Review on the Technology for the Production of Activated Carbons

TANZIL H. USMANI, M. TAHIR MOTAN AND A.H.K. YOUSUFZAI
PCSIR Laboratories Complex,
Off University Road, Karachi-75280, Pakistan

(Received 18th August, 1998, revised 25th January, 2000)

Summary: The term activated carbon in its broadest sense includes a wide range of carbon-based materials prepared to exhibit a high degree of porosity and an extended interparticulate surface area. These are obtained by combustion, partial combustion, and thermal decomposition of various carbonaceous substances of cellulosic, mineral and polymeric nature. Activated carbon may be in powdered, granular or fibrous forms. The granular form is characterized by large internal surface and small pores, whereas the finely divided powdered form is associated with larger pore diameters but a smaller internal surface. Fibrous activated carbons are particularly outstanding in their physico-mechanical properties and high chemical resistance. In this article, successive stages of technology development, of activated carbons in powdered, granular and fibrous forms from precursors of different origin, have been thoroughly reviewed.

Introduction

The term active carbon or carbonaceous adsorbents stands for highly carbonaceous materials consisting mostly of carbon, exhibiting large internal surface and which, due to their surface properties, adsorb all organic and other non polar compounds from the gaseous or liquid phase [1].

Activated carbons are unique and versatile adsorbents because of their extended surface area, microporous structure, high adsorption capacity and large degree of surface reactivity. These are extensively used in treatment of water and waste-water, for solvent recovery, in improvement of environment and in a variety of gas phase applications. Moreover, active carbons have their uses in diversified industries like food processing, pharmaceuticals, chemicals, petroleum, mining, nuclear, automobiles etc. According to a survey, the annual per capita consumption (in kg) of active carbon is about 0.5 in Japan, 0.4 in U.S.A., 0.2 in Europe and 0.03 in the developing world, generally reflecting the degree of awareness among the comity of nations for a safer and cleaner environment [2]. Carbon is generally used in two forms, powdered and granular. The principal uses of granular activated carbon are in air purification, solvent, recovery, recovery of gold and in cigarettes filters. About 80% of the granular carbon produced worldwide is used in liquid phase purifications, and the rest is used in gas phase applications. It is known from visual and microscopic studies that all carbonaceous materials have a system of pores. The art of making an activated carbon is to enlarge these pores and also to develop new pores by the removal of volatile matter [3].

Early history of technology development for activated carbon

The use of charcoal for purposes other than as a fuel in metallurgy is very old, the use in medicine being mentioned in an ancient Egyptian papyrus from 1550 B.C. [4]. The earliest recorded date at which adsorptive power of carbon was recognized appears to be 1773, when Scheele described experiments on gases exposed to charcoal [5]. In 1785, Lowitz called attention to the decolorizing effect of charcoal on solutions [6]. During the 19th century, a number of attempts were made to develop decolorizing carbon from other sources. Bussy produced a carbon from blood having decolorizing power fifty times to that of bone char [7]. Hunter noted the gas adsorbing power of coconut charcoal [8]. Stenhouse prepared and got patented a decolorizing char by heating an intimate mixture of flour, tar and magnesium carbonate [9]. Lee also got a patent on decolorizing carbon prepared by the action of superheated steam and heated air on peat [10]. In 1862, Lipscombe first time prepared an active carbon to purify potable water [11]. This application, later on, became an important industrial use and market for active carbon.

A Swedish chemist Ostrejko got two patents in 1900 and 1901, covering the basic concepts of 'chemical' and 'physical' activation processes [12]. These two patents later on paved the way for the development of modern commercial active carbons. The first powdered commercial active carbon, 'EPONITE' was produced in Europe in 1909, to be followed by 'NORIT' in 1911 and 'CARBORAFFIN' in 1915. The first American carbons introduced in the market were 'CARBROX' in 1917, 'KELPCHAR' in 1920, 'DARCO' in 1921 and 'NUCHAR' and 'SUCHAR' in 1922. In 1915, during World War I, Germans first time used poisonous chlorine gas against the Allied forces which caused great problems. In the mean time, allied forces developed relatiatory measures against the chemical warfare in the form of gas masks containing active carbon 1929. Spalding demonstrated that active carbon could improve taste conditions in municipal water supplies at a very limited cost [13]. Ray first reported the recovery of varpours of organic solvents by active carbon which involves billions of pounds of solvent each year [14].

