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## Waste biomass as sources for activated carbon production-A review

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### Abstract

A review of the production of activated carbons from waste biomass has been presented. The effects of various process parameters on the pyrolysis stage have been reviewed. Influences of activating conditions, physical and chemical, on the active carbon properties have been discussed. Under certain process conditions several active carbons with BET surface areas, ranging between 250 and 2410 m<sup>2</sup>/g and pore volumes of 0.022 and 91.4 cm<sup>3</sup>/g, have been produced. A comparison in characteristics and uses of activated carbons from waste biomass with those of commercial carbons has been made. Waste biomass being highly efficient, low cost and renewable sources of activated carbon production.

**Keywords:** Activated carbons; Waste biomass; Pyrolysis; Renewable sources

### Introduction

Thermo-chemical processes such as pyrolysis or gasification have been widely applied to biomass gain due to its energy content. Pyrolysis is one form of energy recovery processes, which has the potential to generate char, oil and gas product (Putun *et al.*, 2005). Because of the thermal treatment, which removes the moisture and the volatile matters of the biomass, the remaining solid char shows different properties than the parent biomass materials. The remarkable differences are mainly in porosity, surface area, pore structures (micropores, mesopores and macropores) and physicochemical properties such as composition, elemental analysis and ash content (Haykiri-Acma *et al.*, 2005). These changes in the properties usually lead to high reactivity, and hence, an alternative usage of char as an adsorbent material becomes possible (Putun *et al.*, 2005). Thus, the char becomes an attractive by-product, with applications including production of activated carbons (ACs), which is useful as a sorbent for air pollution control as well as for wastewater treatment (Fan *et al.*, 2004). ACs are carbons of highly microporous form with both high internal surface area and porosity, and commercially the most common adsorbents used for the removal of organic compounds from air and water streams. They also often serve as catalysts and catalyst supports.

The process parameters, which have the largest influence on the products of pyrolysis, are the particle size, temperature and heating rate. The process conditions can be optimized to

maximize the production of the pyrolytic char, oil or gas, all of which have potential uses as fuels. Any cheap material, with a high carbon content and low inorganics, can be used as a raw material for the production of AC (Tsai *et al.*, 1997); agricultural by-products have proved to be promising raw materials for the production of ACs because of their availability at a low price. They can be used for the production of AC with a high adsorption capacity, considerable mechanical strength, and low ash content (Savova *et al.*, 2001). Literature survey indicates that there have been many attempts to obtain low-cost AC or adsorbent from agricultural wastes such as *wheat* (Lanzetta and Di Blasi, 1998), *corn straw* (Lanzetta and Di Blasi, 1998), *olive stones* (Minkova *et al.*, 2001) and (Minkova *et al.*, 2000), *bagasse* (Minkova *et al.*, 2001) and (Minkova *et al.*, 2000), *birch wood* (Minkova *et al.*, 2001) and (Minkova *et al.*, 2000), *miscanthus* (Minkova *et al.*, 2001) and (Minkova *et al.*, 2000), *sunflower shell*, *pinecone*, *rapeseed* (Haykiri-Acma *et al.*, 2005) and (Predel and Kaminsky, 1998), *cotton residues*, *olive residues* (Haykiri-Acma *et al.*, 2005), *pine raved*, *eucalyptus maculata*, *sugar cane bagasse* (Cetin *et al.*, 2004) and (Ahmedna *et al.*, 2000), *almond shells* (Savova *et al.*, 2001), (Aygun *et al.*, 2003) and (Marcilla *et al.*, 2000), *peach stones* (Tsai *et al.*, 1997), *grape seeds* (Savova *et al.*, 2001), *straw* (Minkova *et al.*, 2001), (Minkova *et al.*, 2000) and (Jensen *et al.*, 2001), *oat hulls* (Fan *et al.*, 2004) and (Zhang *et al.*, 2004), *corn stover* (Fan *et al.*, 2004) and (Zhang *et al.*, 2004), *apricot stones* (Savova *et al.*, 2001) and (Aygun *et al.*, 2003), *corn stalk* (Putun *et al.*, 2005), *cherry stones* (Savova *et al.*,

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2001), *peanut hull* (Girgis *et al.*, 2002), *nut shells* (Savova *et al.*, 2001), (Lua *et al.*, 2004), (Ahmadroup and Do, 1997), (Yang and Lua, 2003) and (Ahmedna *et al.*, 2004), *rice hulls* (Ahmedna *et al.*, 2000), *corn cob* (Tsai *et al.* 1997), (Tsai *et al.*, 1998), (Tsai *et al.*, 2001) and (El-Hendawy *et al.*, 2001), *corn hulls* (Zhang *et al.*, 2004), *hazelnut shells* (Aygün *et al.*, 2003), *pecan shells* (Ahmedna *et al.*, 2000), *bamboo waste* (Mahanim *et al.*, 2011), *rice husks* (Malik, 2003) and (Yalcin and Sevinc, 2000) and *rice straw* (Ahmedna *et al.*, 2000) and (Oh and Park, 2002). The purpose of the present review is the evaluation of the experimental data that were determined for various types of residues, reported in the literature. Given that solid devolatilization is always a fundamental step, Thermo gravimetric analysis (TGA) technique has been applied in several cases. Bangladesh has enormous amount of biomass resources, but not much scientific research has yet been done to produce activated carbon from the substance. The literature review on activated carbon production will therefore, be useful for the development of research of activated carbon and its applications in Bangladesh.

#### Experimental conditions for carbon production from waste biomass

##### Pyrolysis

Waste biomass are produced in huge amounts worldwide, their proximate and ultimate analysis are presented in Table I, while Table II presents some carbonization and activation

conditions for the production of the ACs from waste biomass.

Corn stover with oat hulls for activated carbon production by TGA was studied (Fan *et al.*, 2004). There was no pre-treatment prior to fast pyrolysis that was held in a nitrogen fluidized bed reactor at a typical biomass feed of 7 kg/h. Zhang *et al.*, (2004) studied oak wood wastes, corn hulls and corn stover carbonization in a fluidized bed reactor at 500 °C. In the study of Haykiri-Acma *et al.* 2005, TGA was used to pyrolyse and then gasifies chars obtained from sunflower shell, pinecone, rapeseed, cotton and olive residues pyrolysis. The chars obtained were heated in order to gasify under steam and nitrogen atmosphere and in equal volumetric ratio. For pinus radiata, eucalyptus maculate and sugar cane bagasse, atmospheric reactivity measurements were performed under isothermal conditions, using a thermogravimetric analyser (Cetin *et al.*, 2004). The heat up was carried out at a nominal heating rate of 40 °C min<sup>-1</sup>. Sugarcane bagasse, rice hulls, rice straw, and pecan shells were also studied (Ahmedna *et al.*, 2000), in an atmosphere of nitrogen gas at 750 °C using an inert atmosphere furnace with retort. Chars were activated until approximately 30% burn-off was achieved.

