

# Preparation of Carbonaceous Adsorbents from Lignocellulosic Biomass and Their Use in Removal of Contaminants from Aqueous Solution

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The feasibility of using lignocellulosic biomass as a source for preparing carbon adsorbents has received rigorous attention over the last few decades. Many studies have discussed its great potential as a renewable feedstock for preparation of carbonaceous adsorbent materials. This review paper provides an overview of the different types of carbonization techniques that so far have been applied to convert lignocellulosic biomass to carbon adsorbents. The effects of various process parameters on the conventional pyrolysis process are reviewed. The paper focuses on the mechanism for the formation of carbons, its wide variety of applications for waste effluents, and the regeneration techniques so far adopted by researchers. Low-cost carbons derived from lignocellulosic biomass have demonstrated excellent capabilities for the removal of organic and inorganic contaminants, including some pharmaceutical compounds, from the waste aqueous stream.

*Keywords:* Biomass; Adsorption; Hemicellulose; Cellulose; Lignin; Carbon

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## INTRODUCTION

Lignocellulosic biomass is considered one of the most abundant and bio-renewable feedstock which has great potential for sustainable production of activated carbon. The use of inexpensive and eco-friendly biomass has been considered as a replacement for commercial activated carbon (Dias *et al.* 2007). Different types of organic materials such as agricultural crops and their residues, wood, and algae are generally categorized as biomass. These materials are initially developed from the photosynthesis process using atmospheric CO<sub>2</sub>, sunlight, and water. Because they are the products of photosynthesis, they are also called photomass. Various types of biomass are annually deposited in large quantities and considered to be solid pollutants to the environment (El-Hendawy 2005; Fiol *et al.* 2006). Thus, from an environmental point of view, the innocuous disposal of these residues is immensely important. These biomasses or their residues are usually light weight and porous, containing carboxylic and hydroxyl functional groups on their surface. Previously, activated carbons had been prepared mainly from coal, lignite, wood, and animal bones, but recently there is a growing interest in utilizing biomass residues to produce activated carbon (Mohammadi *et al.* 2010). A wide range of biomass types have been considered very effective for producing carbonaceous adsorbent due to its low ash and high volatile content. Thus, preparation of

activated carbon (char) from lignocellulosic biomass can be justified by three factors: the unique features of the biomass in terms of porosities and surface functional groups for producing adsorbent, the possibility of mass production at low cost, and the resolution of the waste disposal problem with the addition of value added products. However, the applicability of these types of materials in their original state has been found to be constrained by their relatively small surface area per unit mass with inadequate pore size distribution and leaching of some organic chemicals into the process stream (Chowdhury *et al.* 2012a). In this context, different types of physicochemical techniques have been adopted to prepare activated carbon from lignocellulosic biomass.

The activated carbon consists of hexagonal graphite flat plates in which each carbon atom is held by covalent linkages to three other neighboring carbon atoms. Some hetero atoms including oxygen, hydrogen, nitrogen, sulfur *etc.* are incorporated in the carbon matrix to enhance their sorption performance for specific types of contaminants. Activated carbon contains a significant number of pores. The presence of micro, meso, and macro pores are contributing to its widespread surface area. Carbonaceous adsorbents used for gaseous phase applications usually have more micropores and macro pores in their structure, whereas liquid phase carbons have a significant number of mesopores or a transitional range of pores that allow easy access of the aqueous solution to the internal microporous region through the macropores and mesopores. Macropores have little contribution to the development of surface area (Sudaryanto *et al.* 2006). However, the development of micropores and mesopores is vital, as they entrap and retain various types of adsorbate either from gas or liquid phases (Wu *et al.* 2005; Eckenfelder 2000). The effectiveness of activated carbon as an adsorbent material is also attributed to its surface chemistry containing surface functional groups (Ismadji and Bhatia 2001). It is anticipated that by the restricted oxidation or activation technique, the presence of carboxylic and phenol groups on the surface of activated carbon particles can be enhanced.

