^2\ g^{-1}$, total pore volume = $0.469\ cm^3\ g^{-1}$ and micropore surface area = $783.58\ m^2\ g^{-1}$).

Keywords: Activated carbon; Bituminous coal; Physical activation; Chemical activation; BET surface area; T-plot

1. Introduction

The resolution of ecological problems and the increase in environmental pollution of waste matter caused by expansion of human activity, have recently gained global significance. If materials with purifying ability could be prepared from these wastes, they would be highly useful in overcoming both the pollution and waste problems simultaneously. Porous materials are generally used for such applications as they show excellent properties for the adsorption, separation and/or decomposition of harmful gases and solutions in the environment. Highly functional porous materials are therefore in great demand for these purposes [1,2].

In order to be commercially attractive, an adsorbent should embody a number of features: (i) the adsorbent should have a large internal surface area, which should be accessible through pores big enough to admit the molecules to be adsorbed; (ii) the adsorbent should have high affinity and capacity for target compounds; (iii) the adsorbent should be capable of being easily regenerated; (iv) the adsorbent should not age rapidly, that is lose its adsorptive capacity through continual recycling; (v) the adsorbent should have tolerance for a wide range of wastewater parameters; (vi) the adsorbent should be mechanically strong enough to withstand the bulk handling and vibration that are feature of any industrial unit [3,4].

Any material having a high surface area and a highly porous structure can be considered as an adsorbent. Such a highly porous material maybe carbonaceous or inorganic in nature, synthetic or naturally occurring. The surface area and the chemical nature of the adsorbent surface are important factors that affect the performance of the adsorbent, with the former being the most

---

* Corresponding author. Tel.: +44 7746394012/2890974172; fax: +44 2890974627.
E-mail address: g.walker@qub.ac.uk (G.M. Walker).

1385-8947/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.cej.2007.11.008

important. Adsorbent can be made with internal surface areas which range from about 100 $m^2 g^{-1}$ to 3000 $m^2 g^{-1}$. For most adsorbents, the internal surface area is created from pores of various sizes [5].

On account of the above facts, carbon adsorbents have attracted special attention due to their well-developed porous structure, large surface area and good mechanical properties. In this respect, activated carbon is the most widely used adsorbent for environmental applications such as gas separation, solvent recovery and water purification [6,7]. However, activated carbon is produced from natural carbonaceous materials such as coal, coconut shell, agricultural waste, wood and polymer scrap [8,9]. Coal is the most commonly used precursor due to its low cost and large supply, and also activated carbon prepared from coal is superior to those derived from lignocellulosic materials in terms of mechanical properties [10,11]. Chemically, coal is a macromolecular network composed of groups of polynuclear aromatic ring structures of high molecular weight, to which are attached subordinate rings connected by oxygen, sulphur and aliphatic bridges [12]. More recently, coal has been advocated for production of activated carbon. Sun et al. [13] produced granular activated carbons from Illinois bituminous coal using chemical and physical activation processes for natural gas storage. Microporous activated carbons using CO_2 and chemical activation were obtained by Carrasco-Marín et al. [14] using bituminous coal as a precursor material for the production process. Skodras et al. [15] developed three sequential stages for the production of suitable activated carbon from Greek lignite.

2. Production of activated carbon

Two basic methods are available for the production of activated carbon; physical and chemical activation. The challenge is to produce activated carbon with the desired pore size distribution and surface chemistry from low cost carbons [16,17]. Physical activation includes carbonization of the precursor in an inert atmosphere and activation of the resulting char by an activation agent such as CO_2, steam or air. The carbonization (pyrolysis) process is usually conducted in the absence of air. During the carbonization step, most of the non-carbon elements, mainly volatiles are removed, leaving a char with high carbon content and slight porosity. In addition, a large number of repaired electrons are trapped in the microcrystallite structure of activated carbon due to bond breakage at the edge of the planar structure. Foreign atoms such as oxygen and hydrogen interact with these electrons to form surface complexes or functional groups. The type of the starting material and the method of activation determines to large extent, the nature of surface functional groups. The oxygen-containing surface groups are the most important due to their probable effect on the adsorption process [18].

The porosity of the char can be increased by the activation process. Activation is a controlled gasification process, using an oxidising agent at elevated temperature. The role of the oxidising agent is to burn away the tarry pyrolysis off-product trapped within the pores and initialising the porosity development. It also increases the surface area and enlarges the pore volume; (i) by burning away carbon atoms from the walls of open pores; (ii) by perforating closed pores and thereby providing access to pores formed initially without an inlet. As the oxidising agent burns away the more active area of the carbon skeleton, the microporous structure is then developed. The presence of oxygenated constituents in source materials aids in forming a porous structure [19]. The characteristics of the activated carbon produced by physical activation depend on the activation temperature, the precursor, the oxidising agent used and the degree of activation [20]. According to Faust and Aly [18] carbons activated at low temperatures, 200–400 °C, termed L-carbons, generally will develop acidic surface oxides and will lower the pH value of neutral or basic solutions. Such carbons sorb bases from solution, are considered hydrophilic and exhibit a negative zeta potential. Carbons activated at higher temperatures, 800–1000 °C, termed H-carbons, will develop basic surface oxides, will raise the pH value of neutral or acidic solutions, sorb acids and exhibit a positive zeta potential.

Chemical activation is a single-step process including the impregnation of the carbonaceous material with dehydrating agent prior to activation. The significance of the impregnation is to enhance the pore structure of precursor and hence increases its surface area. The chemical agents used in the chemical process are normally alkali and alkaline earth metal containing substances and some acids such as KOH, K_2CO_3, NaOH, Na_2CO_3, $ZnCl_2$, $MgCl_2$ and H_3PO_4. Although, phosphoric acid is shown to be the most environmentally sound chemical for the activation processes, most studies have used zinc chloride due to its effective activating capability [28]. Chemical activation of carbonaceous materials has been the subject of considerable interest in the past because activated carbon, with a well-developed porosity, can be produced by this process in a single operation. Also, it has been found that the effect of some chemicals on the carbon precursor yields more char and less tar than the untreated sample [10]. If chemical activation is essentially considered as a reaction between the solid precursor and the chemical, it is clear that concentration, temperature and activation time determine the extent of the reaction. However, such reaction cannot proceed to completion because it would mean the destruction of the precursor [21]. The extent of the chemical activation can significantly alter the characteristics of the carbons produced.

In a comparison in physical activation, elimination of a large amount of internal carbon mass is necessary to obtain a well-developed carbon structure, whereas in the chemical activation process all the chemical agents used are dehydrating agents that influence pyrolytic decomposition and inhibit formation of tar thus enhancing the yield of the carbon. The temperatures used in the chemical activation are also lower than that used in the physical activation process, and therefore the development of a porous structure is better in the case of the chemical process [10].

Recently, considerable attention has been paid to the production of activated carbon using a combination process of the chemical and physical activation processes, as this process leads to the production of activated carbon of specific surface properties [22]. A study conducted by Gañan et al. [23] showed that high-porosity carbons were prepared from bituminous coal pitches by combining chemical and physical activation.

In general, the activation process has a decisive effect on the most important properties of activated carbon, as illustrated in Fig. 1. The degree of activation has a profound effect on the micropore system. The micropore volume increases almost linearly with the degree of activation. The macropore volume undergoes a relatively moderate increase in the course of activation. The inner surface area does not increase uniformly over the whole activation process. A sharp initial increase is followed by a slight decrease as activation continued beyond a maximum value. The bulk density decreases almost linearly with increasing activation due to the pore system becoming larger with increasing activation. The decrease of bulk density is due

