

Preparation of activated carbons from corn cob catalyzed by potassium salts and subsequent gasification with CO₂

W.T. Tsai^{a,*}, C.Y. Chang^b, S.Y. Wang^b, C.F. Chang^b, S.F. Chien^a, H.F. Sun^a

^a Department of Environmental Engineering and Health, Chia Nan College of Pharmacy and Science, Tainan 717, Taiwan, ROC

^b Graduate Institute of Environmental Engineering, National Taiwan University, Taipei 106, Taiwan, ROC

Received 6 February 2000; received in revised form 7 August 2000; accepted 7 August 2000

Abstract

In the present study, granular activated carbons were prepared from agricultural waste corn cob by chemical activation with potassium salts and/or physical activation with CO₂. Under the experimental conditions investigated, potassium hydroxide (KOH) and potassium carbonate (K₂CO₃) were effective activating agents for chemical activation during a ramping period of 10°C/min and subsequent gasification (i.e., physical activation) at a soaking period of 800°C. Large BET surface areas (>1600 m²/g) of activated carbons were thus obtained by the combined activation. In addition, this study clearly showed that the porosity created in the acid-unwashed carbon products is substantially lower than that of acid-washed carbon products due to potassium salts left in the pore structure. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Activated carbon; Activation; Gasification; Corn cob; Agricultural waste; Recycling; BET surface area

1. Introduction

Activated carbon is a predominantly amorphous solid that has extraordinarily large internal surface area and pore volume. These unique pore structures play an important role in many different liquid- and gas-phase applications because of their association with adsorptive properties. Although most types of industrial activated carbons are produced from naturally occurring carbonaceous materials such as coal, wood and coconut shell by some form of activation process (Bansal et al., 1988; Noll et al., 1992), some agro-industrial by-products can be used as precursor materials for preparing activated carbons in the laboratory (Pollard et al., 1992; Tsai et al., 1997).

For every 100 kg of corn grain, 18 kg of corn cob is approximately produced (Bagby and Widstrom, 1987). A large quantity of corn cob thus generated remains unused as cellulosic wastes in fields and factories. This poses a serious problem not only in storage but also for

disposal. Utilization of this agricultural waste as a renewable source for energy production (Lin et al., 1995), as a carbohydrate source for producing bacterial protein (Perotti and Molina, 1988), and conversion into valuable activated carbon (Tsai et al., 1997; Aggarwal and Dollimore, 1997) has been researched and developed in the past decade.

In our previous works (Tsai et al., 1997; Tsai et al., 1998), corn cob was found to be a suitable precursor for the preparation of activated carbons by zinc chloride (ZnCl₂) activation owing to its high carbon (i.e., 45.21%) and low ash (i.e., 0.91%) contents. It was also demonstrated that the optimal conditions of operating pyrolysis temperature and impregnation ratio (i.e., the ratio of weight of ZnCl₂ added to weight of corn cob) for the production of large surface area (greater than 1400 m²/g) activated carbon are approximately 500°C and up to 175 wt% at a pre-pyrolytic heating rate of 10°C/min under an inert atmosphere of flowing nitrogen (300 cm³/min at STP). The advantages of this activation method over physical activation include completion in only one step and at a relative low temperature and also a yield of higher carbon content product (Philip and Girgis, 1996). It should be pointed out that the complete removal or recovery of the activating chemicals (e.g., ZnCl₂ and H₃PO₄, which are the most widely used

* Corresponding author. Tel.: +886-6-266-4911; fax: +886-6-266-6411.

E-mail address: wwttsai@mail.chna.edu.tw (W.T. Tsai).

chemical agents) from the resulting carbon products presents significant difficulties. As a result, this chemical activation process will generate serious pollution problems related to environmental contamination with zinc compounds and ecological problems of environmental eutrophication with phosphorus compounds, which increase the overall manufacturing costs and have been limited recently in view of the environmental requirement (Jankowska et al., 1991).

