

Flexible adsorptive fiber from activated carbon powder

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ABSTRACT

Flexible adsorptive polymeric fiber was prepared from a mixture of activated carbon powder, paraffin wax and polypropylene. Activated carbon powder was first coated with paraffin wax. The optimum amount of wax was found to be about 23% by weight of activated carbon. The activated carbon-wax mixture was then mixed with polypropylene with the ratio of PP:activated carbon of 87:13 by weight. The best method to produce adsorptive fiber is, first, to melt-spin the mixture into continuous fiber. Then this as-spun fiber is drawn to the highest possible draw ratio in order to give it adequate strength for further processing. Finally the paraffin wax is extracted with hexane. The performance of the fibers prepared in this way was evaluated from methylene blue adsorption capacity. After extraction the fiber could adsorb more methylene blue than before. Drawing also enhanced the adsorption capacity. The adsorption capacity of the activated carbon in the drawn and extracted fiber is approximately 97% that of the starting activated carbon powder. The adsorptive fiber displays mechanical strength that is high enough for further processing in general textile machineries.

Keywords: activated carbon, adsorptive fiber, methylene blue adsorption

INTRODUCTION

Activated carbon (AC) is a high-porosity and high surface area material which is useful in adsorption of both solutes from solution and gases. It has long been widely used for the recovery of solvents, the separation of gases, the removal of organic pollutants from drinking water and as a catalyst support. As environmental pollution is becoming a more serious problem, the need for AC is growing. AC can be produced from various raw materials such as sugarcane bagasse (Bernard *et al.*, 1997), natural cellulose (Phan *et al.*, 2006), waste tires (Ariyadejwanicha *et al.*, 2003), coal (Sun *et al.*, 1997), wood (Mukherjee *et al.*, 2007; Barkauskas *et al.*, 2004), post consumer plastic (Marzec *et al.*, 1999) and so on. It has many forms such as powder, granular and extruded. One of the main drawbacks of these forms is that it must be held in some kind of containing materials. Recently activated carbon fiber (ACF) has been developed and considered to be the substitute of conventional AC due to its higher sorption characteristics, as well as very high rates of adsorption, plentiful micropores, and high surface area in comparison to the granular form (Zhu *et al.*, 2009; Li and Zhang, 2009; Bui *et al.*, 2009; Zhang *et al.*, 2009). The production of ACF is

similar to conventional AC except that the starting material has to be in fiber form. ACF can be used in various forms such as fabric, filler and felt in different applications. Nevertheless, the drawbacks of ACF are the complication of the manufacturing process and the brittleness of the fiber. Since there are plentiful AC granules or powders on the market, it would be very useful if the powder could be incorporated into a flexible polymeric fiber. This AC containing polymeric fiber would provide much easier handling than conventional AC and thus widen its utilization. The purpose of this work is to present a method to prepare such adsorptive fiber.

For AC to be adsorptive, its porous structure has to be accessible. If AC powder is incorporated directly into a polymeric matrix these pores would just be blocked and it would be rendered inactive. To preserve these accesses, a special concept as shown in Figure 1 is needed. A protective coating must be applied to the AC powder before it is incorporated into the polymeric carrier. This protective coating will then be extracted out with an appropriate solvent in order to provide accessible path to the pores. In addition, the amount of AC powder has to be high enough so that a solvent percolation path is formed throughout. To our knowledge, there is only one patent literature (Lopatin *et al.*, 1997) that discloses a similar concept. However, very limited detail was presented regarding the effect of various parameters on the performance of the adsorptive fiber. In this research the effects of the drawing process and of the protective coating extraction on the adsorption capacity of the fiber were investigated. In addition, mechanical properties and morphology of the fibers were also studied.

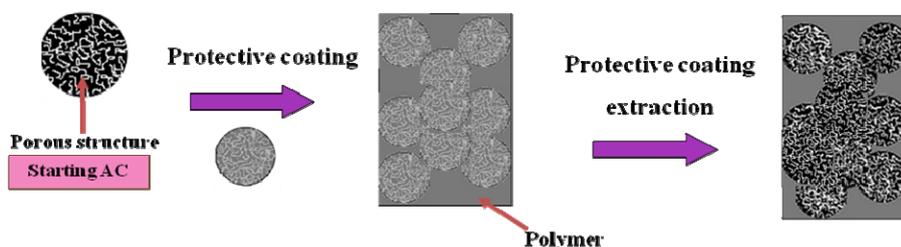


Figure 1 A concept to produce adsorptive fiber from mixture of activated carbon (AC) and polymeric matrix.