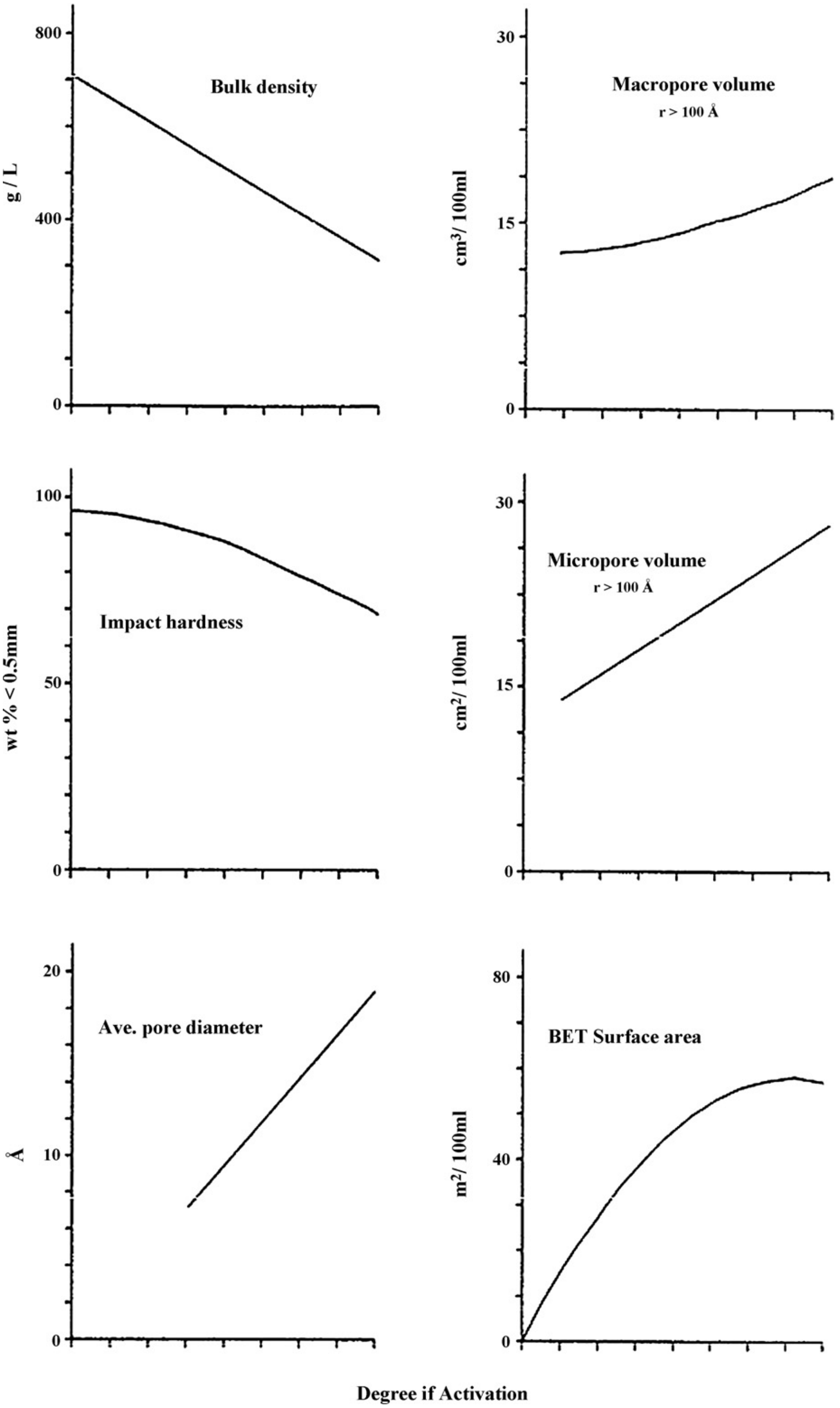

Fig. 1. Influences of degree of activation [18].

to the decrease in apparent density and the constant real density of the carbon. With increasing micropore and macropore volume, the carbon structure becomes more fragile and the impact hardness decreases, first fairly slightly, and then at a more pronounced rate beyond medium values of degree of activation [18].

The focal theme of this research is directed to evaluate the potential use of bituminous coal as precursor material for the production of highly effective natural adsorbents, and to explore the adsorbents characteristics. This is to be accomplished by preparing chars from different types of bituminous coal using pyrolysis methods at different temperatures and for different time intervals and by production of activated carbons using both physical and chemical activation processes.

3. Experimental

The present work focuses on the evaluation of the potential use of an inexpensive material which is available at large quantities (bituminous coal) as precursor material for the production of highly effective activated carbons using both physical and chemical activation processes. Different types of chars and activated carbons produced in small laboratory scale and large industrial scale were investigated.

Five dehydrating agents were used to treat the coals prior to pyrolysis to further improve the porous properties of the activated carbon. Table 1 lists these agents. The dehydrating agents (chemical activators) were used in different concentrations to assess the effect of dehydrating agent/coal ratio on the characteristics of the activated carbons.

3.1. Production of chars

Different types of bituminous coal from different sources were used as precursor materials to produce chars and this includes; contaminated Columbian coal, pure Columbian coal and New Zealand coal. Pyrolysis studies were carried out at different ranges of temperature and for different time intervals. 60 ± 0.1 g of the raw material was placed in a crucible, covered with a lid and introduced into a Carbolite LMF4 muffle furnace after the furnace reached the designated temperature and held for the required period of time. At the end of charring process, the furnace was switched off and the crucible was kept in the furnace overnight to get cooled. Once cooled, the crucible was removed and weighed. The char produced was washed with deionised water and dried.

Table 1
Dehydrating agents for the production of activated carbon

Name	Formula	Molecular weight
Zinc chloride	$ZnCl_2$	136.29
Potassium chloride	KCl	74.56
Ferric sulphate hydrate	$Fe_2\,(SO_4)_3{\cdot}xH_2O$	399.88 + aq
Potassium hydroxide	KOH	56.00
Sodium hydroxide	NaOH	40.00

3.2. Production of activated carbons

Three methods were adopted in the production process of activated carbons and these include.

3.2.1. Production in the muffle furnace

A one-step pyrolysis/activation procedure was used for the activation of raw materials. The pre-treated coal was prepared by mixing 60 ± 0.1 g of the raw coal with 600 ± 0.5 ml of metal salt solution and stirred for 1 h. Then the slurry was filtered using a Buchner flask and funnel. During the filtration process, 1000 ± 0.5 ml of deionised water were used to wash the slurry from any residual metal salt solution. The coal was then placed in an oven to dry at 60 °C overnight. The dried coal was subjected to a pyrolysis process in a muffle furnace at 800 °C for 4 h. A range of metal salt solutions were prepared: $Fe_2(SO_4)_3 \times H_2O$ (10 wt%, 20 wt% and 25 wt%), KCl (10 wt%, 20 wt% and 25 wt%) and $ZnCl_2$ (10 wt%, 20 wt% and 25 wt%).

3.2.2. Production in the tube furnace

A simple process was proposed based on a combination of carbonization and activation processes in a single step. The production process pass through different stages which include preparation of the raw material and this included drying, crushing and sieving into the desired size (1.18–2 mm). 12–15 g of raw bituminous coal was placed to a Carbolite CTF 12/65/550 tube furnace. Low flow of nitrogen (150 ml min^{-1}, STP) was allowed to pass through the system. Then the furnace was heated (10 °C min^{-1}) to the final carbonization temperature (885 °C). During this step all the volatile materials were repelled out from the system. Steam was then allowed to get into the furnace to activate the coal. H_2 and CO were vented into the fume hood. The sample was held for 4 h at the final temperature. Then the system was turned off and was allowed to cool down under the flow of nitrogen until the temperature reached 450–500 °C. After that, the nitrogen was switched off and the system was allowed to cool overnight. Finally the activated carbon was removed from the furnace and was tested for apparent density and yield. Fig. 2 shows schematic layout of the apparatus setup. PAC1 will refer

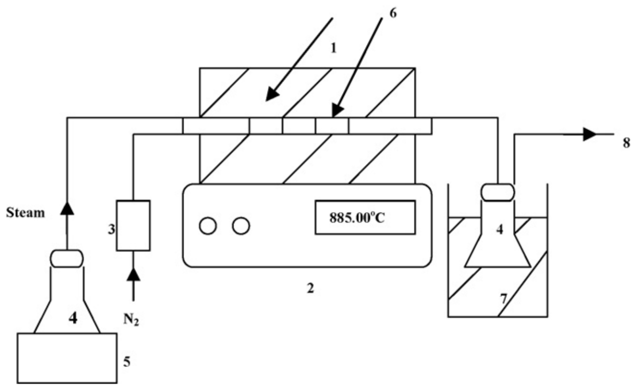

Fig. 2. Schematic layout of the tube furnace setup. (1) Tube furnace, (2) temperature controller, (3) flow meter, (4) conical flask, (5) stirring and hot plate, (6) cal samples, (7) condenser arrangement and (8) vent to fume hood.

to the activated carbon produced in the tube furnace using steam activation process.

For activated carbon produced in the tube furnace using chemical activation process, the following procedure was carried out; the pre-treated coal was prepared by mixing 15 ± 0.1 g of the raw coal with 150 ± 0.5 ml of prepared dehydrating agent solution and stirred for 4 h at 85 °C. Then the slurry was filtered using a Buchner flask and funnel. The coal was then placed in an oven to dry at 100 °C overnight. It has been found that drying of the mixture of coal and chemicals in the oven at 100 °C prior to carbonization dehydrates the sample and provides a uniform reaction [10]. The dried coal was subjected to a pyrolysis process in Carbolite CTF 12/65/550 tube furnace at 800 °C for 4 h. Low flow of nitrogen (150 ml min^{-1}, STP) was allowed to pass through the system. Then the system was turned off and was allowed to cool down under the flow of nitrogen until the temperature reached 450–500 °C. After that, the nitrogen was switched off and the system was allowed to cool overnight.