Activated carbon from wood and agrowastes

Rao and Rao worked on the preparation of decolorizing carbons from baggasse by the use of chemical as well as physical activation methods [15]. Musser and Engel performed experiments on manufacturing activated carbons of higher adsorptive capacity by steam activation of cotton seed hull bran [16]. Ts'ai and Chuang studied the effect of zinc chloride and hydrochloric acid on the activity of charcoals prepared from coconut shells [17]. Mukherjee and Bhattacharya prepared medicinal charcoal of quite a good activity by chemical activation of coconut and groundnut shells [18]. The same authors also prepared decolorizing carbons from the above raw materials by activation with different inorganic salts [19]. Puri *et al.*, established working parameters for producing activated carbon from different tropical raw materials by activation with phosphoric acid [20]. Saqib *et al.*, developed and patented two processes for the production of activated carbon from fruit shells and coniferous tree wastes [21,22]. Later on Beg *et al.*, got patented a process for producing activated carbon from rice husk [23]. Jain and Sharma studied the effect of concentrations of zinc chloride and phosphoric acid on the properties of charcoals prepared from basmati rice husk [24]. Ettling *et al.*, prepared granular carbon of good activity by zinc chloride activation of whole wheat [25]. Marsh *et al.*, studied the adsorptive properties of chars prepared by carbon dioxide activation of plum stones [26]. Eusuf *et al.*, utilized jute sticks and coconut husks for preparation of activated charcoals by their chemical activation [27]. The same authors also obtained zinc chloride activated chars from cellulose and lignin and had inferred, that the activating agent increased the activity as well as yield of the product [28]. A similar study was also conducted by Samad *et al.*, on saw dust [29]. Dandy produced and characterized activated carbons prepared by physical and chemical activation of different agricultural waste products [30]. Shobaky *et al.*, studied the effect of different metallic chlorides on the properties of charcoals prepared from wood of Eucalyptus tree [31]. Nacco *et al.*, prepared and evaluated activated carbon from yeast by chemical activation method [32]. Gonzalez *et al.*, prepared and characterized active carbons from carbon dioxide activation of olive stones and olive wood [33-35]. Bevia *et al.*, had done comprehensive work on chemical activation and selection of optimum working parameters for preparing activated carbons from almond shells [36,37]. Kirubakaran *et al.*, studied the resultant properties of activated carbon obtained in fluidized as well as static bed reactor [38]. Usmani *et al.*, prepared powdered and granular activated carbons from different agrowastes and inferior woods and evaluated them for their liquid phase characterization [39-47].

Activated carbon from coals

Good quality of hard coals like anthracite and bituminous types have been found to be satisfactory base materials for the preparation of active carbon [48]. Most of the R & D work so far done on the development of process technology for the preparation of active carbon from coals is covered by patent literature [49-51]. Wennerberg *et al.*, prepared active carbon of high surface area from coal by chemical impregnation with potassium hydroxide [52]. Schafer prepared active carbon from brown coal after pretreatment with hydrochloric acid and a potassium salt and subsequent steam activation [53]. Nishino *et al.*, observed that the activity of carbons obtained from coal after cooking with potassium salt and steam activation depends largely upon the grain

size of the precursor and amount of salt [54]. Kwok and Miller suggested a method for preparing chemically activated carbon from petroleum coke by treatment with polyphoshoric acid [55]. Das obtained activated carbon from bituminous coal by preleaching it with hydrofluoric and nitric acid [56]. Tourkow *et al.*, studied the activation of two brown coals by activation with water varpours, carbon dioxide and oxygen [57]. Hari Murty obtained several patents on obtaining granular activated carbon from black lignite [58], low grade fat coal [59], and lignites [60]. Johnson *et al.*, obtained active carbon from sized coal by pretreatment with hydrochloric acid [61]. The same workers also used bituminous and sub-bituminous coals for the preparation of active carbon by steam activation [62]. Robinson obtained active carbon from coal containing $\leq$ 60% ash and $\leq$ 40% volatiles by grinding, agglomerating and steam activation [63]. Repik *et al.*, obtained active carbon by using bituminous coal as source material by activation in a fluidized bed with an oxidizing gas [64]. Yan *et al.*, prepared active carbon by chemical activation of coke with potassium hydroxide [65]. Durie *et al.*, pyrolyzed potassium salts of a brown Australian coal for the preparation of active carbon of high surface area [66]. Lukyanova *et al.*, obtained active carbon by zinc chloride activation of brown coal [67]. Danz *et al.*, used ash rich salt containing brown coal for activated carbon by its physical activation [68]. Hoppe *et al.*, pyrolyzed brown coal with steam or ammonia for preparing active carbon [69]. High quality active carbon was obtained from lignite by Greatzer [70]. Chodynki *et al.*, used hard cola with certain binder for preparation of active carbon [71]. Hoppe *et al.*, prepared active carbon by chemical activation of coke of brown coal with potassium carbonate [72]. Active carbon was also obtained by pulverization and zinc chloride activation of coal by Hsiao *et al.*, [73]. Brown coal was used for obtaining activated carbon capable of adsorbing dyes and colorants by its physical activation [74]. Usmani *et al.*, prepared and characterized powdered activated carbon from a low rank Pakistani coal [75].