EXPERIMENTAL

Materials

Polypropylene (PP) was commercially available HP400H manufactured by HMC Polymers (Rayong, Thailand) in the form of pellets. AC was water purification grade (Coconut shell based, steam activated, Mazuma (Thailand) Co. Ltd., Bangkok, Thailand). AC was ball-milled to particle size of about 8-15 μm . Paraffin wax (PE Wax H109) was purchased from SQI group Co. Ltd. (Bangkok, Thailand), and used as protective coating. Hexane was used as a solvent to extract paraffin wax.

Preparation of adsorptive PP fiber

Mixtures containing different amounts of PP, paraffin wax and AC powder were prepared using a small scale laboratory mixer (Haake Rheocord 90, Thermo Electron Corporation; Waltham, MA, USA). The ratio of PP:AC was fixed at 87:13 by weight. The amount of paraffin wax was based on that of AC and varied from 0-32% by weight.

AC powder was first added to the mixer set at 180 °C. Then the paraffin wax was added and mixing continued for 10 min. Afterwards, the PP was slowly added, and the mixing continued until uniform. The mixture was taken out and allowed to cool. It is transformed into fiber by extrusion using a Randcastle monofilament line (Randcastle Extrusion Systems, Inc., Cedar Grove, NJ, USA). There were three heating zones along the barrel of the single screw extruder and one at the die exit. The temperatures were set at 130, 190, 195 and 215 °C for zones 1, 2, 3 and die, respectively. Screw speed was 3 rpm. The as-spun fiber was air-cooled and then hot drawn in a glycerol bath set at 145 °C to different draw ratios (DR) with two sets of rollers running at different speeds. DR is defined as the ratio of the final length of the fiber to the starting length and can be simply calculated from the ratio of the speed of the fast rollers to the slow rollers. Fiber with a draw ratio of X will be coded as DR- X fiber. Finally, the fiber was extracted with hexane and dried under vacuum.

Methylene blue adsorption capacity

Methylene blue (MB) was chosen as adsorbate to test the adsorption capability of the AC. MB stock solution was prepared by dissolving accurately weighed MB in distilled water to a concentration of 50 ppm. The experimental solution was obtained by diluting the MB stock solution. Adsorption of MB on AC was carried out using batch experiment methods. 50 ml of MB solution was added into Erlenmeyer flasks containing fiber sample and stirred at room temperature until equilibrium was obtained. Then, the concentrations of the MB solution were determined spectrophotometrically using a UV-Vis spectrophotometer at a wavelength of 610 nm (Lambda 35, Perkin Elmer, Shelton, CT, USA). MB adsorption capacity is evaluated based on the weight of AC in the fiber since it is AC that is capable of adsorbing.

Tensile properties measurement

Tensile properties of the drawn fibers were measured by tensile testing machine Instron 5569 (Instron, High Wycombe, England) at room temperature. The sample gauge length was 10 cm and the cross head speed was 5 cm/min. For each samples, ten specimens were measured and the averaged values were reported.

Scanning electron microscopy (SEM)

SEM images of fibers for morphological studies were obtained using a Hitachi S-2500 electron microscope (Hitachi, Tokyo, Japan) operating at an

accelerating voltage of 15 kV. The fibers were sputtered coated with gold to ensure good electrical conductivity. In order to examine the fiber internal structure, the fiber was embedded in thermoplastic rubber and the surface was removed using a microtome. Internal structures both before and after solvent extraction were examined.

RESULTS AND DISCUSSION

Effect of paraffin wax

First, it is important to demonstrate the necessity of using a paraffin wax protective coating for AC powder in the fiber to remain adsorptive. Figure 2 shows MB adsorption capacity for unextracted as-spun fiber, extracted as-spun fiber, drawn fiber and AC powder. It can be seen that AC powder displays the highest MB adsorption capacity. On the other hand, unextracted as-spun fiber displays a negligibly small MB adsorption capacity. After extraction, the MB adsorption capacity of the fiber increases significantly to about 45% that of the starting AC powder.