After that, the activated carbon was removed from the furnace, washed with 0.5 M HCl to remove any residual of dehydrating agent and to dissolve any ash in the sample. Finally the sample was washed with hot distilled water (85 °C) until the pH of the filtrate was approximately 6 and dried overnight at 100 °C and then tested for apparent density and yield. A range of dehydrating agent solutions were prepared: KOH (10 wt%, 20 wt%, 25 wt% and 30 wt%) and NaOH (10 wt%, 20 wt%, 25 wt% and 30 wt%).

3.2.3. Production in rotary kiln

New Zealand bituminous coal was used as a precursor material for the production of activated carbon using steam activation at temperature = 1000 °C for 6 h in a pilot scale rotary kiln. The kiln can produce up to 50 kg of activated carbon per hour. It is approximately 10 m in length, has an internal diameter of 87 cm and is capable of reaching temperatures up to 1000 °C. It has four burners, a fan system and an exhaust pipe into the plant scrubber. Fig. 3 shows simplified schematic diagram of the kiln. The weigh belt feeder WBF feeds coal at a controlled rate into the kiln. Fan F_1 feeds air to burners B_1–B_4, which indirectly heat the rotating kiln tube from the outside. The exhaust gases from the end of the tube, which will contain combustible volatiles from the coal and/or product hydrogen and carbon monoxide from reaction of steam with the coal, pass via a recycle loop (poorly drawn) back into the burner cavity of B_1 where they will be burned. The exhaust gases from burners B_1–B_4 pass into the exhaust pipe going down the side of the kiln, and out into the exhaust fan. A thermocouple is attached to the end of the steam pipe so that a temperature inside the tube can be obtained, together with temperatures T_1–T_4 in the heating cavities outside the tube, T_{rec} measured in the recycle loop, and T_{ex} in the exhaust before the exhaust fan, which then pumps the exhaust gases into the scrubber. The temperatures can then be read from data acquisition software on the adjacent portable P.C. Not shown in the diagram is that, the outlet end of the kiln is fitted with wheels, the large exhaust pipe down the side with bellows, and expansion joints have had to be put in before the fan to cope with the expansion of the system when heated to 1000 °C. The kiln tube expands by over 20 cm when heated to 1000 °C. The kiln is presently elevated by between 8 cm and 9 cm at the inlet end, giving an elevation of approximately 0.5°. The kiln can turn at speeds varying from 2 rpm down to around 0.15 rpm giving residence times from just under 2 h up to 12 h. Steam is fed into the system from the boiler via a central pipe, fitted with a valve and a Spirax Sarco DIVA steam flow meter system to measure the flow rate in kg/h. The outlet end is fitted with a flexible joint to be able to facilitate the expansion of the system, and then attached to a water-cooled vibrating exit feeder, which empties the product into a bucket, which this is then bagged. Presently, there is no oxygen meter fitted to the system, there are sample points and pressure measurement points fitted before the exhaust fan, but these are very hot, typically around 600–700 °C, making gas measurement by Drager tube difficult/impossible. PAC2 will refer to the activated carbon produced in the rotary kiln using steam activation process.

3.3. Physical characteristics

3.3.1. Surface area and pore size distribution

Analysis of the surface physical properties of the carbon includes determination of the total surface area, total pore volume and pore size distribution. Gas sorption analysis can be considered as one of the most important techniques used to determine the physical characteristics of the activated carbon. The adsorption of nitrogen gas at liquid nitrogen temperature (77 K) is routinely used to characterise the porous texture of the activated carbons. Surface area, total pore volume and pore size distribution of the chars and activated carbons were determined from N_2 adsorption/desorption isotherms using an adsorption

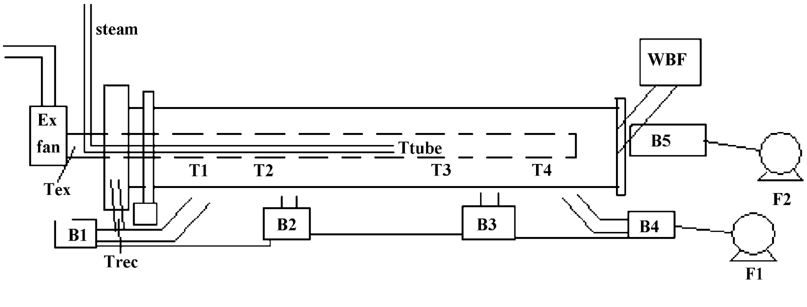

Fig. 3. Simplified schematic diagram of the kiln.

apparatus (Nova 4200, Quantachrome Instruments, UK). The measured relative pressure and adsorbed volume of nitrogen gas were used in BET mathematical model to calculate the monolayer coverage of nitrogen adsorbed on the adsorbent surface from which total surface area was then calculated. The characteristics of pore structure and pore size distribution of mesopores were identified using t-plot and BJH methods. Pore size distributions were evaluated by applying the BJH method whereas the t-plot method was used to estimate V_{micro}. Before the adsorption process commences, all the samples were outgassed for 5 h at 300 °C. Outgassing signifies the exposure of the adsorbent to the vacuum, very often at elevated temperature, in order to remove previously adsorbed gases (especially water vapour) from the surface. According to Sing [24], this process is usually performed to reach a well-defined intermediate state by removing the physisorbed molecules and to avoid any drastic changes as a result of ageing or surface modification.

3.3.2. *Scanning electron microscopy (SEM)*

Texture and surface properties of the adsorbents play an essential role in determining their performance and the final application of carbon materials will depend on their characteristics. Electron microscopy is widely used technique to probe the surface topography of activated carbon. Joel Scanning Electron Microscope, JOEL-JSM 6400, was used to characterise surface properties of the chars and activated carbons. A fine layer of the sample was set on a circular aluminium stub where it was coated with a layer of carbon and a layer of gold. The sample was then placed into the microscope chamber, evacuated and then photographed at different magnifications of range X500–X1000.

4. Results and discussions

In this study, different types of bituminous coal were used as precursor materials in an attempt to produce chars and activated carbons with high surface area, well-developed porous structure and match the requirements of industry. Physical activation alongside chemical activation process was adopted. The effects of precursors, chemical activators and various activating conditions on the structure and texture properties of the resulting activated carbons were investigated.

4.1. *Char characteristics*

A wide range of chars were prepared at different charring temperature and charring time in an attempt to investigate the influence of such parameters on the quality of the chars produced and to choose the optimum conditions under which the chemical activation process can proceed. Three types of bituminous coal were used namely, contaminated Columbian, pure Columbian and New Zealand bituminous coal, to produce chars by a pyrolysis process in a muffle furnace.

Fig. 4 depicts the effect of charring temperature and charring time on the burn-off of the chars produced from the contaminated Columbian bituminous. Burn-off can be defined as a measure of the raw material which has either been driven off in the form of volatiles or burnt off during the pyrolysis process.

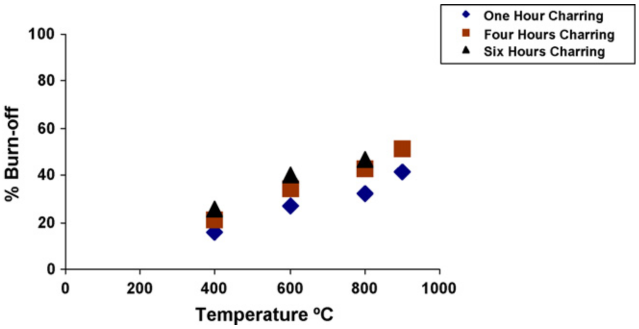

Fig. 4. The effect of charring temperature and charring time on the burn-off of the chars produced from the contaminated Columbian bituminous coal (muffle furnace).

The percentage of %burn-off was defined as follows:

$$\%\text{burn-off} = \frac{(w_1 - w_2)}{w_1} \times 100 \tag{1}$$

where w_1 is the initial weight of coal (g) and w_2 the weight of the obtained char (g).

It can be seen from the figure that by increasing charring temperature, burn-off increases. This is due to more volatile materials removed as the temperature increased. Al-Khalid [8] reported similar behaviour while activating olive-seed waste residue. Pure Columbian and New Zealand bituminous show a very similar trend. It was also noticed that when the charring time was increased, the burn-off increased, i.e., the reaction proceeds with an almost linear weight loss.

Since there is a relevant relationship between the yield and the burn-off; as the burn-off increases, the yield decreases; it is obvious that the yield increases with decreasing charring temperature and with decreasing charring time. Eq. (2) below represents the percentage of yield,

$$\%\text{yield} = \left(\frac{w_2}{w_1}\right) \times 100 \tag{2}$$

where w_1 is the initial weight of coal (g) and w_2 the weight of the obtained char (g).