Pyrolysis temperature has the most significant effect followed by pyrolysis heating rate, the nitrogen flow rate and

**Table I. Waste biomass availability, proximate and ultimate analysis (Skoulou and Zabaniotou, 2007)**

Agricultural wastes	Moisture, % (w/w)	Ash, % (w/w)	Volatiles, % (w/w)	C, % (w/w)	H, % (w/w)	O, % (w/w)	N, % (w/w)	S, % (w/w)	HHV, kcal/kg
Olive tree prunings	7.1	4.75	-	49.9	6	43.4	0.7		4500
Cotton stalks	6	13.3	-	41.23	5.03	34	2.63	0	3772
Durum wheat straw	40	-	-	-	-	-	-	-	4278
Corn stalks	0	6.4	-	45.53	6.15	41.11	0.78	0.13	4253
Soft wheat straw	15	13.7	69.8	-	-	-	-	-	4278
Vineyard prunings	40	3.8	-	47.6	5.6	41.1	1.8	0.08	4011
Corn cobs	7.1	5.34	-	46.3	5.6	42.19	0.57	0	4300
Sugar beet leaves	75	4.8	-	44.5	5.9	42.8	1.84	0.13	4230
Barley straw	15	4.9	-	46.8	5.53	41.9	0.41	0.06	4489
Rice straw	25	13.4	69.3	41.8	4.63	36.6	0.7	0.08	2900
Peach tree prunings	40	1	79.1	53	5.9	39.1	0.32	0.05	4500
Almond tree prunings	40	n.a	-	-	-	-	-	-	4398
Oats straw	15	4.9	-	46	5.91	43.5	1.13	0.015	4321
Sunflower straw	40	3	-	52.9	6.58	35.9	1.38	0.15	4971
Cherry tree prunings	40	1	84.2	-	-	-	-	-	5198
Apricot tree prunings	40	0.2	80.4	51.4	6.29	41.2	0.8	0.1	4971

Table II. Carbonization and activation conditions of waste biomass

Raw material	Particle size	Carbonization conditions (°C/h)	Activation conditions (°C/h)	Chemical/physical treatment	Additional information	Reference
Bamboo waste		300-400°C	750/2	Steam	One-step pyrolysis/activation	(Mahanim <i>et al.</i> , 2011)
Wheat	100 µm	127-375°C	-	-	-	(Lanzetta and Di Blasi, 1998)
Corn straw	100 µm	127-375°C	-	-	-	(Lanzetta and Di Blasi, 1998)
Olive	-	-	750/2	Steam/CO <sub>2</sub>	One-step pyrolysis/activation	(Minkova <i>et al.</i> , 2001), (Minkova <i>et al.</i> , 2000)
Straw	-	-	(10°C/min.) 750/2	Steam/CO <sub>2</sub>	One-step pyrolysis/activation	(Minkova <i>et al.</i> , 2001), (Minkova <i>et al.</i> , 2000)
Birch	-	-	(10°C/min.) 750/2	Steam/CO <sub>2</sub>	One-step pyrolysis/activation	(Minkova <i>et al.</i> , 2001), (Minkova <i>et al.</i> , 2000)
Bagasse	-	-	(10°C/min.) 750/2	Steam/CO <sub>2</sub>	One-step pyrolysis/activation	(Minkova <i>et al.</i> , 2001), (Minkova <i>et al.</i> , 2000)
Miscanthus	-	-	750/2	Steam/CO <sub>2</sub>	One-step pyrolysis/activation	(Minkova <i>et al.</i> , 2001), (Minkova <i>et al.</i> , 2000)
Sunflower shell	<0.250 mm	1000°C	1000 °C	Steam	Gasification up to 1000 °C after pyrolysing	(Haykiri-Acma <i>et al.</i> , 2005)
Pinecone	<0.250 mm	1000°C	1000 °C	Steam	Gasification up to 1000 °C after pyrolysing	(Haykiri-Acma <i>et al.</i> , 2005)
Rapeseed	<0.250 mm	1000°C	1000 °C	Steam	Gasification up to 1000 °C after pyrolysing	(Haykiri-Acma <i>et al.</i> , 2005)
Cotton refuse	<0.250 mm	1000°C	1000 °C	Steam	Gasification up to 1000 °C after pyrolysing	(Haykiri-Acma <i>et al.</i> , 2005)
Olive refuse	<0.250 mm	1000°C	1000 °C	Steam	Gasification up to 1000 °C after pyrolysing	(Haykiri-Acma <i>et al.</i> , 2005)
Radiata pine	1-2 mm	950°C (20°C/s)	-	-	Suite of reactors (a wire mesh reactor, a tubular reactor and a drop tube furnace)	(Cetin <i>et al.</i> , 2004)
Eucalyptus	1-2 mm	950°C (20°C/s)	-	-	Suite of reactors (a wire mesh reactor, a tubular reactor and a drop tube furnace)	(Cetin <i>et al.</i> , 2004)
Sugarcane bagasse	1-2 mm	950°C (20°C/s)	-	-	Suite of reactors (a wire mesh reactor, a tubular reactor and a drop tube furnace)	(Cetin <i>et al.</i> , 2004)
Sugarcane bagasse	10-20 mesh and 12-40 mesh	750°C/1 h	900/4 and 20	CO <sub>2</sub> /N <sub>2</sub>		(Ahmedna <i>et al.</i> , 2000)
Apricot stones/product	0.2-1 mm	800/1 h (15°C/min)	800/1 h	Steam	One-step pyrolysis/activation	(Savova <i>et al.</i> , 2001)
Apricot stones	1-1.25 mm		800/1h	Chemical (ZnCl <sub>2</sub> )		(Aygun <i>et al.</i> , 2003)
Cherry	0.2-1 mm	800/1 h (15°C/min)	800/1 h	Steam	One-step pyrolysis/activation stones/product	(Savova <i>et al.</i> , 2001)
Grape seeds/product	0.2-1 mm	800/1 h (15°C/min)	800/1 h	Steam	One-step pyrolysis/activation	(Savova <i>et al.</i> , 2001)
Nut Shells/product	0.2-1 mm	800/1 h (15°C/min)	800/1 h	Steam	One-step pyrolysis/activation	(Savova <i>et al.</i> , 2001)

Table II. To be contd.