The process for manufacturing activated carbons involves two steps: the carbonization of raw carbonaceous materials in an inert atmosphere and the activation of the carbonized product. Chemical activation of coke and charcoal by potassium hydroxide (KOH) for the preparation of large surface area active carbons was reported in the 1980s (Marsh et al., 1982; Marsh et al., 1984; O'Grady and Wennerberg, 1986). Since then, there have been a number of works describing KOH or other potassium salts activation to obtain the carbons (Laine and Calafat, 1991; Laine and Yunes, 1992; Verheyen et al., 1995; Hu and Vansant, 1995; Ahmadpour and Do, 1996; Otowa et al., 1997; Ahmadpour and Do, 1997; Evans et al., 1999; Hu and Srinivasan, 1999). In addition, potassium salts are known to catalyze the partial gasification of carbonaceous materials with CO₂ (Walker et al., 1968; Laine and Calafat, 1991). These features suggest a possible application of such chemical activators for the preparation of large-surface-area activated carbons from corn cob. The chemical activation with potassium salts could be also considered as a cleaner production technology while compared to that with ZnCl₂ or H₃PO₄. The objective of the present work attempted to investigate the preparation of activated carbon from corn cob. The pyrolysis process involved impregnation of the precursor with different potassium salts and activation by passing CO₂ as the activating gas at the specified temperature. Some of these results were also compared with those obtained by chemical activation with effective potassium salts using N₂ gas. In addition, we studied the influence of acid-washing vs no acid-washing on the physical property of the carbon products under the activation of potassium salts/CO₂.

2. Methods

The apparatus and experimental methods employed in the present work are similar to those for the chemical activation with ZnCl₂ as reported previously (Tsai et al., 1997; Tsai et al., 1998). Corn cob was obtained from a Chia Yi production zone in Taiwan, and then crushed and sieved to 1.0–2.0 mm. Twenty grams of this material was mixed with 200 ml of the potassium solution (e.g. KOH or K₂CO₃) of known concentration. Impregnation was carried out at approximately 80°C on a stirrer/

hot plate with boiler-reflux condenser for 2 h. Afterward, the sample solution was filtered in a vacuum filter flask and dried overnight at 120°C.

Prior to activation experiments, the influence of the flow rates (i.e., 200, 500 and 800 cm³/min at STP) of nitrogen and the heating rates (i.e., 5, 10 and 20°C/min) on the carbon products were studied. The results of the preliminary experiments indicate that these activation parameters are not significant factors affecting the porosity of the final carbon products. To assure the reliability of carbon products and measurement data, the raw materials were well mixed and sampled for the activation experiment. In addition, prior to the measurement of physical properties of the carbon products, the calibration of the analyzer was performed by standard operational procedures. Also, for the purpose of reproducibility test, the BET surface area 348 ± 21 m²/g (i.e., mean \pm standard deviation) of the carbon sample, conducted at an activation temperature of 500°C and a N₂ flow of approximately 500 cm³/min, was obtained for three measurements. Based on the above operations, one sample was used for each experiment in the present work. Thus, pyrolysis temperature was increased at a ramp rate of 10°C/min in a N₂ flow (200 cm³/min at STP) as reported previously (Tsai et al., 1997; Tsai et al., 1998), then switched to CO₂ flow (200 cm³/min at STP) after reaching the specified temperature (i.e., 800°C), which was adopted for the catalytic experiments of Laine and Calafat (1991). After activation with CO₂ for 1 h, cooling to room temperature was carried out under N₂ flow before taking the sample for washing with 3 N hot HCl solution. The acid washed sample was filtered in a vacuum flask followed by washing repeatedly with 80°C distilled water to remove residues attached to the resulting activated carbon. Finally, the product of activated carbon was dried overnight at 120°C and placed in a desiccator for further analyses. For preliminary comparisons, some of the activated carbons were also prepared by chemical activation with KOH or K₂CO₃ in the present study. The heating procedure was similar to that employed as mentioned, but only using 200 cm³/min N₂.