Maximum yield obtained was 84% for contaminated Columbian, 85% for pure Columbian and 90% for New Zealand bituminous, all of which were charred at 400 °C and for 1 h.

Due to the relatively small molecular diameter of nitrogen [25], nitrogen adsorption was used at 77 K to analyse porosity and surface area of the chars. Table 2 shows the characterization results for chars produced form contaminated Columbian bituminous coal.

It is clear from Table 2 that as the temperature was increased from 400 °C to 800 °C, the surface area and total pore volume increased. While increasing the charring temperature enhances surface area and pore volume, it destroys char structure as the temperature was increased to 900 °C. A rapid decrease in the surface area (164.27–78.05 $\mathrm{m^2\,g^{-1}}$) and total adsorbed volume (62–30 $\mathrm{cm^3\,g^{-1}}$) was observed, this is due to the high temperature (900 °C) causing the external surface area to be destroyed, resulting in an overall loss of surface area. Lua and Yang [26] reported similar effect of temperature on the characteristics of

Table 2
Chars characteristics for contaminated Columbian coal (data from muffle furnace)

Temperature (°C)	Time (h)	Surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$) × 10^2	Burn-off (%)	Yield (%)
400	1	0.290	0.158	16.10	83.90
400	4	7.980	0.918	21.05	78.95
400	6	9.050	0.987	25.85	74.15
600	1	47.55	3.659	27.16	72.83
600	4	49.12	3.722	34.15	65.85
600	6	51.26	3.803	39.82	60.18
800	1	80.53	5.409	32.56	67.43
800	4	138.1	8.656	42.86	57.14
800	6	164.3	9.797	46.61	53.09
900	1	78.05	4.931	41.23	58.76
900	4	19.82	1.487	61.22	38.78

activated carbon and attributed this to excessive carbon burn-off, resulting in the widening of pores and even the loss of some walls between the pores. Prolonged activation time (4 h) at 900 °C, causes more destruction to the surface area and causes overactivation, accelerating surface erosion in preference to pore formation [27]. The decrease in the total pore volume ($4.931 \times 10^{-0.2}\ cm^3\ g^{-1}$ to $1.487 \times 10^{-0.2}\ cm^3\ g^{-1}$) reiterates the observation, i.e., the characteristics of the chars produced at 900 °C were inferior to that obtained at 800 °C. Pyrolysis temperature (400 °C) was insufficient to produce chars with effective surface area.

Generally speaking, longer pyrolysis time produced chars with higher surface area and total pore volume. Among all the chars produced, contaminated Columbian has the highest surface area and total pore volume of $164.3\ m^2\ g^{-1}$ and $9.797 \times 10^{-0.2}\ cm^3\ g^{-1}$, respectively.

Figs. 5 and 6 illustrate the relationships between charring time versus surface area and total pore volume of the chars produced from contaminated Columbian coal. Chars produced from pure Columbian coal shows better characteristics than those obtained for chars produced from New Zealand coal. However, charring temperature of 800 °C proved to be the best temperature for producing chars with superior physical characteristics, (i.e., surface area and total pore volume) for the three precursors used; contaminated Columbian, pure Columbian and New Zealand coal.

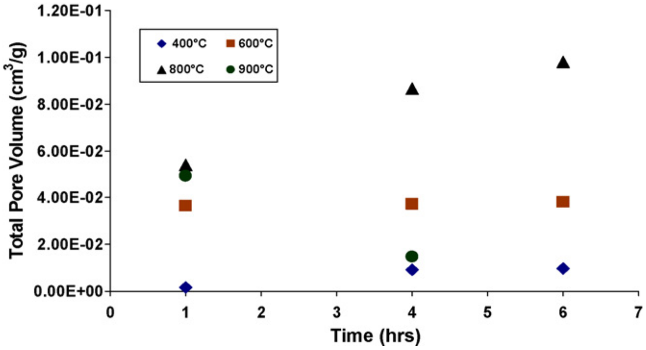

Fig. 6. Relationship between charring time and total pore volume of chars produced from contaminated Columbian coal (muffle furnace).

Fig. 7 shows the nitrogen adsorption isotherms for contaminated Columbian chars produced at different charring temperatures for time interval of 4 h. It is evident from the figure that as the charring temperature increases, the amount of nitrogen adsorbed increases with the exception of char produced at 900 °C. This indicates that the surface area was destroyed as the temperature increased to 900 °C. It is also obvious as the charring temperature increases, the shape of the isotherm turns from type II to type I with the monolayer completed at $P/P_o < 6 \times 10^{-0.2}$. The slight nitrogen uptake at higher relative pressure reflects the fact that slight micropore filling occurs at lower relative pressure and multi-layer adsorption and condensation are predominant on the non-microporous material at higher relative pressure. This is very clear as the temperature is raised from 600 °C to 800 °C and indicates the progress in the development of the micropore structure within the chars (i.e., at $T = 600$ °C,

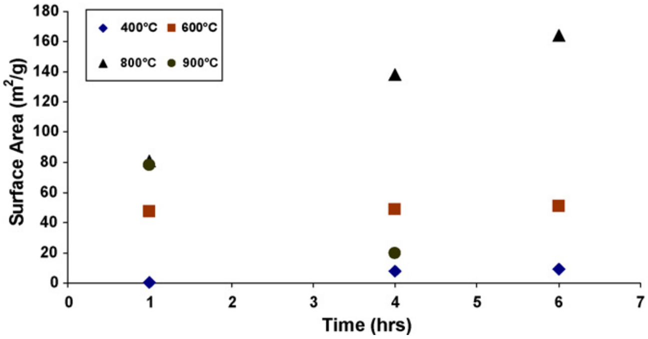

Fig. 5. Relationship between charring time and surface area of chars produced from contaminated Columbian coal (muffle furnace).

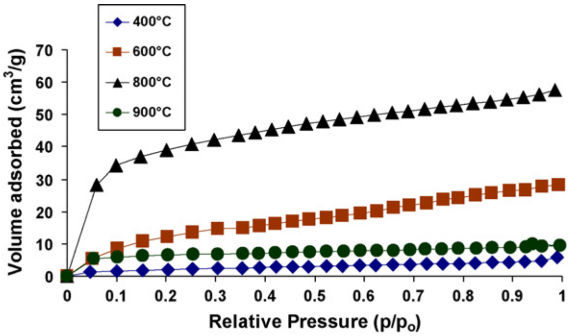

Fig. 7. Nitrogen adsorption isotherms for contaminated Columbian chars produced at different charring temperatures and for 4 h (muffle furnace).

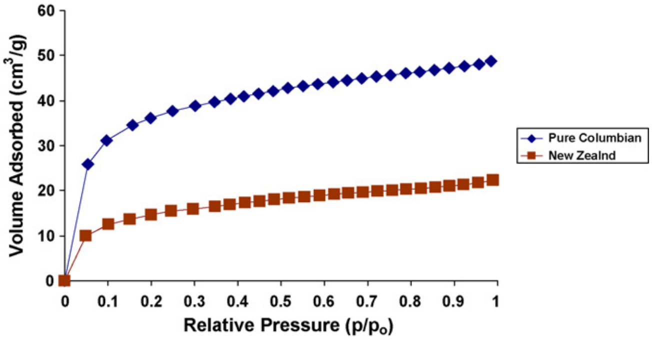

Fig. 8. Nitrogen adsorption isotherms for chars produced at 800 °C and for 4 h (muffle furnace).

the isotherm exhibits type II, non-porous char, at $T = 800\,^\circ\mathrm{C}$, isotherm exhibits type I, microporous char). Chars produced from pure Columbian exhibit the same behaviour as contaminated Columbian, whereas, and New Zealand coal exhibits type II isotherm. Fig. 8 shows such isotherms for pure Columbian and New Zealand coal charred at 800 °C and for 4 h.

A relevant relationship exists between the surface area and carbon porosity. As the porosity increases, the surface area increases especially for carbons with high microporosity since the microporous region contains the majority of the surface area. It is well-known that adsorption is possible only in those pores that can be accessed by molecules, i.e., the carbon adsorption process is dependent on the physical characteristics of the activated carbon and molecular size of the adsorbate. Fig. 7 confirms these observations and illustrates that as the charring temperature was increased, pore propagation became more evident. It is noted that compared to the characteristics of raw materials (analyses show approximately 0–0.12 $\mathrm{m^2\,g^{-1}}$ surface area for the three types of coal used in this work), the pyrolysis process was successful in creating chars with better characteristics (surface area and total pore volume). Fig. 9 shows the pore size distribution for the chars produced at 800 °C and for 4 h.