Raw material	Particle size	Carbonization conditions (°C/h)	Activation conditions (°C/h)	Chemical/physical treatment	Additional information	Reference
Pistachio-nut shells	2.0-2.8 mm	500/2 (10°C/min)	900/30 min (10 °C/min)	Physical CO <sub>2</sub>	-	(Lua <i>et al.</i> , 2004)
Pistachio-nut shells	1-2 mm	500/2	800/2.5 (10 °C/min)	Physical CO <sub>2</sub>	Two-step physical method	(Yang and Lua, 2003)
Macadamia nutshell	212-300 µm	1 h	500	Chemical (ZnCl <sub>2</sub> )	Chemical activation with both ZnCl <sub>2</sub> and KOH	(Ahmadroup and Do, 1997)
-	212-300 µm	1 h	800	Chemical (KOH)	-	-
Hazelnut shell	1-1.25 mm	-	750/10	Chemical (ZnCl <sub>2</sub> )	-	(Aygun <i>et al.</i> , 2003)
Peanut hulls (Girgis <i>et al.</i> , 2002)	-	500/2	700-900 °C	Physical	-	Two-step process
-	-	-	600/2	Pure steam	-	One-step process
-	-	-	300-750/6	Chemical (ZnCl <sub>2</sub> )	-	-
-	-	-	500-700/3	Chemical (KOH)	-	-
-	-	-	500/3-6	Chemical (H <sub>3</sub> PO <sub>4</sub> )	-	-
Almond shells	1-1.25 mm	-	750/10	Chemical (ZnCl <sub>2</sub> )	-	(Aygun <i>et al.</i> , 2003)
Almond shells shells/product	-	-	-	Chemical (H <sub>3</sub> PO <sub>4</sub> )	-	(Ahmedna <i>et al.</i> , 2004)
Almond	0.2-1 mm	800/1 h (15°C/min)	800/1 h	Steam	One-step pyrolysis/activation	(Savova <i>et al.</i> , 2001)
Almond shells	1.5-2 mm	400/1	850/1	Physical	Different samples (either with CO <sub>2</sub> or N <sub>2</sub> )	(Marcilla <i>et al.</i> , 2000)
Oat hulls	<1 mm	500°C/(1.5 s residence)	800/30 min	Steam	-	(Fan <i>et al.</i> , 2004)
-	-	-	800/60 min	Steam	-	-
-	-	-	800/90 min	Steam	-	-
-	-	-	800/120 min	Steam	-	-
Corn cob	1.435 mm	400-800	-	Chemical (ZnCl <sub>2</sub> )	The impregnation ratio fluctuates 20-175%wt	(Tsai <i>et al.</i> , 1997)
Corn cob	1.44 mm	500/0.5 h soak time	-	Chemical (ZnCl <sub>2</sub> )	Carbonization and activation are carried out simultaneously, optimal soaking time and temperature, impregnation ratio 175wt%	(Tsai <i>et al.</i> , 1998)
-	1.44 mm	500/2 h soak time	-	Chemical (ZnCl <sub>2</sub> )	Carbonization and activation are carried out simultaneously	-
-	1.44 mm	700/0.5 h soak time	-	Chemical (ZnCl <sub>2</sub> )	Carbonization and activation are carried out simultaneously	-

Table II. To be contd.

Raw material	Particle size	Carbonization conditions (°C/h)	Activation conditions (°C/h)	Chemical/physical treatment	Additional information	Reference
-	1.44 mm	700/2 h soak time	-	Chemical (ZnCl <sub>2</sub> )	Carbonization and activation are carried out simultaneously	-
-	1.44 mm	800/0.5 h soak time	-	Chemical (ZnCl <sub>2</sub> )	Carbonization and activation are carried out simultaneously	-
-	1.44 mm	800/2 h soak time	-	Chemical (ZnCl <sub>2</sub> )	Carbonization and activation are carried out simultaneously	-
Corn cob	1.19- 1.68 mm	500-800/1 h soak time	-	Chemical (KOH)	Chemical and physical activation	(Tsai <i>et al.</i> , 2001)
-	1.19- 1.68 mm	500-800/1 h soak time	-	Chemical (K <sub>2</sub> CO <sub>3</sub> )	Chemical and physical activation	-
Corn cob	0.5-2 mm	500/2	850/1	Steam	Physical activation/two-steps	(El-Hendawy <i>et al.</i> , 2001)
-	0.5-2 mm	-	500/2	Chemical (H <sub>3</sub> PO <sub>4</sub> )	Chemical activation	-
-	0.5-2 mm	-	600-700/2	Pure steam	Steam-pyrolyzed/one-step scheme	-
Straw/Char	5.97 mm	550 (fluidized bed)	-	-	20t/h raw material	(Jensen <i>et al.</i> , 2001)
Cotton stalk	0.25-1.8 mm(1.2)	400°C	-	-	Increase of residence time result in formation of activated carbon	(Putun <i>et al.</i> , 2005)
-	-	500°C	-	-	400-700 with 7 °C/min	-
-	-	550°C	-	-	400-00 with 7 °C/min	-
-	-	700°C	-	-	400-00 with 7 °C/min	-
Oak/oak char	-	-	700/1	-	-	(Zhang <i>et al.</i> , 2004)
-	-	-	700/2	-	-	-
-	-	-	800/1	-	-	-
-	-	-	800/2	-	-	-
Corn hulls/corn hulls char	-	-	700/1	-	-	(Zhang <i>et al.</i> , 2004)
-	-	-	700/2	-	-	-
-	-	-	800/1	-	-	-
-	-	-	800/2	-	-	-
Corn stover/char	-	-	800/1	-	-	(Zhang <i>et al.</i> , 2004)
-	-	-	700/2	-	-	-
-	-	-	800/1	-	-	-
-	-	-	800/2	-	-	-
-	-	-	800/2	-	-	-
Corn stover	<1 mm	500°C/ (1.5 h residence)	800/30 min	Steam	-	(Fan <i>et al.</i> , 2004)
-	-	-	800/60 min	Steam	-	-
-	-	-	800/90 min	Steam	-	-
-	-	-	800/120 min	Steam	-	-

Table II. To be contd.

Raw material	Particle size	Carbonization conditions (°C/h)	Activation conditions (°C/h)	Chemical/physical treatment	Additional information	Reference
Olive-seed/char	125-160 µm	800/1	800/1	Chemical (KOH)		(Stavropoulos and Zabaniotou, 2005)
-	-	-	800/2	-	-	-
-	-	-	900/1	-	-	-
-	-	-	900/2	-	-	-
Olive-waste cakes	0.1-10 mm	400/1	750-850/30-70 min	Steam	Optimal conditions: 68 min and 822°C. Great adsorption capacity and high surface area	(Bacaoui <i>et al.</i> , 2001)
Rice-straw	ca. 3 cm	700-1000/1 (10°C/min)	900	KOH	Two-stage method	(Oh and Park, 2002)
-	ca. 3 cm	-	500-900/1 (10 °C/min)	Chemical (KOH)		One-stage method
Rice-straw	10-20 mesh and 12-40 mesh	750/1	900/4 and 20	CO <sub>2</sub> /N <sub>2</sub>		(Ahmedna <i>et al.</i> , 2000)
Rice-husk	200-16 mesh	400/1	600/1	Steam activation		(Malik, 2003)
Rice-husk	-	-	600/3	ZnCl <sub>2</sub> /CO <sub>2</sub>	Different salt solutions/CO <sub>2</sub> participated to the activation method	(Yalcin and Sevinc, 2000)
Rice-hulls	10-20 mesh and 12-40 mesh	750/1	900/4 and 20	CO <sub>2</sub> /N <sub>2</sub>		(Ahmedna <i>et al.</i> , 2000)
Pecan shells	10-20 mesh and 12-40 mesh	700-800/1	800/2-8	Physical		(Ahmedna <i>et al.</i> , 2000)
-	10-20 mesh and 12-40 mesh	-	450/1	Chemical		-
Pecan shells	-	-	-	Chemical (H <sub>3</sub> PO <sub>4</sub> )		(Ahmedna <i>et al.</i> , 2004)
-	-	-	-	Steam		-
Cassava peel	-	-	750	Chemical (KOH)	For 3 h and 650 °C SBET=1183 m <sup>2</sup> /g, impregnation ratio 1:1	(Sudaryanto <i>et al.</i> , 2006)