BET surface area analyses of the resulting activated carbons were measured as described previously (Tsai et al., 1997; Tsai et al., 1998). Nitrogen adsorption–desorption isotherms at –196°C were obtained employing the Micromeritics ASAP 2000 and BET surface area was determined by means of the standard BET equation applied in a relative pressure range from 0.06 to 0.3 (Gregg and Sing, 1982; Lowell and Shields, 1991). The values of 0.81 g/cm³ and 16.2×10^{-20} m² were used for the density of liquid nitrogen at –196°C and the molecular area of adsorbate nitrogen, respectively, in the measurements of BET surface area. The total pore volumes (V_t) were estimated to be the liquid volumes of N₂ at a high relative pressure of 0.96. The true density (ρ_s) of

the sample was measured by a helium displacement method with a pycnometer (Micromeritics, AccuPyc 1330) (Lowell and Shields, 1991), where the measurement was repeated ten times for each sample. The particle density (ρ_p) was thus calculated from V_t and ρ_s (Smith, 1981)

$$\rho_p = 1/(V_t + 1/\rho_s). \quad (1)$$

Therefore, the particle porosity (ε_p) can be computed from ρ_s and ρ_p .

$$\varepsilon_p = 1 - \rho_p/\rho_s. \quad (2)$$

Analysis of main elements for carbon products was performed by using a CHN-O rapid analyzer (Heraeus Co.) for two measurements. The inductively coupled plasma-atomic emission spectrometer (ICP-AES) of ICAP 9000 (JARREL-ASH Co.) was used to determine the trace elements for three measurements.

All characterization determinations of the resulting activated carbons except surface area, pore volume and pore size distribution from N_2 adsorption-desorption measurement were replicated at least two times. By using the Microsoft Excel[®] computer package, the procedures most commonly used to estimate the statistical parameters (i.e., mean and standard deviation) of measurement data were made.

3. Results and discussion

From the data in Table 1, it is clear that the potassium hydroxide (KOH) and potassium carbonate (K_2CO_3) are effective catalysts for activation of the corn cob among the potassium compounds studied. It is also noted that the BET surface area of the activated carbon prepared without catalyst was smaller than that with catalyst. In order to study the substantial influence of CO_2 gasification on the porosity development, the chemical activations of corn cob impregnated with 15 wt% KOH and 37.5 wt% K_2CO_3 were carried out at a temperature of 800°C in a N_2

atmosphere. The condition of the impregnation ratios selected in the present study was based on the results of the previous experiments, where the carbon products could not be obtained at higher impregnation ratios (i.e., 20 wt% KOH and 50 wt% K_2CO_3) due to serious sintering or excess burn-off (Laine and Calafat, 1991). In Table 2 the BET surface areas of carbon products obtained by chemical activation accompanied with N_2 are compared with those of chemically and subsequently physically activated samples with CO_2 . The results show that the process of combined chemical and physical activation is superior to that of chemical activation only.

The nitrogen adsorption isotherms on the resulting activated carbons are shown in Fig. 1. It is seen that the knee of the adsorption isotherm is sharp and its plateau is also horizontal with nearly no hysteresis. Evidently, the carbon product thus obtained is of type I according to the Brunauer, Deming, Deming and Teller (BDDT) classification for the types of the adsorption isotherm (Gregg and Sing, 1982). The major uptake occurs at low relative pressures (less than 0.1), indicating the formation of highly porous material with narrow pore size distribution that is essentially microporous as listed in Table 3. It should be noted that the interaction potential in a microporous solid might be strong enough to bring about a nearly complete filling of pores at a quite low relative pressure (Laine and Calafat, 1991).

The main effect of gasification with CO_2 is the creation and widening of the existing pores, indicating the increase in adsorptive properties such as the BET surface area. As discussed by Laine and Calafat (1991) in the preparation of activated carbons from coconut shell with potassium compounds, the relatively large surface area found in the K_2CO_3 - and KOH-impregnated samples could be attributed to carbon gasification with the gaseous products (i.e., CO_2 and H_2O) of the decomposition of potassium compounds and partial reaction of the salts with the cellulose constituting corn cob.