4.2. Activated carbons characteristics

Since activated carbons were prepared using different types of precursor and different activating agents, their physical characteristics could be compared to select the most suitable precursor and activating agent. (CAC: chemically activated carbon; 1, contaminated Columbian bituminous coal; 2, pure Columbian bituminous coal; 3, New Zealand bituminous coal.) Table 3 lists the burn-off and yield percentages of activated carbons produced from contaminated Columbian pre-treated with different types of dehydrating agents. By comparing the burn-off percentages of the chars produced at 800 °C and for 4 h (Table 2), with that of the activated carbons produced form the same coal pre-treated with different concentrations of the chemical activators and at the same charring temperature and charring time (Table 3), it was observed that chemical treatment processes prior to the activation reduces burn-off from 45% to 38% and increased the yield. This behaviour was more pronounced when the coal was pre-treated with $\mathrm{ZnCl_2}$. This accentuates the effect of the impregnation process on the evolution of carbonization off-product. It is well-known in the literature that zinc chloride promotes the decomposition of carbonaceous material during the pyrolysis process, restricts the formation of tar and increases the carbon yield [22]. Burn-off percentage of around 38–39% was obtained irrespective of the concentration of the chemical activators. This means that after the volatile matter has been removed in the first stage of the carbonization process, no further volatilization took place [8]. Similar trends were observed for activated carbons produced from pure Columbian and New Zealand coal.

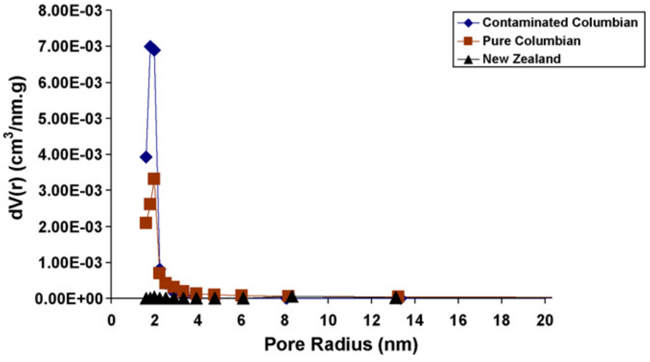

Fig. 9. Pore size distribution for chars produced at 800 °C and for 4 h (muffle furnace).

Table 3
Burn-off and yield percentages of activated carbons produced from contaminated Columbian pre-treated with different types of dehydrating agents (contaminated Columbian coal, muffle furnace at 800 °C for 4 h)

Activated carbon	Burn-off (%)	Yield (%)
CAC1$_{10\%\mathrm{ZnCl2}}$	38.25	61.75
CAC1$_{20\%\mathrm{ZnCl2}}$	38.46	61.54
CAC1$_{25\%\mathrm{ZnCl2}}$	38.63	61.37
CAC1$_{10\%\mathrm{KCl}}$	38.77	61.22
CAC1$_{20\%\mathrm{KCl}}$	39.15	60.84
CAC1$_{25\%\mathrm{KCl}}$	39.69	60.30
CAC1$_{10\%\mathrm{Fe_2(SO_4)_3}}$	39.88	60.22
CAC1$_{20\%\mathrm{Fe_2(SO_4)_3}}$	39.69	60.30
CAC1$_{25\%\mathrm{Fe_2(SO_4)_3}}$	39.22	60.77

In this study, to explore the surface characteristics of the activated carbons, $\mathrm{N_2}$ adsorption isotherms were employed. S_{BET} and t-plot methods were used to specify the total surface area and micropore surface area and micropore volume, respectively. The total pore volumes were estimated to be the liquid volume of adsorbate ($\mathrm{N_2}$) at relative pressure about 0.99.

Regardless of the dehydrating agents, all samples produced from contaminated Columbian show an approximation of a type I isotherm according to IUPAC classification. This indicates that all the activated carbons are essentially microporous [28]. In contrast, samples produced from pure Columbian and New Zealand coal show type II isotherms attributed to non-porous characteristics. A wide range of surface area and total pore volumes were obtained confirming the significant influence of the preparation conditions on the porosity development. No overall trends were observed with the dehydrating agents and precursors used in this study. For zinc chloride and contaminated Columbian, as the concentration of the pre-treatment solution increases from 10% to 25% (w/w), the surface area and total pore volume decreases from 231.50 $m^2\ g^{-1}$ to 161.51 $m^2\ g^{-1}$ and from $1.227 \times 10^{-0.1}$ $cm^3\ g^{-1}$ to $9.446 \times 10^{-0.2}$ $cm^3\ g^{-1}$, respectively. On the contrary, for zinc chloride and pure Columbian, an increase in surface area (71.29–102.63 $m^2\ g^{-1}$) and total pore volume ($5.066 \times 10^{-0.2}$ to $6.339 \times 10^{-0.2}$) was observed with increasing zinc chloride concentration. Similar trends were obtained in the case of KCl. As the concentration of the pre-treatment solution increases, the surface area and total pore volume of contaminated Columbian decreased; and an increase in surface area and total pore volume of pure Columbian was observed with increasing pre-treatment solution concentration with the exception of 25% KCl. $ZnCl_2$ has the same effects on the New Zealand coal as it has on contaminated Columbian and KCl has the same effects on the New Zealand coal as it has on pure Columbian. Pre-treatment with ferric sulphate gave poor results regarding to the surface area and total pore volume compared to potassium chloride and zinc chloride, except in the case of contaminated Columbian. Whitten [27] reported that the degree of burn-off dictates the final structural properties of the activated carbon. Although the burn-off percentages were approximately constant, the activated carbons produced show a wide variety of surface area and total pore volume. For example, CAC1$_{10\%\text{KCl}}$ shows higher BET surface area than CAC1$_{20\%\text{KCl}}$, but CAC1$_{20\%\text{KCl}}$ has higher micropore area than CAC1$_{10\%\text{KCl}}$. These contradictions can be attributed to the pore distribution developed within the carbon, whether the pores are in the macro, meso or micropores range. Contaminated Columbian treated with 10 wt% $ZnCl_2$ displayed the highest surface area and total pore volume (surface area = 231.5 $m^2\ g^{-1}$, and total pore volume = 0.1227 $cm^3\ g^{-1}$) with well-developed microporisity (micropore area = 92.336 $m^2\ g^{-1}$). Table 4 summarizes the results. It is obvious from the table that for activated carbons that exhibited type II isotherms (pure Columbian and New Zealand coal), there is excellent agreement between the surface area values calculated using BET theory and t-plot method.

Fig. 10 depicts the nitrogen adsorption isotherms for contaminated Columbian, pure Columbian and New Zealand coal pre-treated with 25% (w/w) of ferric sulphate with dehydrating agent/coal ratio of 1:1 and for 1 h. Microporosity is evident for contaminated Columbian and non-porous structure evident for pure Columbian and New Zealand coal. The shape of the

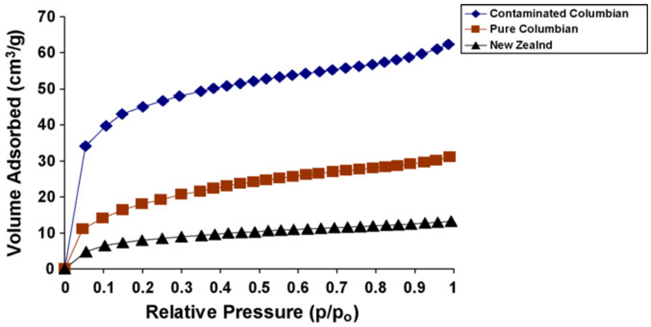

Fig. 10. Nitrogen adsorption isotherm for activated carbons pre-treated with 25% (w/w) of ferric sulphate for 1 h (muffle furnace at 800 °C).