Fibrous activated carbon or active carbon filament from different precursors

From mid 1971, much of the R&D efforts done worldwide in the area of adsorbent carbon have been directed towards the development of technology for preparing active carbon fiber or filament. In this connection, different cellulosic as well as polymeric precursors have been investigated. Most of the worked abstracted in scientific literature in this particular field like that of 'coal as raw material' is covered by patents.

Minoru copolymerized acrylonitrile and then oxidized and steam activated it to obtain fibrous activated carbon of high surface area of 1200 m^2/g [76]. The same author also got a patent on using acrylic fibers for active carbon filament by extruding, air oxidizing and steam activating it at 850°C for 40 minutes. The product had tensile strength 1.81g, elongation 15.2% and surface area of 1400 m^2/g [77]. PANAC (fibrous polyacrylonitrile active carbon) was also manufactured by Katsuji *et al.*, by initially air heating the polymeric precursor at 200°C and finally activating at 1000°C in carbon dioxide or steam atmosphere [78]. Active carbon fiber capable of adsorbing various waste gases like sulfur dioxide etc., was prepared by Nobio *et al.*, by chemical impregnation and steam activation of unwoven cloth of Polynosic fiber [79]. A filter cloth capable of adsorbing odour and toxic gases was prepared from viscose cloth by initial chemical treatment with a Lewis acid and further activation with carbon dioxide for 2-3 hours [80]. Rayon felt was used as a precursor for active carbon fibers of benzene adsorption 53% by direct heating in a reactor at 800°C for 60 minutes [81]. Masatoshi *et al.*, obtained fibrous active carbon of high adsorptivity and mechanical strength from acrylonitrile fibers [82]. A brush like adsorbent for waste gas treatment was prepared by Kozo *et al.*, from fibers of acrylonitrile copolymer [83]. Fibrous activated carbon for waste water treatment was prepared by mixing acrylonitrile copolymer with zeolite powder in a certain proportion [84]. Hiroshi, *et al.*, obtained active carbon filament in 32% yield from a cellulosic plant precursor by preheating and chemical activation with zinc chloride or phosphoric acid [85]. The same authors also got a patent on activated carbon filament from plant filament. The product in 46.7% yield had BET surface area of 890 m^2/g [86]. Fibrous activated carbon suitable for gas masks, air conditioners and medical equipment was obtained by chemical as well as physical activation of a cellulose fabric [87]. A filament of surface area 1100 m^2/g and benzene adsorption 40% was also obtained by Shigeru *et al.*, from acrylonitrile precursor [88]. A

Japanese Company also got a patent on fibrous activated carbon from polyacrylonitrile and an oxide [89]. The same company also patented a method for obtaining fibrous activated carbon having fiber strength of 38.2 Kg/mm^2 by copolymerization and steam activation of the acrylonitrile [90]. An apparatus for producing fibers of active carbon was described by Roman *et al.*, [91]. Regenerated cellulose fibers were used for obtaining short fibrous activated carbon having iodine adsorption of 1200 mg/g [92]. Fibrous activated carbon for dechlorination of water upto 67% efficiency was obtained and got patented by a Japanese company [93]. A method for obtaining long filament active carbon fiber was patented by Atrushi *et al.*, [94]. William *et al.*, got a patent on preparing fibrous activated carbon by chemical activation of cellulose fibers [95]. Fibrous activated carbon having strength of 611 Kg/mm^2 was prepared by Juni [96]. Polymeric precursors were used for getting activated carbon fibers after copolymerization and fluidized bed activation [97]. The technology for high strength active carbon fibers was also patented by Hasuo [98]. The preparation, properties and uses of fibrous activated carbon were discussed in detail by Yoshikazi [99]. Bulky spherical activated carbon fiber was prepared by Fumihiro from isotropic pitch fibers [100]. Toshi got a patent on preparing activated carbon fiber for use in filters and deodorants [101]. The preparation and properties of filament active carbon was also studied by Shubao *et al.*, [102]. Minoru *et al.*, [103] got a patent on manufacture of activated spherical carbon fibers from coal tar pitch. The change in microporosity of fibrous activated carbon obtained by steam as well a carbon dioxide activation have been studied [104].