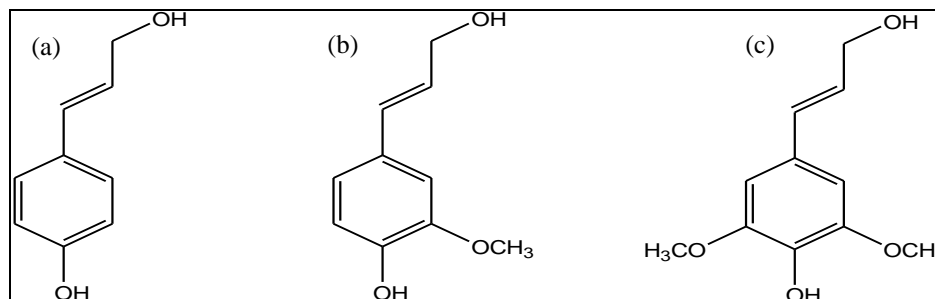
The extensive application of activated carbon for the sorption process is due to its effective surface area, wide availability, surface reactivity, and versatility to modify its physicochemical properties for specific applications (Haro *et al.* 2011). A literature review has found that various types of lignocellulosic residues such as mangostene fruit shell (Chowdhury *et al.* 2012a), fir wood (Wu *et al.* 2005), kenaf core (Chowdhury *et al.* 2012b), bamboo (Chan *et al.* 2009), kenaf fiber (Chowdhury *et al.* 2012c), cedar wood (Cuerda-Correa *et al.* 2006), pecan shell (Dastgheib and Rockstraw 2001), orange seed (Elizalde-Gonzalez and Hernández-Montoya 2008), and rubber wood sawdust (Kalavathy *et al.* 2005), *etc.* are effectively used to prepare carbon-based adsorbent.

Numerous studies have dealt with the reclamation of municipal and industrial waste waters to safe potable water by the application of activated carbons. It is not possible here to discuss each such observation; however, some important findings will be discussed herein illustrating the sorption of different types of pollutants over the surface of the activated carbon. The purpose of this review paper is to present experimental data that were evaluated by previous researchers to obtain carbonaceous adsorbent and its application as adsorbent material in the liquid phase system. An overview is also given regarding the percentage composition of the biomass for carbon preparation and the fundamental principles including process parameters involved in the pyrolysis process. Literature depicting the regeneration process using activated carbons obtained from lignocellulosic precursors loaded with organic and inorganic pollutants will be discussed.

## Chemical Structure of Lignocellulosic Biomass

### Lignin

Lignocellulosic biomass contains 10% to 30% lignin. However, some materials such as coir have approximately 45% lignin, whereas softwood contains 25% to 31% and hardwood contains 16% to 24% lignin (Suhās *et al.* 2007). In the case of hardwoods, lignin is covalently attached with xylans, and in softwood it is bonded with galactoglucomannans. The complex matrix of lignin contains many hydroxyl, methoxyl, and carbonyl groups, which impart high polarity to this macromolecule. Lignin is a natural polymer that is produced from enzyme-initiated dehydrogenative polymerization. It is a macromolecule containing alkyl-phenol in its structure. Lignin is an insoluble, resin-like substance consisting of phenyl propane building blocks usually having a hydroxyl group in the para position and a methoxyl group in the meta position to the side chain. In addition, there may be carbon-to-carbon or carbon-to-oxygen bonds that join the aromatic ring with the rest of its structure. The three major components from which lignin are produced are sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol. The structure of these three alcohols is illustrated in Fig. 1.



**Fig. 1.** Constituent elements of lignin: (a) sinapyl alcohol, (b) coniferyl alcohol, and (c) p-coumaryl alcohol (Suhās *et al.* 2007)

### Hemicellulose

Different types of monosaccharide units join together to yield a polymer chain of hemicelluloses. The main monomer unit of hemicellulosic backbone is pentose sugar. The pentose sugar holds the cellulose micells and fiber in the biomass and acts as cementing material. It also contains xylose sugar, which is bonded by  $\beta$ -(1, 4)-glycosidic bonds and branched by  $\alpha$ -(1, 2)-glycosidic bonds containing 4-methyl glucuronic acid groups. Contrary to lignin, it is partially soluble in water but mostly soluble in alkalis. It can be easily hydrolyzed. The chain of hemicelluloses may consist of homopolymer having a repetitive unit of a single type of sugar or it may have a heteropolymer unit where the constituent monomers are different types of sugar. Basically it is a collection of polysaccharides with a lower degree of polymerization than cellulose. Its structure is similar to that of cellulose, as 5 or 6 carbon sugars are arranged in the hemicellulose chain. However, its chains are relatively short and less regular compared with cellulose, making them soluble to a certain extent.