Table 4
Characterization results of activated carbon produced in the muffle furnace (Venezuelan bituminous coal, 800 °C for 4 h)

Activated carbon	Surface area (BET) ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$) × 10^2	Micropore surface area ($m^2\ g^{-1}$)	Micropore volume ($cm^3\ g^{-1}$)	External surface area ($m^2\ g^{-1}$)
CAC2$_{10\%\text{ZnCl}_2}$	231.5	12.27	92.34	0.046	139.2
CAC1$_{20\%\text{ZnCl}_2}$	164.7	10.00	38.00	0.019	126.7
CAC1$_{25\%\text{ZnCl}_2}$	161.5	9.446	0.000	0.000	161.5
CAC1$_{10\%\text{KCl}}$	228. 9	12.30	76.00	0.038	152.9
CAC1$_{20\%\text{KCl}}$	224.4	12.05	111.1	0.056	113.2
CAC1$_{25\%\text{KCl}}$	147.5	8.436	32.04	0.016	115.4
CAC1$_{10\%\text{Fe}_2(\text{SO}_4)_3}$	159.2	9.701	22.89	0.011	136.3
CAC1$_{20\%\text{Fe}_2(\text{SO}_4)_3}$	212.7	12.01	70.41	0.035	142.3
CAC1$_{25\%\text{Fe}_2(\text{SO}_4)_3}$	155.6	9.638	19.17	0.010	136.5
CAC2$_{10\%\text{ZnCl}_2}$	71.29	5.066	0.000	0.000	71.28
CAC2$_{20\%\text{ZnCl}_2}$	85.64	5.681	0.000	0.000	85.64
CAC2$_{25\%\text{ZnCl}_2}$	102.6	6.339	0.000	0.000	102.6
CAC2$_{10\%\text{KCl}}$	120.8	7.674	0.000	0.000	120.7
CAC2$_{20\%\text{KCl}}$	126.2	8.071	0.000	0.000	126.2
CAC2$_{25\%\text{KCl}}$	16.41	1.356	0.000	0.000	16.41
CAC2$_{10\%\text{Fe}_2(\text{SO}_4)_3}$	48.45	3.431	0.000	0.000	48.45
CAC2$_{20\%\text{Fe}_2(\text{SO}_4)_3}$	60.86	4.073	0.000	0.000	60.80
CAC2$_{25\%\text{Fe}_2(\text{SO}_4)_3}$	68.21	4.800	0.000	0.000	68.21
CAC3$_{10\%\text{ZnCl}_2}$	53.52	3.861	0.000	0.000	53.52
CAC3$_{20\%\text{ZnCl}_2}$	36.24	2.416	0.000	0.000	36.24
CAC3$_{25\%\text{ZnCl}_2}$	29.56	1.899	0.000	0.000	29.56
CAC3$_{10\%\text{KCl}}$	10.91	0.726	0.000	0.000	10.91
CAC3$_{20\%\text{KCl}}$	63.98	3.923	0.000	0.000	63.98
CAC3$_{25\%\text{KCl}}$	51.08	3.560	0.000	0.000	51.07
CAC3$_{10\%\text{Fe}_2(\text{SO}_4)_3}$	36.99	2.598	0.000	0.000	36.98
CAC3$_{20\%\text{Fe}_2(\text{SO}_4)_3}$	34.11	2.578	0.000	0.000	34.11
CAC3$_{25\%\text{Fe}_2(\text{SO}_4)_3}$	30.30	2.056	0.000	0.000	30.29

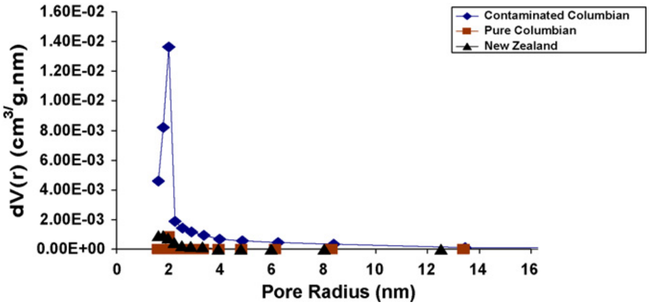

Fig. 11. Pore size distribution of activated carbons pre-treated with 25% (w/w) of ferric sulphate for 1 h (muffle furnace at 800 °C).

isotherms and amount of nitrogen adsorbed emphasized the results listed in Table 4. Contaminated Columbian acquired the highest amount of N_2 adsorbed, this in good agreement with the nature of the pore structure (i.e., microporous, which contains the majority of the surface area available for adsorption). It is important to note that during the activation processes New Zealand and pure Columbian form hard cake due to the melting of the coal. This inhibits proper activation of coal. The presence of petroleum coke in the contaminated Columbian coal may prevent the formation of cake and enhances activation process as evident from the high surface area and pore volume. Fig. 11 shows the pore size distribution for the three activated carbons pre-treated with 25% (w/w) of ferric sulphate calculated by BJH method using desoprtion isotherms. Fig. 11 shows that contaminated Columbian exhibits a maximum, which extend towards pore of 2 nm. This steep increase of the PSD towards micropore region corresponds to the high BET surface area in this carbon. The pore size distribution (PSD) confirmed again the non-porosity of activated carbons produced from pure Columbian and New Zealand coal.

Another range of activated carbon was produced in tube furnace using KOH and NaOH and under the flow of nitrogen. Venezuelan bituminous coal was used as a precursor material for the production of activated carbons. The coals were first crushed to size 1.18–2.00 mm. To ensure complete reaction between dehydrating agent and coal, coal and dehydrating agent were mixed at 85 °C for 4 h. It was then activated for 2 h at 800 °C. $\mathrm{CACV}_{(\mathrm{suf})}$ will be the adopted nomenclature for the activated carbons produced from Venezuelan bituminous coal using chemical activation method and (suf) refers to the type and concentration of the activating agent used. The effect of process variables such as chemical agents, and impregnation ratio on the chemical activation process was studied in order to optimize these preparation parameters. Table 5 summarizes the results.

Although it is well-known in the literature that chemical activation processes usually produce activated carbon with well-developed microporosity, it is evident from Table 5 that the chemical treatment was not effective in creating activated carbon with micropore structure except in the case of 20% (w/w) of KOH. As the concentration of KOH increased from 10% to 20% (w/w), a great enhancement in the characteristics of the activated carbon was obtained. Further increase in the concentration led to over load the activated carbon and hampered rather than enhanced the activation process. Pre-treatment coal with 25% (w/w) NaOH produced activated carbon with surface area equal to $171.8\ \mathrm{m^2\,g^{-1}}$. Higher concentration of NaOH seems to be detrimental. Shawabkeh [29] attributed this to the decomposition of excessive NaOH and KOH molecules into water, which thence dissolved the carbon content in the material and blocked the pores.

All the activated carbons produced were tested for apparent density, burn-off and yield. It was recognized that all the activated carbons gave fairly similar results in terms of burn-off (30–35%) and yield (65–70%). Apparent density was around 0.41 g ml. Comparing to the results obtained by researchers in this field, the carbon appear to have comparatively poor characteristics and this may be attributed to the relatively large quantity (mass) of coal treated each batch (10 g), especially there is no mixing facility in the tube furnace as opposed to a rotary kiln and this gives rise to the poor heat transfer. As a result, only the coal particles located on the top of the crucible has been well activated. In general, treatment with KOH produces activated carbon with higher BET surface area and total pore volume than treatment with NaOH. Okada et al. [1] observed the same influence of KOH and NaOH regarding surface area and pore volume on the activated carbon produced from waste newspaper prepared by chemical activation. These differences in activated carbon characteristics were related to the ionic radii of the alkalis used. The reason for higher BET surface area in the case of KOH was attributed to the formation of atomic K according to the following equation:

$$\mathrm{C + 2KOH \rightarrow 2K + CO + H_2O} \tag{3}$$

Table 5
Characterization results of activated carbons produced in the tube furnace (Venezuelan bituminous coal, 800 °C for 4 h)

Activated carbon	Surface area (BET) ($\mathrm{m^2\,g^{-1}}$)	Total pore volume ($\mathrm{cm^3\,g^{-1}}$) × 10^3	Micropore surface area ($\mathrm{m^2\,g^{-1}}$)	Micropore volume ($\mathrm{cm^3\,g^{-1}}$)	External surface area ($\mathrm{m^2\,g^{-1}}$)
$\mathrm{CACV}_{10\%\mathrm{KOH}}$	8.200	9.548	0.0	0.0	8.189
$\mathrm{CACV}_{20\%\mathrm{KOH}}$	347.5	313.8	142.5	0.063	205.0
$\mathrm{CACV}_{25\%\mathrm{KOH}}$	28.07	31.33	0.0	0.0	28.07
$\mathrm{CACV}_{30\%\mathrm{KOH}}$	27.48	20.23	0.0	0.0	27.47
$\mathrm{CACV}_{10\%\mathrm{NaOH}}$	6.690	0.567	0.0	0.0	6.691
$\mathrm{CACV}_{20\%\mathrm{NaOH}}$	11.84	16.13	0.0	0.0	11.89
$\mathrm{CACV}_{25\%\mathrm{NaOH}}$	171.8	251.3	0.0	0.0	171.8
$\mathrm{CACV}_{30\%\mathrm{NaOH}}$	23.65	19.74	0.0	0.0	23.65

Thus atomic K (large cation) may intercalate and expand the interlayers of adjacent hexagonal network planes consisting of C atoms, enhancing pore formation.