Table 1

BET surface area of activated carbons produced from corn cob impregnated with different potassium compounds (10.5 wt% K), employing CO_2 flow at 800°C for 1 h

K-compounds	BET surface area (m ² /g)	Pyrolysis yield ^a (%)
unimpregnated	437	22.9
KCl	490	27.6
K_3PO_4	732	23.1
KNO_3	903	20.4
K_2CO_3	1266	18.7
KOH	1682	14.7

^a The yield is defined as the ratio of the mass of impregnated sample to that of activated product.

Table 2

Effects of CO_2 on BET surface area of the resulting activated carbon prepared from corn cob with activation using impregnation ratio of 15 wt% and 37.5 wt% for KOH and K_2CO_3 , respectively

Carbon samples		BET surface area (m ² /g), S_{BET}
Chemical activator	Gas flow	
KOH	N_2	369
KOH	CO_2	1682 ^a
K_2CO_3	N_2	506
K_2CO_3	CO_2	1541 ^b

^a The carbon yield, defined as the ratio of the mass of impregnated sample to that of activated product, is 14.7%.

^b The carbon yield is 17.4%.

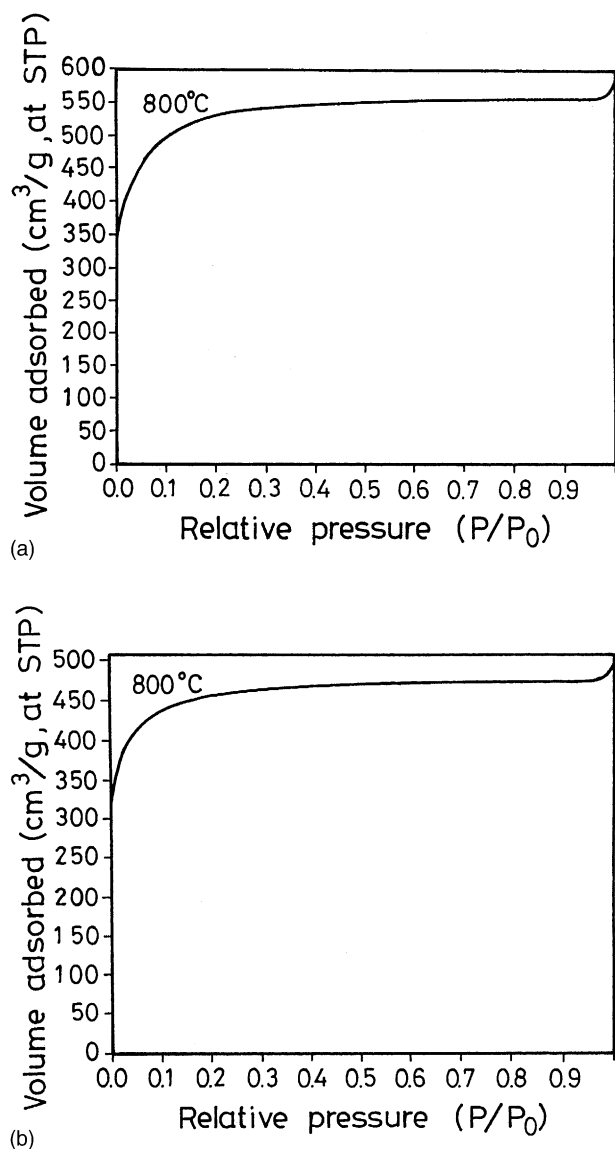


Fig. 1. Adsorption isotherms of nitrogen of the resulting activated carbons produced at activation temperatures of 800°C, impregnation ratios of (a) 15 wt% KOH and (b) 37.5 wt% K_2CO_3 , followed by soaking time of 1 h under flow of CO_2 .