Since as-spun PP-AC fiber was relatively thick and not so strong, attempts were made to increase its strength by drawing the fiber to increase molecular orientation of the PP matrix. It is seen, as shown in Figure 2, that drawing of the fiber (even to DR of only 5) could also enhance the MB adsorption capacity further to about 55% that of the starting AC powder. This shows that the extraction process could remove the paraffin wax protective coating and clear the paths to pores of AC powder. The fact that the MB adsorption capacity for AC in the fiber is only about half that of the starting AC powder would suggest that either pores of the powder are still blocked or particles are isolated and not extracted and, therefore, inaccessible for the adsorbate molecules. Drawing improves the process by causing separation, thus creating voids between AC particles and polymer matrix and increase percolation path for the solvent. The occurrence of voids in drawn or deformed polymer containing particulate fillers are not unexpected (Kausch *et al.*, 2000; Kwon *et al.*, 2002; Wang *et al.*, 2002; Parsons *et al.*, 2005). The optimum amount of paraffin wax and draw ratio were determined in the following sections.

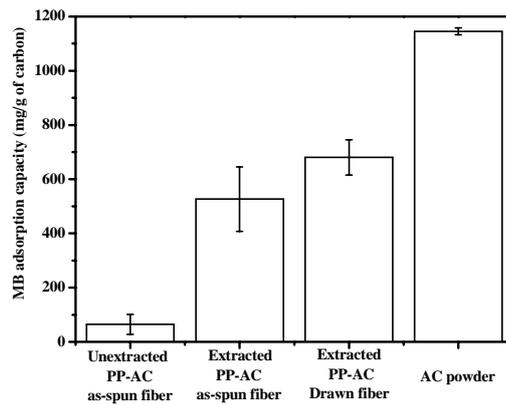


Figure 2 Methylene blue (MB) adsorption capacity (mg/g of carbon) of unextracted as-spun fiber, extracted as-spun fiber and extracted drawn fiber (with a draw ratio of 5) and starting AC powder.

In order to visually observe the effect of paraffin wax extraction and drawing, the surfaces of the fibers and the internal structure of the fiber before and after the extraction were examined with scanning electron microscope. The surfaces of as-spun and drawn fibers and internal structure of the drawn fiber are displayed in Figures 3-5, respectively. For as-spun fiber, the extraction did not appear to change the surface of the fiber significantly (Figure 3). AC particles are seen slightly clearer for the extracted fiber. For drawn fiber (Figure 4), much rougher surface with many longitudinal grooves and AC particles are clearly seen after extraction indicating that the soluble paraffin wax must have been removed. Similar changes are also observed for the internal structures of drawn fiber as shown in Figure 5. No AC particles were observed before extraction. On the other hand, AC particles are seen distributed over the surface after extraction. These observations confirmed the effect of paraffin wax extraction on the MB adsorption capacity.

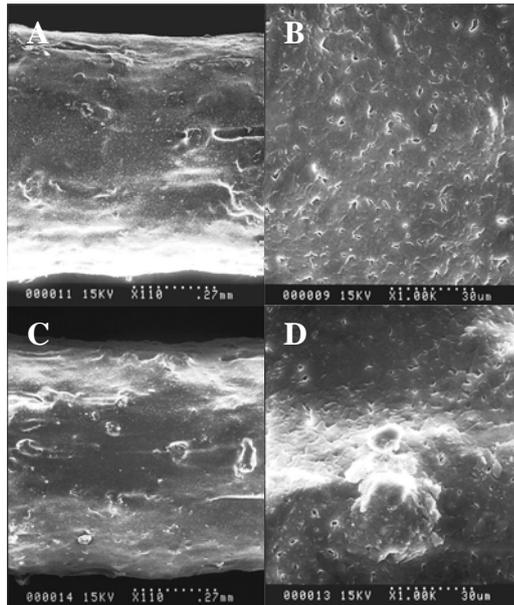


Figure 3 Scanning electron micrographs at two levels of magnification (X100 and X1000 times) of surfaces of as-spun fibers before (A and B) and after (C and D) paraffin wax extraction.