Conclusion

The use of activated carbon in diversified fields in increasing rapidly due to its vital role in combating environmental degradation. Their important applications relate to their use in the removal of colour, odour, taste and other undersirable organic impurities from potable waters, in the treatment of domestic and industrial wastewater, solvent recovery, air purification in inhabited spaces, food processing and chemical industries, in purification of air, chemical, pharmaceutical and food products and in a variety of gas phase applications. The uses of activated carbons in hydromettalurgy, in medicines for combating certain types of bacterial ailments, catalyst support and in modern chemical warfare have also been explored. Therefore activated carbons have a pivotal role to play in future industry, medicine and protection fields.

References

1. H. Juntgen, *Carbon*, **15**, 273 (1977).
2. R.C. Bansal, T.P. Donnet and F.H. Stoeckli, 'Active Carbon' (Marcel Dekker Inc., N.Y., 1988).
3. Sato Euchi, U.S. Patent 4, 616, 001, June (1985).
4. J.R. Partington, 'Origin and Development of Applied Chemistry, Longmans, Green Co., London (1935).
5. V.R. Deitz, 'Bibliography of Solid Adsorbents', United States Cane Sugar Refiners and National Bureau of Srtandards, Washington, D.C., (1944).
6. Lowitz, Crell's *Chem. Ann.*, **1**, 211 (1786).
7. A. Bussy, *J. Pharm. Sci. Accessories*, **8**, 257 (1822).
8. J. Hunter, *J. Chem. Soc.*, **18**, 285 (1865).
9. J. Stenhouse, British Patent 1395 (1856).
10. T.V. Lee, British Patent 528 (1863).
11. F. Lipscomb, British Patent 2887 (1862).
12. R. Von Ostrejko, British Patents 14224 (1900), 18040 (1900), German Patent 136, 792 (1901).
13. G.R. Spalding, *J. Am. Water Works Assoc.*, **22**, 646 (1930).
14. A.B. Ray, *Ind. Eng. Chem.*, **39**, 12 (1947).
15. A.N. Rao and S.N.G. Rao, *J. Indian Chem. Soc., Ind. and News Ed.*, **2**, 161 (1939).
16. D.M. Musser and H.C. Engel, *Ind. Eng. Chem.*, **32**, 1636 (1940).
17. L.S. Ts'ai and K.Y. Chuang, *Ind. Eng. Chem.*, **34**, 7, 812 (1942).
18. S. Mukherjee and S. Bhattacharya, *J. Sci. & Ind. Res.*, **4**, 235 (1945-46).
19. S. Mukherjee and S. Bhttacharya, *J. Am. Chem. Soc.*, **71**, 1725 (1949).
20. B.R. Puri, M.L. Lakhanpal and P.C. Gupta, *J. Ind. Chem. Soc., Ind. and News Ed.*, **17**, 1, 35 (1954).
21. Saqib Ahmad, m. Alauddin, S.A. Khan and A.H. Khan, Pak. Patent 118, 187, April 3, (1967).