From the view of industrial use, the properties of activated carbon, such as total pore volume, true density, particle density, particle porosity and major/trace element contents, are also important. The results of these properties of resulting activated carbons are given in Table 4. Based on the data in Table 4, it appears that the carbon is characteristic of high porosity and possesses high true density compared with those (i.e., 2.24 and 2.22 g/cm^3 , respectively) of commercial activated carbons BPL and PCB (Calgon Co., U.S.A.) (Tsai and Chang, 1994a). It is also seen from Table 4 that the carbon products contain nearly 90 wt% of carbon, which are approximate to those (i.e., 87.88 and 94.85

wt%, respectively) of carbons BPL and PCB (Tsai and Chang, 1994b). However, based on the major trace metal composition of carbon products (Table 4), it can also be seen that the Si and Al elements are the two highest sources of trace metal.

As mentioned in the experimental section, after the combined chemical and physical activation the crude carbon products were subjected to washing with hydrochloric acid and distilled water. It is known that washing with acid removes the alkali and alkaline earth metals, and washing with water removes the basic and water-soluble components in the carbon (Ahmadpour and Do, 1996). Thus, the final carbon products obtained by washing will yield well-developed porosity in the carbon structure. This point had been confirmed in our study of corn cob employing the combined activation. The test was performed on two samples with the impregnation ratios of 20 wt% KOH and 25 wt% K_2CO_3 . The results of BET surface area before and after washing of samples are presented in Table 5. The results clearly show that the approximate 50% of porosity (reflected by the BET surface area) created in the carbon samples should be occupied by potassium salts in the structure. Small surface areas of the unwashed carbons are because of potassium salts left in the carbon products, blocking pore entrances to the nitrogen molecules based on the analysis of adsorption and desorption isotherms of nitrogen for determining BET surface area. Also, the values of BET surface area of the resulting activated carbons increase with the increase in the impregnation ratio of K_2CO_3 activating agent from the data in Tables 1, 2 and 5, i.e., 1266 m^2/g (21.2 wt% of K_2CO_3 or 10.5 wt% K) < 1424 m^2/g (25 wt% of K_2CO_3) < 1541 m^2/g (37.5 wt% of K_2CO_3). This result is consistent with the result reported for the chemical activation of $ZnCl_2$ (Tsai et al., 1997).

In conclusion, the combined chemical and physical activation process was attempted to prepare activated carbon from corn cob catalyzed by potassium salts and subsequent gasification with CO_2 in the present study. It was found that KOH and K_2CO_3 were effective catalysts for the activation with CO_2 among all the potassium compounds studied. The carbon products thus obtained possess a large surface area of about 1700 m^2/g . The BET surface areas of the combined activated carbon products were also compared with those obtained purely by chemical activation. In addition, the washing treatment was an important factor affecting the pore entrances and thus the physical properties of the resulting carbon products. Due to their large adsorption capacity (i.e., large BET surface area), low cost (i.e., agricultural waste) and cleaner production process (i.e., KOH/ K_2CO_3 instead of $ZnCl_2$ or H_3PO_4), the corn cob-derived activated carbon products may offer potential as substitutes for commercial activated carbons.

Table 3
List of adsorption pore distribution of the resulting carbons^a

Activated carbon (15 wt% KOH)		Activated carbon (37.5 wt% K ₂ CO ₃)	
Pore diameter (<i>D</i> , Å)	Pore volume ^b (<i>V</i> , cm ³ /g)	Pore diameter (<i>D</i> , Å)	Pore volume ^b (<i>V</i> , cm ³ /g)
2120	0.040	2160	0.004
805	0.007	830	0.003
420	0.001	518	0.001
215	0.002	216	0.003
150	0.004	122	0.005
120	0.007	95	0.013
97	0.021	68	0.022
52	0.047	52	0.031
42	0.086	41	0.056
32	0.140	33	0.102
27	0.325	26	0.207
22	0.955	21	0.551

^a Produced at activation temperature of 800°C, impregnation ratio of 15 wt% KOH and 37.5 wt% K₂CO₃, respectively, followed by soaking time of 1 h under CO₂ flow.

^b Performed as the form of $dV/d \log(D)$.