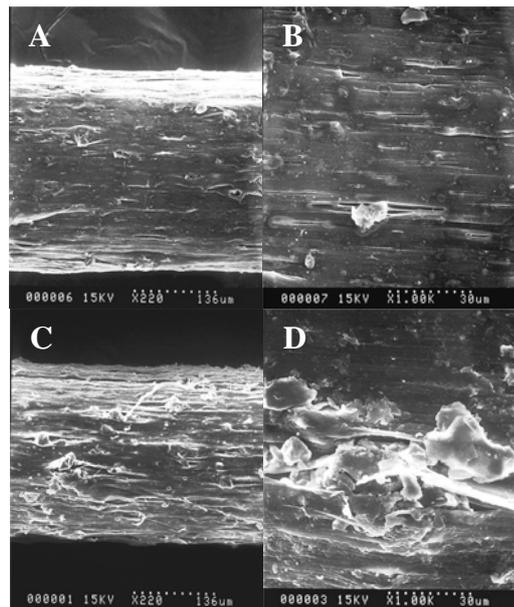


Figure 4 Scanning electron micrographs at two levels of magnification (X100 and X1000 times) of surfaces of drawn fibers (draw ratio of 5) before (A and B) and after (C and D) paraffin wax extraction.

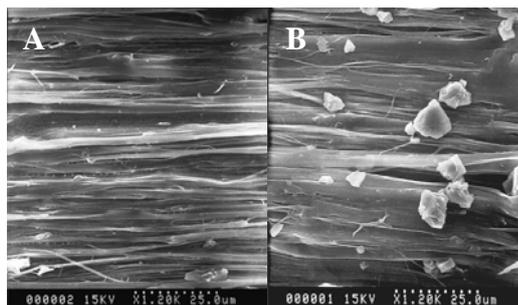


Figure 5 Scanning electron micrographs of internal structure of fibers drawn to a draw ratio of 5 before (A) and after (B) paraffin wax extraction.

Effect of paraffin wax loading

From the previous section, it is shown that it is important to have paraffin wax protective coating. It is conceivable that there should be an optimum amount of paraffin wax which just enough for all AC particles to be covered. At too low the amount, some particles would not be covered and the polymer matrix will block the pores. Since the paraffin wax is required to coat the AC powder, the amount of it will be based on the amount of AC powder. Figure 6 displays the effect of the amount of paraffin wax on the MB adsorption capacity of extracted drawn fibers. All fibers were drawn to the draw ratio of 10. When no paraffin wax was added (PP-AC), the fiber displays about 310 mg of MB per g of AC. This value is larger than expected as compared with the unextracted as-spun fiber (64 mg of MB per g of AC) shown in Figure 2. The increase may be explained by voiding in the system caused by drawing as mentioned in the previous section. These voids would certainly increase the percolation path for the extraction solvent.

When paraffin wax loading was increased, the MB adsorption capacity increased significantly and then peaked at about 23 wt%. At this point, the MB adsorption capacity was about 954.4 mg of MB per g of AC which is about 84% of starting AC powder under the same condition. This MB adsorption capacity is equal to 123.6 mg MB per g of fiber. This value is considered rather high when compared with that reported for granular form which are less than 70 mg per g of material but still low when compared with that of ACF (Yamashita *et al.*, 2001; Weng *et al.*, 2009).

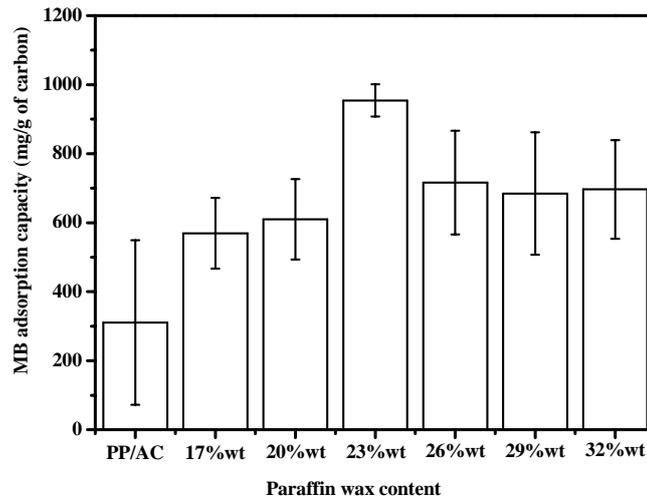


Figure 6 MB adsorption capacity (mg/g of carbon) of extracted PP-AC fibers containing different amount of paraffin wax and drawn to a draw ratio of 10.