22. Saqib Ahmed, M. Alauddin, S.A. Khan and A.H. Khan, Pak. Patent 118, 569, April 3, (1967).
23. M.A.A. Beg and Samiuzzaman, Pak. Patent 125, 583, July 26 (1975).
24. K.D. Jain and M.K. Sharma, *J. Ind. Chem. Soc.*, **48**, 12, 1155 (1971).
25. B.V. Ettling, M.F. Adam and D.J. Schecter, *Ind. Eng. Chem., Prod. Res. Develop.*, **11**, 4, 461 (1972).
26. H. Marsh, M. Iley, I. Berger and T. Siemieniewska, *Carbon*, **13**, 103 (1975).
27. M. Eusuf, A.M. Hasan, R. Khan, M.S. Haque and T.A. Bhuiyan, *BJSIR*, **12**, (3-4), 171 (1977).
28. M. Eusuf, A.M. Hasan, R. Khan and M.S. Haque, *BJSIR*, **12** (3-4), 180 (1977).
29. S.A. Samad, M. Rehman and M.N. Hasan, *BJSIR*, **12**(3-4), 224 (1977).
30. A.J. Dandy, *Newzeland J. Sci.*, **20**, 291 (1977).
31. G.A. El-Shobaky and A.M. Youseef, *Surface Technology*, **7**, 209 (1978).
32. R. Nacco and E. Aquarone, *Carbon*, **16**, 31 (1978).
33. J. De D. Lopez - Gonzalez, F.M. Vilchez and F.R. Reinoso, *Carbon*, **18**, 413 (1980).
34. J. De D. Lopez-Gonzalez, C.V. Calahorro, A.N. Guijosa and V.G. Serrano, *Adsorp. Sci. and Tech.*, **2**, 263 (1985).
35. J. De D. Lopez - Gonzaloz, C.V. Calahorro, A.N. Guijosa and V.G. Serrano, *Adsorp. Sci. & Tech.*, **3**, 41 (1986).
36. F.R. Bevia, D.P. Rico and A.F.M. Gomis., *Ind. Eng. Chem., Prod. Res. Dev.*, **23**, 266 (1984).
37. F.R. Bevia, D.P. Rico and A.F.M. Gomis, *Ind. Eng. Chem., Prod. Res. Dev.*, **23**, 269 (1984).
38. C.J. Kirubakaran, K. Krishnaiah and S.K. Seshadri, *Ind. Eng. Chem. Res.*, **30**, 2411 (1991).
39. M.A.A. Beg and T.H. Usmani, *Pak. J. Sci. Ind. Res.*, 28(4), 282 (1985).
40. T.H. Usmani, T.W. Ahmed and S.Z. Ahmad, *Pak. J. Sci. Ind. Res.*, **31**(3) 221 (1988).
41. T.H. Usmani, T.W. Ahmd and S.Z. Ahmed, *Pak. J. Sci. Ind. Res.*, **32**(4) 282 (1989).
42. T.W. Ahmed, T.H. Usmani and S.Z. Ahmed, *Pak. J. Sci. Ind. Res.*, **33**(4) 177 (1990).
43. T.W. Ahmed, T.H. Usmani and M. Mumtaz, *Pak. J. Sci. Ind. Res.*, **34**(4), 121 (1991).
44. T.H. Usmani, T.W. hmed, S.Z. Ahmed and A.H. Yousufzai, *Pak. J. Sci. Ind. Res.*, **36**(6-7) 236 (1993).
45. T.H. Usmani, T.W. Ahmed, S.Z. Ahmed and A.H.K. Yousufzai, *Pak. J. Sci. Ind. Res.*, **36**(6-7), 240 (1993).
46. T.H. Usmani, T.W. Ahmed and A.H.K. Yousufzai, *Bioresource Technology*, **48**(1), 31 (1994).
47. T.H. Usmani, T.W. Ahmed, M. Mumtaz, M. Tahir Motan and A.H.K. Yousufzai, *Pak. J. Sci. Ind. Res.*, **37**(9), 371 (1994).
48. J.J. Morgen and C.E. Fink, *Ind. Eng. Chem.*, **38**, 219 (1946).
49. A. Godel, *Chimie et industrie*, **29**, 3 (1933), **59**, 437 (1948).
50. A.C. Fieldner, R.E. Hall and A.E. Golaway, *Bur. Mines. Tech. Paper*, 479 (1930).
51. A.E. Williams, *J. Mining (London)*, **227**, 1026 (1946).
52. A.N. Wennerberg and T.M. O'Grady, U.S. Patent 4, 082, 694, Apr. 4, (1978).
53. H.N.S. Schafer, U.S. Patent 4, 039, 473 Aug. 2, (1977).
54. H. Nishino, H. Kubo and H. Ichukawa, U.S. Patent 2, 764, 561, Oct. 9, (1973).
55. J. Kwok and A. Miller, U.S. Patent 2, 767, 592, Oct. 23 (1973).
56. S.K. Das, U.S. Patent 4, 083, 801, April. 11, (1978).
57. K. Tourkow, T. Siemieniewska, F. Czeckowskai and A. Gankowska, *Fuel*, **56**, 121 (1977).
58. N. Hari Murty, *Ger. Offen.*, **2**, 621, 530, 16 May (1975).
59. N. Hari Murty, *Ger. Offen.*, **2**, 625, 625, 23 Dec., (1976).
60. N. Hari Murty *Ger. Offen.*, **2**, 624, 779, 16 Dec., (1976).
61. B.C. Johnson, R.K. Sinha and J.E. Urbanic, U.S. Patent 4, 014, 817 Mar., (1977).
62. B.C. Johnson, R.K. Sinha and J.E. Urbanic, Belg., 839, 918, 16 July, (1977).
63. M. Robinson, D.B. Mobbs and K. Talati, *Ger. Offen.*, **2**, 644, 520, 14 April, (1977).
64. J.A. Repik and C.E. Miller, U.S. Patent 4, 107, 084, Aug., (1978).
65. S. Yan and H. Marsh, *Carbon*, **14**, 20 (1979).
66. A.R. Durie, A. Schafer and N..S. Harry, *Fuel*, **58**(6), 412 (1979).