Table 4
Physical properties and element analysis of resulting activated carbons prepared from corn cob with activation using impregnation ratio of 15 wt% KOH and 37.5 wt% K₂CO₃, and employing CO₂ flow at 800°C for 1 h

Physical properties/element analysis		Carbon products	
		15 wt% KOH/CO ₂	37.5 wt% K ₂ CO ₃ /CO ₂
Total pore volume (cm ³ /g), <i>V_t</i>		0.84	0.74
True density ^a (g/cm ³), ρ_s		2.506 ± 0.004	2.417 ± 0.004
Particle density ^b (g/cm ³), ρ_p		0.82	0.86
Particle porosity ^c (-), ϵ_p		0.673	0.645
Major elements ^d (wt%)	C	89.20 ± 0.59	85.11 ± 0.53
	H	0.77 ± 0.08	0.99 ± 0.13
	N	0.54 ± 0.01	1.58 ± 0.01
	O (by diff.)	9.49	12.32
Trace elements ^e (µg/g)	Si	1176 ± 15	>1000
	Al	171 ± 6	236 ± 8
	K	115 ± 5	201 ± 9
	Fe	1.9 ± 0.5	82 ± 3.3
	Pb	4.4 ± 0.2	12 ± 0.7

^a The true density (ρ_s) was measured by helium displacement method with a pycnometer. The data denote the mean ± standard deviation for ten determinations.

^b The particle density (ρ_p) is calculated from the total pore volume (*V_t*) and true density (ρ_s) (Smith, 1981), i.e., $\rho_p = 1/(V_t + 1/\rho_s)$.

^c The particle porosity (ϵ_p) is computed from the total pore volume (*V_t*) and particle density (ρ_p) (Smith, 1981), i.e., $\epsilon_p = 1 - \rho_p/\rho_s$.

^d The data denote the mean ± standard deviation for two determinations.

^e The data denote the mean ± standard deviation for three determinations.

Table 5
Variation in BET surface area of carbon products prepared by KOH/CO₂ and K₂CO₃/CO₂ activation before and after washing

Carbon samples			BET surface area
Chemical activator	Impregnation ratio	Treatment	(m ² /g), <i>S_{BET}</i>
KOH	20 wt%	Unwashed	779
		Washed	1628 ^a
K ₂ CO ₃	25 wt%	Unwashed	846
		Washed	1424 ^b

^a The carbon yield is 15.8%.

^b The carbon yield is 18.0%.

Acknowledgements

This research was supported by National Science Council (NSC), Taiwan, under contract number NSC 87-2211-E-041-005.