then finally the pyrolysis residence time. Generally, increasing pyrolysis temperature reduces yields of both chars and ACs. According to Putun *et al.*, 2005, increased temperature leads to a decreased yield of solid and an increased yield of liquid and gases. As the temperature is raised, there is a rise in ash and fixed carbon percentage and there is a decrease in volatile matter. Consequently, higher temperature yields charcoals of greater quality. The decrease in the char yield with increasing temperature could either be due to greater primary decomposition of biomass at higher temperatures or through secondary decomposition of char residue. The secondary decomposition of the char at higher temperatures may also give some non-condensable gaseous products, which also contributes to the increase in gas yield. Indeed, as the temperatures of primary degradation are increased or the residence times of primary vapours inside the cracked particle has to stay shorter, the char yields decrease (Putun *et al.*, 2005). Temperature dependence was also studied (Tsai *et al.*, 1997) and (Tsai *et al.*, 1998) for preparation of ACs with chemical activation ( $ZnCl_2$ ), where it was noticed that char yield decreases with temperature, while soaking time had no effect on the char yield.

#### Activation

Basically, there are two main steps for the preparation and manufacture of AC: (1) the carbonization of the carbonaceous raw material below 800 °C, in the absence of oxygen,

and (2) the activation of the carbonized product (char), which is either physical or chemical. The types of activation are represented in Table III.

#### Physical activation

Physical activation is a two-step process. It involves carbonization of a carbonaceous material followed by the activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures, as it can be seen in Table IV. The activation gas is usually  $CO_2$ , since it is clean, easy to handle and it facilitates control of the activation process due to the slow reaction rate at temperatures around 800 °C (Zhang *et al.*, 2004). Rice husk, corn cob, oak, corn hulls, corn stover, rice straw, rice hulls, pecan shells, peanut hulls and almond shells (Haykiri-Acma *et al.*, 2005), (Ahmedna *et al.*, 2000), (Marcilla *et al.*, 2000), (Zhang *et al.*, 2004), (Girgis *et al.*, 2002), (Lua *et al.*, 2004), (Yang and Lua, 2003), (El-Hendawy *et al.*, 2001), (Malik, 2003), (Yalcin and Sevinc, 2000) and (Oh and Park, 2002), were the raw materials studied by this method. Carbonization temperature range between 400 and 850 °C, and sometimes reaches 1000 °C, and activation temperature range between 600 and 900 °C.

**Table III. Types of activation**

Material	Activation	Steps of process	Reference
Pistachio-nutshells, sunflower shells, pinecone, rapeseed, cotton residues, olive residues, peanut hulls, almond shells, oak, corn hulls, corn stover, rice straw, rice husk, rice hulls, pecan shells, sugarcane bagasse, olive-waste cakes	Physical	Two-steps	(Haykiri-Acma <i>et al.</i> , 2005), (Ahmedna <i>et al.</i> , 2000), (Marcilla <i>et al.</i> , 2000), (Zhang <i>et al.</i> , 2004), (Girgis <i>et al.</i> , 2002), (Lua <i>et al.</i> , 2004), (Yang and Lua, 2003), (El-Hendawy <i>et al.</i> , 2001), (Malik, 2003), (Oh and Park, 2002) and (Bacaoui <i>et al.</i> , 2001)
Corn cob, olive seeds, rice husks, rice straw, cassava peel, pecan shells, Macadamia nutshells, hazelnut shells, peanut hulls, apricot stones, almond shells	Chemical	One-step	(Tsai <i>et al.</i> , 1997), (Aygün <i>et al.</i> , 2003), (Girgis <i>et al.</i> , 2002), (Ahmadroup and Do, 1997), (Ahmedna <i>et al.</i> , 2004), (Tsai <i>et al.</i> , 1998), (Tsai <i>et al.</i> , 2001), (El-Hendawy <i>et al.</i> , 2001), (Yalcin and Sevinc, 2000), (Oh and Park, 2002), (Stavropoulos and Zabaniotou, 2005) and (Sudaryanto <i>et al.</i> , 2006)
Olive, straw, birch, bagasse, miscanthus, peanut hulls, corn stover, apricot stones, cherry stones, grape seeds, nutshells, almond shells, oat hulls	Steam-Pyrolysis	One-step	(Fan <i>et al.</i> , 2004), (Savova <i>et al.</i> , 2001), (Minkova <i>et al.</i> , 2001), (Minkova <i>et al.</i> , 2000), (Girgis <i>et al.</i> , 2002) and (El-Hendawy <i>et al.</i> , 2001)

**Table IV. Physical activation of waste biomass, reported in the literature**

Material	Material	Reference
Steam	Rice husk, corn cob, olive residues, sunflower shells, pinecone, rapeseed, cotton residues, olive-waste cakes, bamboo	(Haykiri-Acma <i>et al.</i> , 2005), (El-Hendawy <i>et al.</i> , 2001), (Malik, 2003) and (Mahanim <i>et al.</i> , 2011)
CO <sub>2</sub>	Oak, corn hulls, corn stover, rice straw, rice hulls, pecan shells, Pistachio nutshells, sugarcane bagasse	(Ahmedna <i>et al.</i> , 2000), (Zhang <i>et al.</i> , 2004), (Lua <i>et al.</i> , 2004) and (Yang and Lua, 2003)
	Peanut hulls, almond shells	(Marcilla <i>et al.</i> , 2000) and (Girgis <i>et al.</i> , 2002)

Physical activation of oak, corn hulls and corn stover chars (Zhang *et al.*, 2004), was performed at temperatures of 700 and 800 °C and durations of 1 and 2 h. For oak, the longer the activation duration, the greater the adsorption capacity of the resultant ACs, and vice-versa for the corn hulls and corn stover. Apparently, the activation durations of 1 and 2 h did not appreciably affect the properties of ACs from oak at 700°C. In contrast, the surface areas, total pore volume, and pore volume of AC obtained upon 1 h of activation were much less than those upon 2 h of activation at 800 °C. Obviously, the pore structure of carbons from oak altered substantially for different durations of activation at 800 °C. The surface areas and pore volumes of ACs from chars generated from corn hulls as well as from corn stover were appreciably greater after 1 h of activation than after 2 h of activation. This was in sharp contrast to the results from the activation of char from oak. Plausibly, in activating the chars from both corn hulls and corn stover, the rate of pore structure formation exceeded that of the destruction due to the pore enlargement and collapse at the earlier stage and vice versa at the later stage. A more thorough research for corn cobs was

made (El-Hendawy *et al.*, 2001). The char was carbonized at 500 °C, then soaked for 2 h, and steam-activated at 850 °C in a flow of steam/N<sub>2</sub>, for 1 h.