Effect of drawing

It has been shown above that drawing can influence the MB adsorption capacity. In this section, the effect of drawing was investigated in more details. For this set of data, the amount of paraffin wax was fixed at 23 wt% (of AC) and the draw ratio was varied. First, the amount of extracted paraffin wax was studied for fibers drawn to draw ratios of 5, 7, 10 and 15. The results are shown in Figure 7. It can be seen that the as-spun fiber displayed the lowest amount of extracted wax and when the fiber was drawn, the amount of extracted wax increased and then level off at around 80%. This suggests that the maximum amount of extracted wax is about 80% of the amount loaded into the system. The MB adsorption capacity for these fibers is shown in Figure 6. Slightly different trend is seen that is the as-spun fiber displayed the lowest MB adsorption capacity. However, when the fiber was drawn, the MB adsorption capacity increased with increasing draw ratio. The MB adsorption capacity of DR-10 drawn fiber is about twice that of the as-spun fiber. At draw ratio of 15, the adsorption capacity increases further and is now about 97% that of the starting AC powder. The MB adsorption capacity is now increased to 142.7 mg per g of fiber, more than double that of AC in granular form (Yamashita *et al.*, 2001; Weng *et al.*, 2009). The results also suggest that although the amount of extracted wax had reached the highest value but drawing could still improve the MB adsorption capacity of the fiber. This could be attributed to the development of more and, possibly, elongated and interconnected voids within the fiber during drawing and therefore opening more access to the pores of AC particles.

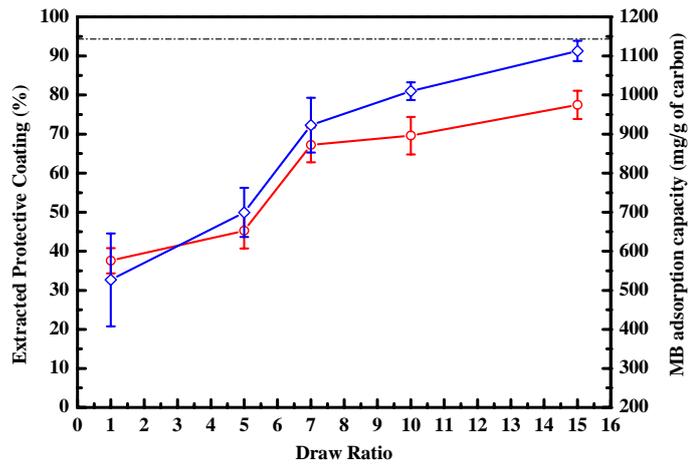


Figure 7 Percentage of extracted paraffin wax (○) from PP-AC fibers of different draw ratios and their corresponding MB adsorption capacity (◇). The dotted line represents the MB adsorption capacity of the starting AC powder included for easy comparison.

Mechanical properties

For the fiber to be processed into different products, its mechanical properties should be high enough. Table 1 displays tensile strength of fibers different paraffin wax loadings and draw ratios. Properties of PP fibers are included for comparison. It can be seen that adding AC and wax causing the strength to drop. Drawing could improve the strength of the fiber and the difference became smaller. The strength at draw ratio of 5 is considered high enough for further processing into different products by conventional textile method. It should be noted that stronger fiber could be obtained by using much finer AC powder and also by adjusting the ratio of paraffin wax. However, this is beyond that scope of this research in which only the concept is illustrated.

Table 1 Tensile strength of the adsorptive PP-AC fibers of different compositions and draw ratios. (PP = Polypropylene, AC = Activated Carbon, Paraffin wax = W).

Materials	Strength (MPa)		
	DR-7	DR-10	DR-15
PP	404.7±15.3	575.5±44.3	610.8±36.2
PP-AC	165.1±12.9	254.7±23.2	-
PP-AC + 17%W	169.1±38.5	212.2±23.1	-
PP-AC + 20%W	175.9±28.9	234.4±26.2	-
PP-AC + 23%W	152.7±16.2	254.7±20.6	-
PP-AC + 26%W	142.8±27.6	250.9±41.5	-
PP-AC + 29%W	154.7± 5.4	282.9±15.8	467.4±47.1
PP-AC + 32%W	197.2±30.5	314.9±67.9	594.8±94.7

CONCLUSIONS

Adsorptive PP fiber containing AC powder was successfully prepared. The fiber can be prepared by melt-spinning of PP-AC-paraffin wax mixture into continuous fiber followed by paraffin wax extraction. The extraction is necessary for clearing pathways into pores of AC particles for adsorption. Drawing could improve the MB adsorption capacity. The adsorptive fibers have enough, although lower than PP fiber, strength for further processing into products.