Physical activation process using steam was also used to activate Venezuelan bituminous coal under flow of nitrogen in small laboratory scale using single step (direct activation). Many trials have been conducted to study effects of activation temperature, steam concentration and activation time on the characteristics of activated carbon. It was observed that activation temperature of 885 °C, activation time of 4 h and steam concentration of 3.8 ml g^{-1} hr^{-1} are the optimum activation conditions to produce activated carbon with good characteristics. Apparent density of 0.26 g ml, burn-off of 70% and yield of 30% were attained. All the activated carbons produced from Venezuelan bituminous coal using steam activation were found to form a cake (stuck together) on removal from furnace. This problem was overcome by carbonising the coal at 250 °C for 2 h prior to the activation process. Physical activation process was successful in producing activated carbon (PAC1) with surface area = 863.50 $m^2\,g^{-1}$, total pore volume = 0.469 $cm^3\,g^{-1}$ and micropore surface area = 783.58 $m^2\,g^{-1}$. Production process in rotary kiln was also successful in producing activated carbon (PAC2) with good physical characteristics (surface area = 857.14 $m^2\,g^{-1}$, total pore volume = 0.446 $cm^3\,g^{-1}$ and micropore surface area = 801.8 $m^2\,g^{-1}$). By comparing physical characteristics of the activated carbons produced in small laboratory scale (PAC1) and large industrial scale (PAC2) using physical activation process with that of the internationally recognized activated carbon F400 (surface area = 1216 $m^2\,g^{-1}$, total pore volume = 0.821 $cm^3\,g^{-1}$ and micropore surface area = 918 $m^2\,g^{-1}$), it is clear that the activated carbons produced show excellent properties and can be used for adsorption processes. Overall, PAC1 (from Venezuelan bituminous), and PAC2 (from New Zealand bituminous) were activated using physical activation methods, also some samples of PAC1 were also activated using KOH and NaOH in a laboratory scale process. However, the experimental data indicated that the physical activation produced activated carbon with better characteristics than the chemical activation.

4.3. Topography of activated carbons

Electron microscopy is commonly used for the characterization of the topography of activated carbons. It provides useful information relating to the porous nature of carbon's exterior and adsorbent porosity. Scanning electron microscopy was conducted to study the surface topography of chars and activated carbons. Fig. 12 depicts the micrographs for a char (Fig. 12a) and an activated carbon produced from contaminated Columbian pre-treated with 25 wt% of ferric sulphate (Fig. 12b). It is obvious from the figure that char has smooth surface with well-developed pore structure (mixture of macro, meso and micropore). On the other hand, activated carbon is quite irregular in nature and more micropores were created. This is consistent with the results obtained from analysing the char and activated carbon using N_2 adsorption isotherm, where the char was found to has a small micropore area and micropore volume (Fig. 12a), (3.36 $m^2\,g^{-1}$ and 0.001 $cm^3\,g^{-1}$, respectively), whereas activated carbon (Fig. 12b) was found to has a well-developed microporisity with micropore area = 155.64 $m^2\,g^{-1}$ and micropore volume = 0.010 $cm^3\,g^{-1}$. The white spheres and

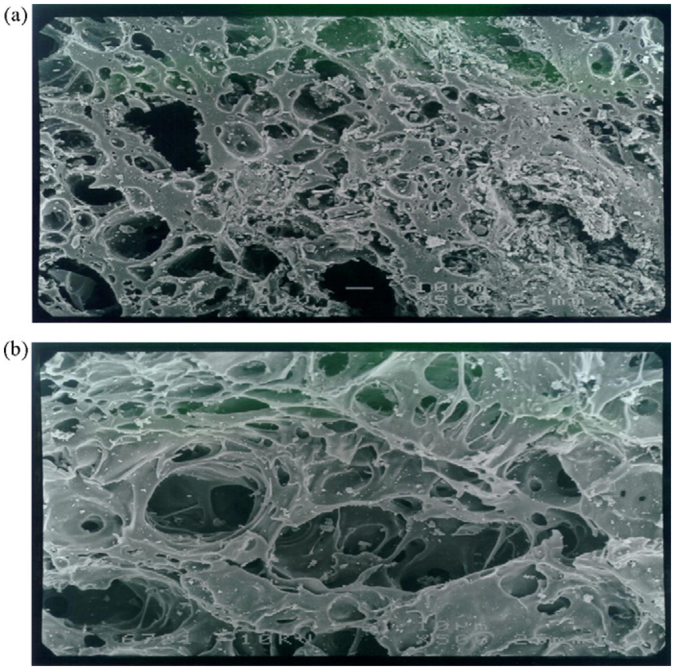

Fig. 12. SEM's (×500) for (a) the char (with optimum condition), (b) activated carbon produced from contaminated Columbian pre-treated with 25 wt% of ferric sulphate (muffle furnace at 800 °C for 4 h).

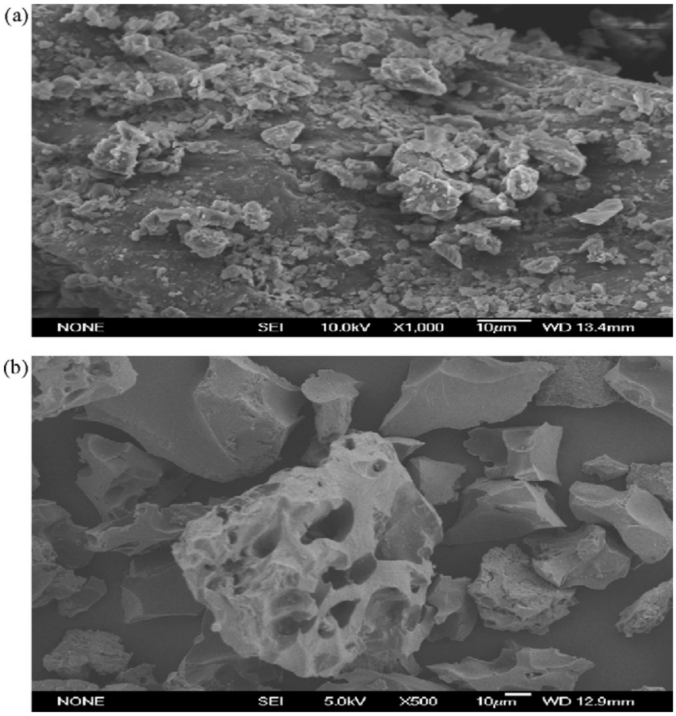

Fig. 13. Electron micrograph (×500) for PAC1 (Venezuelan bituminous coal); (a) raw material and (b) activated carbon (tube furnace at 800 °C for 4 h).

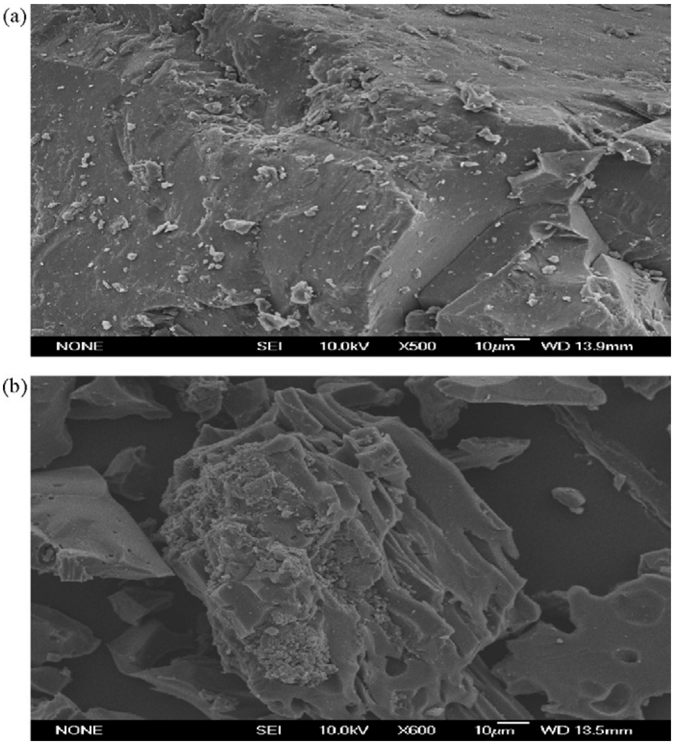

Fig. 14. Electron micrograph for PAC2 (New Zealand bituminous coal; (a) raw material (×500) and (b) activated carbon (×600) (industrial kiln at 1000 °C for 6 h).

some “fluffy” materials may be due to the presence of ferric sulphate residues and some other impurities.

Fig. 13 shows the micrographs for activated carbon produced from Venezuelan bituminous coal using steam activation process (PAC1) and Fig. 14 shows micrograph for activated carbon produced from New Zealand bituminous coal (PAC2). Close inspection of Fig. 13 shows that raw material (Fig. 13a) of PAC1 is irregular in nature and the absence of porosity is evident. Activation process was able to create pore structure within the carbon as it is recognized in Fig. 13b. Raw material of PAC2 (Fig. 14a) shows smooth surface with non-porous structure. Activation process developed the porous structure within the carbon with layers of flakes are obvious. This might be indication of the detrital effect of the activation process in this case (Fig. 14b). All these micrographs support the N_2 adsorption analysis results and indicate the porosity of the activated carbon.