References

- Aggarwal, P., Dollimore, D., 1997. The production of active carbon from corn cobs by chemical activation. *J. Therm. Anal.* 50, 525–531.
- Ahmadpour, A., Do, D.D., 1996. The preparation of active carbons from coal by chemical and physical activation. *Carbon* 34, 471–479.
- Ahmadpour, A., Do, D.D., 1997. The preparation of activated carbon from macadamia nutshell by chemical activation. *Carbon* 35, 1723–1732.
- Bagby, M.O., Widstrom, N.W., 1987. Biomass uses and conversions. In: Watson, S.A., Ramstad, P.E., (Eds.). *Corn: Chemistry and Technology*, American Association of Cereal Chemists Inc., St. Paul, MN, USA, pp. 575–590.
- Bansal, R.C., Donnet, J.B., Stoeckli, F., 1988. *Active Carbon*. Marcel Dekker, New York.
- Evans, M.J.B., Halliop, E., MacDonald, J.A.F., 1999. The production of chemically-activated carbon. *Carbon* 37, 269–274.
- Gregg, S.J., Sing, K.S.W., 1982. *Adsorption Surface Area and Porosity*, second ed. Academic Press, New York.
- Hu, Z., Srinivasan, M.P., 1999. Preparation of high-surface-area activated carbons from coconut shell. *Microporous and Mesoporous Mater.* 27, 11–18.
- Hu, Z., Vansant, E.F., 1995. Chemical activation of elutrilite producing carbon-aluminosilicate composite adsorbent. *Carbon* 33, 1293–1300.
- Jankowska, H., Swiatkowski, A., Choma, J., 1991. *Active Carbon*. Ellis Horwood, Chichester, England.
- Laine, J., Calafat, A., 1991. Factors affecting the preparation of activated carbons from coconut shell catalized by potassium. *Carbon* 29, 949–953.
- Laine, J., Yunes, S., 1992. Effect of the preparation method on the pore size distribution of activated carbon from coconut shell. *Carbon* 30, 601–604.
- Lin, J.L., Keener, H.M., Essenhigh, R.H., 1995. Pyrolysis and combustion of corncobs in a fluidized bed: measurement and analysis of behavior. *Combust. Flame* 100, 271–282.
- Lowell, S., Shields, J.E., 1991. *Powder Surface Area and Porosity*, third ed. Chapman and Hall, New York.
- Marsh, H., Crawford, D.C., O'Grady, T.M., Wennerberg, A., 1982. Carbons of high surface area. a study by adsorption and high resolution electron microscopy. *Carbon* 20, 419–426.
- Marsh, H., Yan, D.S., O'Grady, T.M., Wennerberg, A., 1984. Formation of active carbons from cokes using potassium hydroxide. *Carbon* 22, 603–611.
- Noll, K.E., Gounaris, V., Hou, W.S., 1992. *Adsorption Technology for Air and Water Pollution Control*. pp. 3–6, Lewis, Chelsea, MI, USA.
- O'Grady, T.M., Wennerberg, A., 1986. High-surface-area Active carbon. In: Bacha, J.D., Newman, J.W., White, J.L., (Eds.), *Petroleum-Derived Carbons*, ACS Symp. Ser. 303, ACS, Washington, DC, pp. 302–309.
- Otowa, T., Nojima, Y., Miyazaki, T., 1997. Development of KOH activated high surface area carbon and its application to drinking water purification. *Carbon* 35, 1315–1319.
- Perotti, N.I., Molina, O.E., 1988. Corn cob as a bacterial substrate for the production of forage protein. *Biol. Wastes* 26, 125–131.
- Philip, C.A., Girgis, B.S., 1996. Adsorption characteristics of microporous carbons from apricot stones activated by phosphoric acid. *J. Chem. Tech. Biotechnol.* 67, 248–254.
- Pollard, S.J.T., Fowler, G.D., Sollars, C.J., Perry, R., 1992. Low-cost adsorbents for waste and wastewater treatment: a review. *Sci. Total Environ.* 116, 31–52.
- Smith, J.M., 1981. *Chemical Engineering Kinetics*, third ed. McGraw-Hill, New York.
- Tsai, W.T., Chang, C.Y., 1994a. Adsorption of methylene chloride vapor on activated carbons. *J. Chem. Tech. Biotechnol.* 61, 145–151.
- Tsai, W.T., Chang, C.Y., 1994b. Surface chemistry of activated carbons and its relevance for effects of relative humidity on adsorption of chlorinated organic vapors. *Chemosphere* 29, 2507–2515.
- Tsai, W.T., Chang, C.Y., Lee, S.L., 1997. Preparation and characterization of activated carbons from corn cob. *Carbon* 35, 1198–1200.
- Tsai, W.T., Chang, C.Y., Lee, S.L., 1998. A low cost adsorbent from agricultural waste corn cob by zinc chloride activation. *Bioresource Technol.* 64, 211–217.
- Verheyen, V., Rathbone, R., Jagtoyen, M., Derbyshire, F., 1995. Activated extrudates by oxidation and KOH activation of bituminous coal. *Carbon* 33, 763–772.
- Walker, P.L., Jr, Shelef, M., Anderson, R.A., 1968. Catalysis of carbon gasification. In: Walker, P.L., Jr. (Ed.), *Chemistry and Physics of Carbon*, vol. 4, Marcel Dekker, New York, pp. 287–383.