### Cellulose

Cellulose is a linear polymer consisting of 6 carbon glucose units. The anhydrous glucose units are also linked together by  $\beta$ -(1, 4)-glycosidic bonds. The cellulosic chains are arranged parallel due to the presence of intermolecular and intramolecular hydrogen

bonds between OH groups of the same cellulose chain or neighboring cellulosic chains. It is almost insoluble in most types of solvent. The two terminals of a cellulose molecule contain two different types of terminating groups; one contains a reducing hemiacetal group in position C1, and is therefore known as the reducing end group, whereas the other terminal contains an extra secondary hydroxyl group in position C4 and is known as the non-reducing end group. In contrast to starch, the glucose units are oriented with  $-CH_2OH$  groups alternating above and below the plane of rings. Consequently, it produces long and unbranched chains in cellulose. Due to the absence of a side chain in cellulose, it forms a symmetrical structure, as shown in Fig. 2.

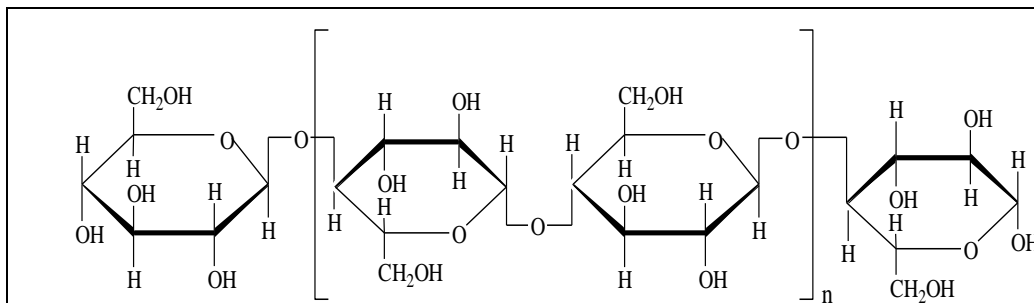


Fig. 2. Typical cellulose molecule

### Properties of Carbon Materials Based on Chemical Constituents of Biomass

In most of the published work on the preparation of activated carbon, the composition of the starting lignocellulosic substrate is not specified. Also in most cases there is little attempt to relate the characteristics of activated carbon or the char obtained after the carbonization stage and its adsorptive properties to the amount of cellulose or lignin present in the biomass matrix. A summary of relevant published data for the properties of activated carbon based on the composition of the biomass is given in Table 1.

Table 1. Influence of Composition of Biomass on the Surface Area and Porosity of the Activated Carbon

Lignocellulosic Biomass	% Lignin	% Cellulose	Carbon Yield %	Char Yield %	BET Surface Area (m <sup>2</sup> /g)	Micropore Surface Area (m <sup>2</sup> /g)	Reference
Palm shell	53.4	29.7	50.0*	-	260	-	Daud and Ali 2004
Coconut shell	30.1	19.8	48.6*	-	183	-	
Wood birch	21.0	42.6	48.6**	5.6	-	-	
Olive waste	28.0	44.8	50.9**	17.5	-	-	Zanzi <i>et al.</i> 2002
Wheat straw	21.7	43.6	45.6**	13.2	-	-	
Jute	11.8	64.4	44.1	24.6	840	396	
Abaca	5.1	63.2	43.7	28.6	860	587	
Flax	2.5	56.5	43.3	25.1	776	436	Reed and Williams
Hemp	3.3	67.0	41.2	28.5	877	555	2004
Coir	41-45	36-43	46.6	34.4	822	685	