5. Conclusions

The focus of this research was to investigate the potential use of bituminous coals as a precursor material for the production of a range of chars and activated carbons with superior characteristics. Chemical activation process alongside with physical activation process was employed for the production processes. The effects of dehydrating agents, type of precursor and the preparation conditions on the physical characteristics of the activated carbon were investigated. Electron microscopy was used for the characterization of the topography of chars and activated carbons. On the basis of present studies, many conclusions can be drawn:

- Comparing the physical characteristics of the raw materials, the chars and activated carbons, all the chars and activated carbon produced were proven to have a reasonable surface area and total pore volume. Therefore, the production of chars and activated carbons using bituminous coals as precursor materials is applicable from practical point of view.
- Charring temperature and charring time had significant role in imparting physical and chemical characteristics of the chars and had great effects on the burn-off and the yield. Increasing charring temperature was accompanied with an increase in burn-off and a decrease in the yield indicating that more volatile materials were removed as the temperature was increased.
- As adsorbent adsorption potential is dependent on the availability of high surface area and total pore volume, longer pyrolysis conditions, (charring temperature and charring time) are favourable as chars with higher surface area and total pore volume were produced at higher charring temperature and charring time. Charring temperature of 800 °C and charring time for 4 h proved to be the optimum charring conditions for producing chars as indicated by the superior physical characteristics. Increasing charring temperature above the optimum value results in a loss in both surface area and pore volume. The destruction in the surface area and pore volume can be linked to the possibility of overactivation, accelerating surface erosion in preference to pore formation.
- Nitrogen adsorption isotherms show a switch in the shape of the isotherm from type II to type I indicating the progress in the development of the micropore structure within the chars.
- Chemical treatment process prior to the activation was found to reduce burn-off from 45% to 38% and increase the yield of activated carbon irrespective of the concentrations or the nature of the activating agents used. This accentuates the effect of the impregnation process on the evolution of carbonization off-product as the dehydrating agents tend to strip away hydrogen and oxygen atoms as water rather than as hydrocarbons leaving the carbon skeleton largely untouched.
- Regardless of the dehydrating agents used, approximately, all samples produced from contaminated Columbian show isotherm of type I indicating that all the activated carbons are essentially microporous. Samples produced from pure Columbian and New Zealand coal show type II which indicates the non-porous characteristics.
- A wide range of surface area and total pore volumes were obtained confirming the significant influence of the preparation conditions on the porosity development.
- Scanning of the surface topography using electron microscope indicates microporosity of the activated carbons produced using physical activation technology and confirms heterogeneity of the activated carbons. This indicates the essential role of the surface characteristics on the adsorption process.

- Physical activation process (in small laboratory scale and large industrial scale) show better physical characteristics of the activated carbons produced.

References

[1] K. Okada, N. Yamamoto, Y. Kameshima, A. Yasumori, Porous properties of activated carbons from waste newspaper prepared by chemical and physical activation, J. Colloid Interface Sci. 262 (2003) 179–193.

[2] K. Gergova, N. Petrov, V. Minkova, A comparison of adsorption characteristics of various activated carbons, J. Chem. Tech. Biotechnol. 56 (1993) 77–82.

[3] J.F. Richardson, J.H. Harker, Backhurst, Chemical Engineering: Particle Technology and Separation Processes, vol. II, fifth ed., Butterworth-Heinemann, Oxford, 2002.

[4] S. Karcher, A. Kornmüller, M. Jekel, Screening of commercial sorbents for the removal of reactive dyes, Dyes Pigments 51 (2001) 111–125.

[5] W.J. Thomas, B. Crittenden, Adsorption Technology and Design, first ed., Butterworth-Heinemann, Oxford, 1998.

[6] Z. Jiang, Y. Liu, X. Sun, F. Tian, F. Sun, C. Liang, W. You, C. Han, C. Li, Activated carbon chemically modified by concentrated H_2SO_4 for the adsorption of the pollutants from wastewater and the dibenzothiophene from fuel oils, Langmuir 19 (2003) 731–736.

[7] F. Banat, S. Al-Asheh, L. Al-Makhadmeh, Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters, Process Biochem. 39 (2003) 193–202.

[8] T. Al-Khalid, N. Haimour, S. Sayed, B. Akash, Activation of olive-seed waste residue using CO_2 in a fluidized-bed reactor, Fuel Process. Technol. 57 (1998) 55–64.

[9] P. Ariyadejwanich, W. Tanthapanichakoom, K. Nakagawa, S.R. Mukai, H. Tamon, Preparation and characterisation of mesoporous activated carbon from waste tires, Carbon 1 (2002) 1–8.

[10] A. Ahmadpour, D. Do, The preparation of active carbons from coal by chemical and physical activation, Carbon 34 (4) (1996) 471–479.

[11] A.K. Mittal, C. Venkobachar, Studies on sorption of dyes by sulfonated coal and ganoderma lucidum, Ind. J. Environ. Health 31 (2) (1989) 105–111.

[12] R.J. Lewis, Hawley's Condensed Chemical Dictionary, fourteenth ed., John Wiley and Sons, Inc., New York, 2001.

[13] J. Sun, M.J. Rood, M. Rostam-Abadi, A. Lizzio, Natural gas storage with activated carbon form a bituminous coal, Gas Sep. Purif. 10 (2) (1996) 91–96.

[14] F. Carrasco-Marín, M.A. Alvarez-Merino, C. Moreno-Castilla, Microporous activated carbons from a bituminous coal, Fuel 75 (8) (1996) 966–970.

[15] G. Skodras, T. Orfanoudalci, E. Kakaras, G. Sakellaropoulos, Production of special activated carbon from lignite for environmental purpose, Fuel Process. Technol. 77 (78) (2002) 75–87.

[16] H. Benaddi, T. Bandosz, J. Jagiello, J. Schwarz, J. Rouzaud, D. Legras, F. Beguin, Surface functionality and porosity of activated carbons obtained from chemical activation of wood, Carbon 38 (2000) 669–674.

[17] J. Díaz-Terán, D.M. Nevskaia, J.L. Fierro, A.J. López-Peinado, A. Jerez, Study of chemical activation process of a lignocellulosic material with KOH by XPS and XDR, Microporous Mesoporous Mater. 60 (2003) 173–181.

[18] S.D. Faust, O.M. Aly, Chemistry of Water Treatment, second ed., Ann Arbor Press, Inc., Michigan, 1998.

[19] J. Hassler, Purification with Activated Carbon: Industrial Commercial Environmental, third ed., Chemical Publishing Co., New York, 1974.

[20] S.J. Allen, L. Whitten, G. McKay, The Production and Characterisation of Activated Carbon: A Review, Dev. Chem. Eng. Mineral Process 6 (5) (1998) 231–261.

[21] M. Molina-Sabio, F. Rodríguez-Reinoso, Role of chemical activation in the development of carbon porosity, Colloids Surf. A 41 (2004) 15–25.

[22] N.R. Khalili, M. Campbell, G. Sandi, J. Golas, Production of micro and mesoporous activated carbon from paper mill sludge: 1 effect of zinc chloride activation, Carbon 38 (2000) 1905–1915.

[23] J. Gañan, C.M. González-García, J.F. González, E. Sabio, A. Macías-García, M.A. Díaz-Díez, Preparation of activated carbons from bituminous coal pitches, Appl. Surf. Sci. 238 (1–4) (2004) 1–8, 347–354.

[24] K. Sing, The use of nitrogen adsorption for the characterization of porous materials: review, Colloid Surf. A 187–188 (2001) 3–9.

[25] Z. Ryu, J. Zheng, M. Wang, B. Zhang, Nitrogen adsorption studies of pan-based activated carbon fibers prepared by different activation methods, J. Colloid Interface Sci. 230 (2000) 312–319.

[26] A. Lua, T. Yang, Effect of activation temperature on the textural and chemical properties of potassium hydroxide activated carbon prepared from pistachio-nut shell, J. Colloid Interface Sci. 274 (2004) 594–601.

[27] L. Whitten, The production and characterisation of sorbents from lignocellulosic materials and their application in No_x/So_x removals. PhD Thesis, Queen's University Belfast, Belfast, UK, 1997.

[28] S. Park, W. Jung, KOH activation and characterisation of glass fibers-supported phenolic resin, J. Colloid Interface Sci. 265 (2003) 245–250.

[29] R. Shawabkeh, Synthesis and characterization of activated carbo-aluminosilicate material from oil shale, Microporous Meso-porous Mater. 75 (2004) 107–144.