#### *Chemical activation*

In the *chemical* activation process the two steps are carried out simultaneously, with the precursor being mixed with chemical activating agents, as dehydrating agents and oxidants. Chemical activation offers several advantages since it is carried out in a single step, combining carbonization and activation, performed at lower temperatures and therefore resulting in the development of a better porous structure, although the environmental concerns of using chemical agents for activation could be developed. Besides, part of the added chemicals (such as zinc salts and phosphoric acid), can be easily recovered (Tsai *et al.*, 1997), (Zhang *et al.*, 2004) and (Tsai *et al.*, 1998). However, a two-step process (an admixed method of physical and chemical processes) can be applied (Oh and Park, 2002), (Table V).

**Table V. Chemical activation of waste biomass**

Activating agent	Material	Reference
ZnCl <sub>2</sub>	Corn cob, Macadamia nutshells, peanut hulls, almond shells, hazelnut shells, apricot stones, rice husks	(Tsai <i>et al.</i> , 1997), (Aygün <i>et al.</i> , 2003), (Girgis <i>et al.</i> , 2002), (Ahmadroup and Do, 1997), (Tsai <i>et al.</i> , 1998) and (Yalcin and Sevinc, 2000)
KOH	Corn cob, Macadamia nutshells, peanut hulls, olive seed, rice straw, Cassava peel	(Girgis <i>et al.</i> , 2002), (Ahmadroup and Do, 1997), (Tsai <i>et al.</i> , 2001), (Oh and Park, 2002), (Stavropoulos and Zabaniotou, 2005) and (Sudaryanto <i>et al.</i> , 2006)
H <sub>3</sub> PO <sub>4</sub>	peanut hulls, almond shells, pecan shells, corn cob	(Girgis <i>et al.</i> , 2002), (Ahmedna <i>et al.</i> , 2004) and (El-Hendawy <i>et al.</i> , 2001)
K <sub>2</sub> CO <sub>3</sub>	Corn cob	(Tsai <i>et al.</i> , 2001)

Chemical activation was used in most of the studies for corn cob, olive seeds, rice husks, rice straw, cassava peel, pecan shells, Macadamia nutshells, hazelnut shells, peanut hulls, apricot stones, almond shells (Tsai *et al.*, 1997), (Aygün *et al.*, 2003), (Girgis *et al.*, 2002), (Ahmadroup and Do, 1997), (Ahmedna *et al.*, 2004), (Tsai *et al.*, 1998), (Tsai *et al.*, 2001), (El-Hendawy *et al.*, 2001), (Yalcin and Sevinc, 2000), (Oh and Park, 2002), (Stavropoulos and Zabaniotou, 2005) and (Sudaryanto *et al.*, 2006). The most common chemical agents are  $ZnCl_2$ ,  $KOH$ ,  $H_3PO_4$  and less  $K_2CO_3$ . As it can be seen almond shells, hazelnut shells and apricot stones (Aygün *et al.*, 2003), were activated with a solution of  $ZnCl_2$  (30 wt%) at 750-800-850 °C, respectively, for 2 h. Zinc chloride was also used in the study (Tsai *et al.*, 1997) and (Tsai *et al.*, 1998), for the activation of carbons from corn cob in the range of 400-800 °C, for 0.5-4.0 h of soaking time, and as well in the study of (Girgis *et al.*, 2002), where a 50% solution was mixed with sample of peanut hulls at 300-750 °C for 6 h. Additionally,  $ZnCl_2$  was used as an activating agent for Macadamia nutshells (Ahmadroup and Do, 1997), and rice husks (Yalcin and Sevinc, 2000), at 500 °C for 1 h, and at 600 °C for 3 h in combination with  $CO_2$ , respectively, and gave the best characteristics of the activated carbons than with any other agent (chemical or physical).

Carbons from Macadamia nutshells (Ahmadroup and Do, 1997), and peanut hulls (Girgis *et al.*, 2002), were activated with  $KOH$  at 800 °C for 1 h and 500-700 °C for 3 h, respectively. ACs that were produced, did not have good quality as the ones produced with  $ZnCl_2$ . Corn cob char (Tsai *et al.*, 2001), that was activated with  $KOH$  at 500-800 °C for 1 h, did not generally give AC with such good BET surface area ( $S_{BET}$ ). Activation of olive seed carbons (Stavropoulos and Zabaniotou, 2005), took place at 800-900 °C for 1-2 h and gave ACs with high surface area and char yield. For rice straw char (Oh and Park, 2002), activation proceeded firstly in one-stage at 500-900 °C for 1 h and secondly in two-stages, at 700-1000 °C for 1 h (carbonization conditions) and

then at 900°C for the activation. Cassava peel char (Sudaryanto *et al.*, 2006), activated at 650 and 750 °C, the higher  $S_{BET}$  appeared in the second case.

From the results, it becomes very obvious that the two-stage process is much more effective, as it gave ACs with higher porosity. In fact, this method (two-step chemical activation process), gave the higher surface area from all the studies being mentioned in the present review.

Activation with  $H_3PO_4$  was used for carbons from peanut hulls (Girgis *et al.*, 2002), corn cob (El-Hendawy *et al.*, 2001), almond shells and pecan shells (Ahmedna *et al.*, 2004). The activating conditions for peanut hull chars were 500 °C for 3 h, while for corn cob chars 500 °C for 2 h. Corn cob gave better characteristics of the ACs in the respective research than peanut hull. Almond shell chars activated with  $H_3PO_4$  gave carbons with a little lower surface area than those mixed with  $ZnCl_2$ .

Carbons from corn cob (Tsai *et al.*, 2001), were activated with  $K_2CO_3$  at 500-800 °C for 1 h, where the ACs produced, comparatively with the results with  $KOH$ , had a lower surface area and gave the maximum char yield.

#### *Steam pyrolysis/activation*

There is also an additional one-step treatment route, denoted as steam-pyrolysis (Table VI) as reported (Fan *et al.*, 2004), (Savova *et al.*, 2001), (Minkova *et al.*, 2001), (Minkova *et al.*, 2000), (Girgis *et al.*, 2002) and (El-Hendawy *et al.*, 2001), where the raw agricultural residue is either heated at moderate temperatures (500-800 °C) under a flow of steam. The residues studied with this method were olive, straw, birch, bagasse, miscanthus, apricot stones, cherry stones, grape seeds, nutshells, almond shells, oat hulls, corn stover, and peanut hulls. The samples in the study of Minkova *et al.*, 2001, were heated with a heating rate of 10 °C/min to a final temperature of 700 °C, 750 °C or 800 °C and kept 1 or 2 h at

**Table VI. Steam-pyrolysis activation in one-step process of waste biomass**

	Material	Reference
Steam	Olive, straw, birch, bagasse, miscanthus, apricot stones, cherry stones, grape seeds, nutshells, almond shells, oat hulls, corn stover	(Fan <i>et al.</i> , 2004), (Savova <i>et al.</i> , 2001), (Minkova <i>et al.</i> , 2001) and (Minkova <i>et al.</i> , 2000)
Pure steam	Peanut hulls, corn cob	(Lanzetta and Di Blasi, 1998) and (El-Hendawy <i>et al.</i> , 2001)

this temperature in the flow of steam, while the final carbonization temperature in the study of Savova *et al.*, 2001 was 80 °C for 1 h

For the preparation and characterization of AC derived from oat hulls or corn stover (Fan *et al.*, 2004), char was heated at 800 °C for 30, 60, 90 and 120 min. The ACs, which had a high pore volume, was weighed to determine activation burn-off or mass loss due to activation.