\* By elemental analysis; \*\*Moisture- and ash-free

It was observed by previous researchers that hydrolytic lignin-based carbon contains more pore volume than cellulosic carbon (Gergova *et al.* 1994). It was reported by González *et al.* (2003) that lignin is the main constituent for char formation, whereas cellulose and hemicellulose are the volatile fraction removed during the pyrolysis process. However, lignin char has low reactivity compared with other biomass constituents due to its highly cross-linked structure (Sharma *et al.* 2004). Others have shown that chemical activation by acid results in an attack on the amorphous lignin first rather than the crystalline cellulosic matrix of the biomass (Jagtoyen and Derbyshire 1998). Dissolution of lignin and other mineral components in rice husk-based activated carbon was responsible for the creation of new pores (Kennedy *et al.* 2004). During production of activated carbon from white oak and yellow poplar, it was observed that activation of lignin produces micropores whereas activation of cellulose produces a mixture of pores (Jagtoyen and Derbyshire 1998). In contrast to that, microporosity developed in activated char derived from powdered wood components (cellulose, xylan, and lignin) is due to cellulose and not due to lignin and hemicellulose (Khezami *et al.* 2005). Review of the literature revealed that palm shell containing more lignin content produced carbon with more surface area than coconut shell (Daud and Ali 2004). The researchers also found that the biomass based-char containing more cellulosic content was easier for the preparation of activated carbon than that having more lignin polymer, which predominantly imparts density or hardness of the biomass matrix. Five types of biomass fiber were activated under identical conditions and it was observed that coir having high lignin content yielded carbon with the highest micropore surface area and char yield (Reed and Williams 2004). A similar trend was seen for wood birch, olive waste, and wheat straw in the percentage of char yield (Zanzi *et al.* 2002).

### **Preparation of Carbon Materials**

There are two main steps involved in the production of activated carbon. The first step is known as carbonization of the carbonaceous precursors in the absence of oxygen to break down the cross-linkage between biomass matrixes. The second step is the activation of the carbonized product, known as char, for the additional improvement of the porous texture of the activated carbon (Ioannidou and Zabaniotou 2007).

### **Carbonization**

Carbonization is carried out by pyrolysis of the precursors in an inert atmosphere to produce char. This will enhance the carbon content from the organic substances. The pores formed during the carbonization process are usually narrow and in some cases blocked by tarry substances. The deposition of tarry substances takes place when volatile components from the carbon matrix diffuse out of the pore structure into the gas main stream. Some substances may collide with the walls of the pores, resulting in hydrocracking and carbon deposition (Kamishita *et al.* 1977). This phenomenon was observed in preparing activated carbon from guava seed which yielded a poorly adsorbing activated carbon due to the partial disintegration of organic constituents as the pores were blocked by carbonization byproducts (Rahman and Saad 2003). The carbonization process is divided into four main stages, based on the temperature reached in each stage (Wereko-Brobby and Hagen 1996). The steps involved in the carbonization process are summarized in Table 2.

**Table 2.** Steps and Range of Temperature in the Carbonization Process (Wereko-Brobby and Hagen 1996)

Stage	Temperature (°C)	Type of Reaction	Process
1	≤200	Endothermic	Initial drying of precursors
2	170<300	Endothermic	Pre-carbonization stage, producing some pyrolygneous liquids (methanol and acetic acid), small quantities of non-condensable gases (CO and CO <sub>2</sub> )
3	250<300	Exothermic	Greater proportion of the light tars and pyrolygneous acids produced in the second stage are released steadily from precursors to produce charcoal
4	>300	-	Increasing the carbon content of the charcoal by driving off the remaining volatile components of the charcoal

### Activation

Technical know-how about different process parameters including different activating agents involved in the activation process is very important in developing suitable activated carbon adsorbent required for a specific application. The activation step is necessary to enhance the porosity and burning off of the deposited tars during carbonization (Turmuzi *et al.* 2004). The activation process can be subdivided into three major stages based on the individual activity of different parts of the carbon configuration. At the preliminary stage, tarry substances that cause pore clogging are eliminated to facilitate the surface of the elementary carbon crystal to come into contact with the activating agent for the reaction. During the second stage, elementary crystals of carbon will burn. The final stage involves oxidation of the carbon particles (Tan 2008). This results in the reduction of the total micropore volume due to the burning of the walls between the adjacent pores. The consequence of damaging the walls is the creation of pores with large diameters. There are three main methods for activation, namely physical, chemical, and physiochemical processes.