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REFERENCES

- Ariyadejwanicha, P., Tanthapanichakoon, W., Nakagawab, K., Mukai, SR. and Tamon, H. (2003). Preparation and characterization of mesoporous activated carbon from waste tires. *Carbon*, *41*, 157–164.
- Bernard, EC., Egashira, R. and Kawasaki, J. (1997). Decolorization of molasses wastewater using activated carbon prepared from cane bagasse. *Carbon*, *35*, 1217-1221.
- Barkauskas, J., Tautkus, S., and Kareiva, A. (2004). Residual content of inorganic ions in activated carbons prepared from wood. *J. Anal. Appl. Pyrolysis*, *71*, 201–212.
- Bui, NN., Kim BH, Yang KS, Dela Cruz ME and Ferraris JP. (2009). Activated carbon fibers from electrospinning of polyacrylonitrile/pitch blends. *Carbon*, *47*, 2538-2539.
- Kausch HH, Beguelin Ph and Fischer M. (2000). Failure of Particulate Reinforced Polymers. *Mech Compos Mater*, *36*, 177-184.
- Kwon S, Kim KJ, Kim H, Kundu PP, Kim TJ, Lee YK, Lee BH and Choe S. (2002). Tensile property and interfacial dewetting in the calcite filled HDPE, LDPE, and LLDPE composites. *Polymer*, *43*, 6901-6909.
- Li Q, Zhang W. (2009). Study on PAN-based activated carbon fiber prepared by different activation methods, in Power and Energy Engineering Conference, APPEEC 2009. *Asia-Pacific* 27-31 March 2009: 1-4.
- Lopatin G, Coplan MJ, Walton JP, US Patent 4342811 (1979).
- Marzec M, Tryba B, Kaleńczuk RJ and Morawski Aw. (1999). Poly(ethylene terephthalate) as a source for activated carbon. *Polym Adv Technol*, *10*, 588-595.
- Mukherjee S, Kumar S, Misra AK and Fan M. (2007). Removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal. *Chem Eng J*, *129*, 133–142.
- Parsons EM, Boyce MC, Parks DM and Weinberg M. (2005). Three-dimensional large-strain tensile deformation of neat and calcium carbonate-filled high-density polyethylene. *Polymer*, *46*, 2257-2265.
- Phan NH, Rio S, Faur C, Le Coq L, Le Cloirec P and Nguyen TH. (2006). Production of fibrous activated carbons from natural cellulose (jute, coconut) fibers for water treatment applications. *Carbon*, *44*, 2569-2577.
- Sun J, Hippo EJ, Marsh H, O'Brien WS and Crelling JC. (1997). Activated carbon produced from an illinois basin coal. *Carbon*, *35*, 341-352.
- Wang KH, Chung IJ, Jang MC, Keum JK and Song HH. (2002). Deformation Behavior of Polyethylene/Silicate Nanocomposites As Studied by Real-Time Wide-Angle X-ray Scattering. *Macromolecules*, *35*, 5529-5535.
- Weng CH, Lin YT and Tzeng TW. (2009). Removal of methylene blue from aqueous solution by adsorption onto pineapple leaf powder. *J Haz Mat*, *170*, 417-424.
- Yamashita J, Shioya M, Kikutani T and Hashimoto T. (2001) Activated carbon fibers and films derived from poly(vinylidene fluoride). *Carbon*, *39*, 207–214.
- Zhang S, Zhang Q, Chen S, Yuan Q and Li P. (2009). Irradiation-induced grafting of acrylonitrile onto activated carbon fiber. *Polym Adv Technol*, *120*, 1168-1173
- Zhu Y, Zuo T, Jiang L, Cai Z, Yan C, Liu X, Malcolm X and Wu Q. (2009). Pore structure analysis on activated carbon fibers—By cluster and watershed transform method. *Appl Surf Sci*, *256*, 587–592.