The burn-off refers to the weight difference between the original char and the AC divided by the weight of original char with both weights on a dry basis. The following relationship is used for calculating the activation burn-off of biomass-derived chars:

Activation burn-off (%) =  $100 - \left\{ \frac{\text{mass after activation (g)}}{\text{original mass (g)}} \times 100 \right\}$

$$\Rightarrow \text{burn-off} = \frac{W_0 - W_1}{W_0} \times 100\%$$

where  $W_0$  is the weight of char and  $W_1$  the mass of the carbon after activation.

The activated carbons, produced by steam gasification, were generally proved to be weakly affective, except the ones from almond shell, apricot and cherry stones (Savova *et al.*, 2001).

### Properties and characteristics of active carbons

#### Surface area

The surface area of char is important because, like other physico-chemical characteristics, it strongly affect the reactivity and combustion behaviour of the char. The chars from pyrolysis above 400 °C had a surface area and a high surface area formed (Putun *et al.*, 2005). In the study of Tsai *et al.*, 1997 and 1998 surface areas were observed to decrease at higher pyrolysis temperature and soaking time. The higher surface areas are probably due to the opening of the restricted pores. The percentage of micropore followed the increase of pyrolysis temperature, but this rate of increase was not as fast as the rate of declination in surface areas. The BET surface areas which calculated in the research of Tsai *et al.*, 1997 and 1998 were observed to increase at higher activation temperature, for both KOH and K<sub>2</sub>CO<sub>3</sub> series, and the maximum rate of increase in BET surface area occurred between 650 and 700 °C.

#### Pore size and volume

Both the size and distribution of micropores, mesopores and macropores determine the adsorptive properties of ACs. For instance, small pore size will not trap large adsorbate molecules and large pores may not be able to retain small adsorbates, whether they are charged polar molecules or uncharged non-polar compounds (Ahmedna *et al.*, 2004).

Materials with a greater content of lignin (grape seeds, cherry stones) develop ACs with macroporous structure, while raw materials with a higher content of cellulose (apricot stones, almond shells) yield AC with a predominantly microporous structure (Savova *et al.*, 2001).

The pore size, in the study of Tsai *et al.*, 1997 and 1998 which was determined after chemical activation with ZnCl<sub>2</sub>, was calculated on the basis of desorption data by employing the Barrett-Joyner-Halenda (BJH) method. As it can be observed in Table VII, the total pore volume is decreasing not only with the increase of the temperature, but also with the increase of the soaking time when the temperature is constant. On the contrary, in the research of Tsai *et al.*, 1997 and 1998 the values of total pore volume increase rapidly with increase in the activation temperature. It is noted that the maximum values (i.e. 0.87 and 0.74 cm<sup>3</sup>/g for 15 wt% KOH and 37.5 wt% K<sub>2</sub>CO<sub>3</sub> ACs, respectively) of total pore volume at 800 °C, are larger than those of commercial ACs, i.e. 0.60 and 0.52 cm<sup>3</sup>/g for BPL and PCB, respectively, (Calgon Carbon Co., Pittsburgh, USA).

All the characteristics from the ACs produced are summed up in Table VII. As it can be seen carbons from corn stover and oat hulls (Fan *et al.*, 2004), give the more pore volume, whereas olive seed carbons (Stavropoulos and Zabaniotou, 2005), when activated have high percentage of char yield (76%). The higher SBET (2410 m<sup>2</sup>/g) can be taken by pyrolyzing rice straw (Oh and Park, 2002), and activate the carbons with KOH, but remarkable surface areas can also be taken from corn cob (Tsai *et al.*, 2001), olive seed (Stavropoulos and Zabaniotou, 2005), and Cassava peel (Sudaryanto *et al.*, 2006).

### Applications and uses of waste based active carbons

ACs have applications in many industries as diverse as food processing, pharmaceuticals, chemical, petroleum, mining, nuclear, automobile and vacuum manufacturing, because of their adsorptive properties they have due to a high available area which is presented in their extensive internal pore struc

**Table VII. Characteristics of activated carbons from waste biomass**

Raw material	SBET (m <sup>2</sup> /g)	V <sub>o</sub> (cm <sup>3</sup> /g)	Yield (%)	Reference
Apricot stones	1190	0.50	18.2	(Savova <i>et al.</i> , 2001)
Cherry stones	875	0.28	11.2	(Savova <i>et al.</i> , 2001)
Grape seeds	497	0.12	26.2	(Savova <i>et al.</i> , 2001)
Nut Shells	743	0.21	17.9	(Savova <i>et al.</i> , 2001)
Pistachio-nut shells	778	0.466	-	(Lua <i>et al.</i> , 2004)
Macadamia nutshell	1718	0.723	-	(Ahmadroup and Do, 1997)
-	1169	0.529	-	-
Peanut hulls	80.8-97.1	0.022-0.043	30	(Girgis <i>et al.</i> , 2002)
-	253	0.079	29	-
-	420	0.173	30	-
-	228-268	0.033-0.076	27-32	-
-	240-1177	0.036-0.57	22-36	-
Almond shells	998	0.40	17.8	(Savova <i>et al.</i> , 2001)
Almond shells	1005.7-1217.7, 1157.4-1315.4	-	15.84-6.34	(Marcilla <i>et al.</i> , 2000)
Oat hulls	349	91.4	-	(Fan <i>et al.</i> , 2004)
-	431	88.4	-	-
-	522	86.8	-	-
-	625	84.2	-	-
Corn cob	400-1410	0.19-0.70	-	(Tsai <i>et al.</i> , 1997)
Corn cob	960	0.486	28.8	(Tsai <i>et al.</i> , 1998)
-	774	0.349	30.4	-
-	747	0.368	27.8	-
-	682	0.335	29.2	-
-	706	0.345	27.8	-
-	721	0.342	28.2	-
Corn cob	0.1-1.806	-	12.8-31.3	(Tsai <i>et al.</i> , 2001)
-	0.2-1.541	-	17.4-33.5	-
Corn cob	607	0.296	8.7	(El-Hendawy <i>et al.</i> , 2001)
-	960	0.629	18.3	-
-	618-786	0.321-0.430	20.1-20.8	-
Straw	-	-	-	(Jensen <i>et al.</i> , 2001)
Cotton stalk	37.28	-	30.30	(Putun <i>et al.</i> , 2005)
-	3.33	-	29.17	-
-	3.32	-	27.93	-
-	3.14	-	25.56	-
Oak	642	0.2704	-	(Zhang <i>et al.</i> , 2004)
-	644	0.2450	-	-
-	845	0.3212	-	-
-	985	0.3792	-	-
Corn hulls	977	0.3352	-	(Zhang <i>et al.</i> , 2004)
-	902	0.3284	-	-
-	1010	0.4348	-	-
-	975	0.3792	-	-
Corn stover	660	0.2817	-	(Zhang <i>et al.</i> , 2004)
-	432	0.1818	-	-
-	712	0.2849	-	-
-	616	0.2343	-	-
Corn stover	424	88.7	-	(Fan <i>et al.</i> , 2004)
-	442	86.2	-	-
-	374	85.0	-	-
-	311	84.2	-	-
Olive-seed	1339	-	76	(Stavropoulos and Zabaniotou, 2005)
-	1334	-	72	-
-	1550	-	65	-
-	1462	-	59	-
Olive-waste cakes	514-1271	0.217-0.557	-	(Bacaoui <i>et al.</i> , 2001)
Rice-straw	2410	1.4	-	(Oh and Park, 2002)
Rice-husk	480	13.652	-	(Yalcin and Sevinc, 2000)
Pecan shells	682	-	32	(Ahmedna <i>et al.</i> , 2004)
-	724	-	18	-
Cassava peel	1378	0.583	-	(Sudaryanto <i>et al.</i> , 2006)

ture. Such high porosity is a function of both the precursor as well as the scheme of activation (El-Hendawy *et al.*, 2001).

The chemical nature of ACs significantly influences its adsorptive, electrochemical, catalytic, and other properties. Generally speaking, ACs with *acidic* surface chemical properties are favourable for basic gas adsorption such as ammonia while ACs with *basic* surface chemical properties are suitable for acidic gas adsorption such as sulphur dioxide (Yang and Lua, 2003). The uses of the AC produced by agricultural residues are summarized in Table VIII.

#### *In gas phase adsorption*

The ACs may be used as adsorbent for air pollution control, as it can effectively treat industrial gas, and indoor air environments (Tsai *et al.*, 1998). Due to their large number of

micropores and the high surface area (high adsorption capacities) they can be used as catalysts for gas purification, separation and deodorization.

Adsorption by commercial ACs offers an efficient technology for removing volatile organic compounds (VOCs) from air pollution sources, owing to their large specific surface areas, high micropore volumes and rapid adsorption capabilities (Yates *et al.*, 2001). Furthermore, several microporous ACs from various manufacturers were selected to study the viability of using monolithic adsorption units, capable of regeneration for the purification of effluent gas streams (Yates *et al.*, 2003).

The removal processes for SO<sub>x</sub> and NO<sub>x</sub> can be designed using activated carbon fiber (ACF) for the environment of busy traffic crossings, parking spaces, and large halls as well

**Table VIII. Uses of activated carbons produced by waste biomass**

Raw material	Uses	Reference
	Treat industrial gas, indoor air (air pollution control)	(Marcilla <i>et al.</i> , 2000)
Peanut hulls, rice straw	Adsorption of methylene blue (liquid purification)	(Ahmadroup and Do, 1997) and (Yalcin and Sevinc, 2000)
	Trace metals	(Ahmedna <i>et al.</i> , 2004)
Rice husk, orange peel	adsorption of acid dyes	(Malik, 2003), (Chuah <i>et al.</i> , 2005) and (Ricordel <i>et al.</i> , 2001)
Palm kernel fibre	Removal of ions	(Ho Y and Ofomaja, 2005) and (Kadirvelu <i>et al.</i> , 2003)
	Removal of Arsenic	(Manju <i>et al.</i> , 1998)
Pitch-based carbons	Adsorption of atrazine	(Gullon and Font, 2001) and (Brown <i>et al.</i> , 2004)
Activated carbons membranes	Clean-up of fruits and vegetables	(Sojo <i>et al.</i> , 1997)
Wheat straw	Removal of nitrate and pesticides	(Aslan and Turkman, 2005), (Kouras <i>et al.</i> , 1995), (Ayranci and Hoda, 2005) and (Murayama <i>et al.</i> , 2003)
	Be as support for noble metals/catalysts	(Besson <i>et al.</i> , 2005)
Rice husks	Wastewater treatment	(Daifullah <i>et al.</i> , 2003)
Jordanian olive stones	Groundwater treatment	(El-Sheikh <i>et al.</i> , 2004)
	Purification of drinking water	(Heijman and Hopman, 1999) and (Pintar, 2003)
	Removal of heavy metals	(Chuah <i>et al.</i> , 2005) and (Ricordel <i>et al.</i> , 2001)
	Purification of effluent gas streams	(Yates <i>et al.</i> , 2003)
	Removal of mercury vapours	(Vitolo and Seggiani, 2002)
	Removal of volatile organic compounds	(Yates <i>et al.</i> , 2001)
	Removal of NO <sub>x</sub> and SO <sub>x</sub>	(Mochida <i>et al.</i> , 2000)
	Removal of phenols and phenolic compounds	(Dabrowski <i>et al.</i> , 2005) and (Dursun <i>et al.</i> , 2005)

as for exhaust gases such as the flue gas from a power plant, catalyst regeneration for fluidized catalytic cracking (FCC) process, and ventilated gas from motorway tunnels (Mochida *et al.*, 2000). Activated carbon are also used for removing mercury vapours from a gas mixture containing H<sub>2</sub>S, O<sub>2</sub> and moisture that is representative of the exhaust gas emissions of the geothermal power plants (Vitolo and Seggiani, 2002).

#### *In liquid phase adsorption*

Liquid phase adsorption applies to many purification processes. The most relevant is the wastewater treatment e.g. by rice husk carbons (Daifullah *et al.*, 2003), the drinking water (Heijman and Hopman, 1999), the industrial effluents purification (Pintar, 2003), and ground water treatment e.g. Jordanian olive stones (El-Sheikh *et al.*, 2004).

Adsorption of methylene blue has been one of the most important means of assessing removal capacity from the aqueous phase. Phosphoric acid-ACs are the best in the uptake of methylene blue from aqueous solution (200-400 mg/g) (Girgis *et al.*, 2002). Porous carbons with high surface area and adsorption capacities for methylene blue and iodine could be obtained from a rice straw precursor (Oh and Park, 2002), particularly by the two-stage method, in which the raw rice straw is carbonized at the first stage and activated with KOH at the subsequent stage. From the one-stage method the porous ACs of only moderate performance could be obtained, because the ash-formation makes it difficult to increase the optimum temperature at which micropores can be created.

ACs are used for the removal of phenols, phenolic compounds (Dabrowski *et al.*, 2005) and (Dursun *et al.*, 2005), heavy metals and dyes (Chuah *et al.*, 2005) and (Ricordel *et al.*, 2001), metal ions (Ho Y and Ofomaja, 2005) and (Kadirvelu *et al.*, 2003) and mercury (II) from aqueous solutions. Phenolic derivatives belong to a group of common environmental contaminants. The presence of these compounds even in low concentrations can be an obstacle to the use and/or reuse of water. Phenols cause unpleasant taste and odour of drinking water and can exert negative effects on different biological processes. Phenolic derivatives are widely used as intermediates in the synthesis of plastics, colours, pesticides, insecticides, etc. Degradation of these substances means the appearance of phenol and its derivatives in the environment (Dabrowski *et al.*, 2005). They can also adsorb arsenic (As) (Manju *et al.*, 1998) and trace metals (Ahmedna

*et al.*, 2004) from drinking water, or be used as support for noble metals or as catalysts per se in liquid phase reactions (Besson *et al.*, 2005).

Adsorption of acid dyes from aqueous solution, like acid violet 17 from waste waters, by orange peel carbons, or acid yellow 36 by rice husk carbons (Malik, 2003), is one of the most efficient methods. Carbons with low dye uptake (30-100 mg/g) are those chemically activated with ZnCl<sub>2</sub>, KOH, steam pyrolyzed or chars (Girgis *et al.*, 2002).

#### *Active carbon for organics-pesticides*

ACs are very efficient in the adsorption of nitrate and pesticides from surface waters (Aslan and Turkman, 2005), (Kouras *et al.*, 1995), (Ayranci and Hoda, 2005) and (Murayama *et al.*, 2003). Pitch-based AC fibres are more effective in the atrazine removal dynamic tests than granular activated carbon if they are highly activated. The rapid adsorption kinetics of the atrazine with the highly activated ACF seems to be the main reason for its having a better performance than granular AC (GAC). This means that a fiber-type structure with micropores directly accessible from the surface is not enough reason to justify the good efficiency of ACF (Gullon and Font, 2001). Another carbon based material, Nyex 100 (Brown *et al.*, 2004), was also used for the removal of atrazine to low levels, below 1 µg<sup>-1</sup>.

The feasibility of using AC membranes as the solid phase for an on-line single step extraction-cleanup of fruits and vegetables for multi residue screening was studied in (Sojo *et al.*, 1997). The type of carbon present in these membranes (an acid-washed coconut charcoal) seems to be able to discriminate between compounds containing benzene rings with small substituents from those with bulky substituents. The origin of this selectivity may be due to the presence of active sites on the carbon surface. It is speculated that these sites are electron deficient sites, which could be deactivated by exposure to reducing agents, such as ascorbic acid. This is a property that could be exploited in the cleanup of samples for the isolation of compounds such as polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) from complex matrices such as soils and sediments.

#### *Comparisons of active carbons*

Commercial carbons can be used satisfactorily, as post treatment in order to adsorb colour, nitrate and dissolved organic carbon from drinking water, effluent water (Aslan and

**Table IX. Uses of commercial activated carbons**

PAC/Chemviron	Dodine (surface waters)	(Kouras <i>et al.</i> , 1995)
ACF/Spectra corp	Atrazine (kinds of pesticides for water waste treatment)	(Ayranci and Hoda, 2005)
Nyex 100	Atrazine (aqueous solutions)	(Brown <i>et al.</i> , 2004)
ACF/KF-175, TOYOBO	Organic chlorine pesticides (water samples)	(Murayama <i>et al.</i> , 2003)

Turkman, 2005). Organic pollutants, like different kind of pesticides, are also being removed by either powdered or granular or fiber ACs. Kouras *et al.*, 1995, showed that powdered active carbon produced by Chemviron was very effective in cleaning surface waters by the adsorption of dodine. The result was even better when using coagulants (polyelectrolyte, Al, Fe). The highest removal observed when mixing 50 mg/l PAC with ferric chloride (>98.2%). Ayranci *et al.*, 2005, supported that ACF, and especially pitch-based, was more effective in the removal of atrazine than granular AC. In their tests for waste-water purification it turned up that ACF (from Spectra corp.) had very high specific surface area, adsorption capacity and mechanical strength. A new collection method of organic chlorine pesticides in water samples (rainwater, river water, seawater) using an ACF filter (KF-175, TOYOBO) was proposed in the study of Murayama *et al.*, 2003, to be effective and economical compared to those by the conventional method. Finally, Brown *et al.*, 2004, used a novel carbon-based adsorbent material (Nyex 100) for the removal of atrazine to low levels, below  $1 \mu\text{g}^{-1}$ , from aqueous solutions, which regenerated electrochemically, and has the ability to reach three times greater adsorptive capacities than originally achieved. This material does not have internal surface and porous, and it has low cost. Table IX summarizes the uses of commercial active carbons.

## Conclusion

### *Concerning type of waste biomass*

Activated carbons from *almond shell, nut shell, apricot and cherry stones*, have low ash content in contrast with the carbon from *grape seeds* which has relatively high ash content. All samples have low sulphur content. The following order of suitability of raw materials for activated carbon production was established: hazelnut shell>apricot stone>almond shell. The higher yields of activated carbons with high  $S_{\text{BET}}$  obtained from olive wastes, birch and bagasse, make these

raw materials suitable for preparation of activated carbon while samples from straw and miscanthus seem more suitable for conversion into liquid and gaseous products.

### *Concerning process parameters*

Both the hydrogen and oxygen contents of char and hence H/C ratio decreases as the temperature is increased indicating an increase in the aromaticity and carbonaceous nature of char. SBET and the total pore volume increase with *pyrolysis temperature*, and reach a maximum at about 500 °C; thereafter, the trend is a decrease with pyrolysis temperature. The rate of declination is not as fast as that of increase. However, increase in temperature from 500 to 800 °C may induce shrinkage in the carbon structure, resulting in a reduction in the surface area and the pore volume.

Moreover, it seems that the *soaking time in the chemical activation* plays a less important role in the production of activated carbon. It is seen that, by increasing soaking time, the surface area and the pore volume were increased as a result of the development of porosity. However, the values thereafter are observed to decrease gradually at longer soaking time, which is possibly attributed to the gasification of the few well developed micropore wall.  $S_{\text{BET}}$  increase with an increase of *the burn-off*, which proved to be the most significant factor, regardless of the activation temperature.

### *Concerning type of activation*

The experimental results of Macadamia nutshells show that surface area and micropore volume of the samples produced by chemical activation with  $\text{ZnCl}_2$  are much higher than those with  $\text{KOH}$ . High-quality of carbon can easily be produced from peanut hulls through chemical activation with  $\text{H}_3\text{PO}_4$  at 500 °C.

### Concerning uses of active carbons

Activated carbons prepared with the pistachio-nut shells can be used for both gas and liquid adsorption applications, depending on the activation conditions. Peanut husks carbon is an effective adsorbent for the removal of  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$  and  $Ni^{2+}$  from aqueous solutions. It would be useful for the economic treatment of wastewater containing these heavy metals, as the adsorbent has a much superior capacity to the commercial activated carbon.

Copper-impregnated coconut husk carbon can be used as an adsorbent for the effective removal of As(III) from aqueous solutions. The carbonized product from beet pulp is an efficient adsorbent for the removal of phenol from aqueous solution.

Three grades of carbons were obtained from *corn cobs*: (a) Those obtained by carbonization yields a poorly developed wide-pored carbon with capacity for iodine and  $Pb^{2+}$  ions; (b) steam-activated carbons (in one or two step schemes) develop porosity with temperature, and are essentially microporous. These exhibit good adsorbing affinity from solution (iodine, phenol, and methylene blue) that depends on their porosity characteristics; (c) chemical activation by  $H_3PO_4$  at 500 °C proved very effective in producing high quality activated carbon with well-developed porosity and high adsorption capacity for both organic and inorganic substrates.

Almond shell-based carbon with steam-activated pecan shell- removed nearly 100% of lead ion, 90-95% of copper ion and 80-90% of zinc ion. Acid activation resulted in higher yield, lower surface area, higher percentage of micropore compared to steam activation. Percent yield is a factor used in cost estimation and commercial potential of activated carbons.

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