#### *Physical activation*

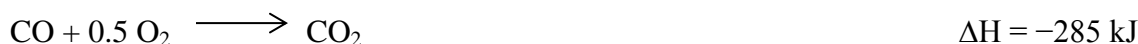
Physical activation comprises a two-step process. After carbonization of carbonaceous materials, the produced char is activated in the presence of activating agents (oxidizing gases) such as CO<sub>2</sub>, steam, air, or their mixtures, at an elevated temperature. Physical activation is carried out by the oxidation of the raw precursors or char using oxidizing gas at 800 °C to 1100 °C to obtain a certain percentage of burnoff (El-Hendawy 2005). The porous texture of the activated carbon is observed due to the exclusion of volatile matters present on the char. The main purpose of gasification is to expand the pores, resulting in meso porosity inside the carbon structure. At lower temperatures, the reactions are too slow. Initially at lower temperatures, reactions take place on the interior surface of the carbon. At higher temperatures, reactions become

diffusion controlled on the outside of the carbon particles. The following reaction takes place between CO<sub>2</sub> and the carbon matrix (Qureshi 2008):



Activation temperature and activation time are the two important parameters for development of porous structure and surface functional groups of activated carbons. Sentorun-Shalaby *et al.* (2006) have reported that the increase in activation temperature and activation time were inversely proportional with the solid yield but directly proportional with the pore volume for activated carbon prepared from apricot stones. In the case of preparing activated carbon from pistachio nutshell using CO<sub>2</sub> activation, it was observed that an increase in activation time or temperature increased the carbon-CO<sub>2</sub> reaction, resulting in the development of new pores together with the expansion of previously developed pores. Nevertheless, there is a precise limit after which increasing the activation time or temperature might cause the destruction of the pores by collapsing some of the pore walls with the formation of ash residues. Some of the previous work carried out on the physical activation of various lignocellulosic biomasses is listed in Table 3.

Steam and air have been shown to react 8 times and 100 times faster respectively with carbon than CO<sub>2</sub>. It is comparatively difficult to use steam or air mixtures containing oxygen for the activation step. Steam and air react with carbon particles to produce CO and CO<sub>2</sub> by the following reactions:



Due to the aggressive reaction of air (oxygen) with carbon, burnout occurs not only inside the pores but also on the external surface of the carbon, resulting in poor yield. Thus, from an economical aspect, utilization of CO<sub>2</sub> is more preferable. CO<sub>2</sub> is the most frequently used activating gas as it is easy to handle and clean, and ensures overall control of the activation process due to the slow reaction rate at temperatures around 800 °C (Ioannidou and Zabaniotou 2007; Tseng and Tseng 2005).

#### *Chemical activation*

In the first step, the carbonaceous precursors are impregnated with a predefined ratio of chemical activating agents for dehydrating purposes. The oxidants used are phosphoric acid, potassium carbonate, zinc chloride, sodium hydroxide, lithium hydroxide, and potassium hydroxide. Chemical activation is usually conducted at a temperature lower than that used in physical activation. The reaction between the chemicals and the carbon residues degrade the cellulosic backbone. This process can improve the pore development in the carbon structure due to the dehydration and oxidation reactions of the chemicals.

**Table 3.** Physical Activation of Lignocellulosic Biomass

Biomass	Carbonization Temperature (°C)	Carbonization Time (h)	Activating agent	Activation Temperature (°C)	Activation Time (h)	Production Steps	References
Jute fiber & coconut fiber	-	-	CO <sub>2</sub>	950	0.5	Stage 1	Phan <i>et al.</i> 2000
Date stone	500-800	1	Steam	500-800	0.5-9	Stage 2	Bouchelta <i>et al.</i> 2008
Oil palm shell	400-900	0.5-3	CO <sub>2</sub>	900	0.5	Stage 2	Lua <i>et al.</i> 2006
Coconut shell	325	2.5	Steam	800	2	Stage 2	Achaw and Aftane 2007
Oil palm fiber and oil palm shell	600	2	CO <sub>2</sub>	500-900	0.17-1	Stage 2	Guo and Lua 2000
Rice straw	900	1	CO <sub>2</sub>	700-900	1-6	Stages 1 and 2	Yun <i>et al.</i> 2001
Pistachio nutshell	500	2	CO <sub>2</sub>	725-825	0.5-3	Stage 2	Yang and Lua 2003
Pecan shell	700	1	Steam	850	2	Stage 2	Ng <i>et al.</i> 2003
Candlenut shell	700	1	CO <sub>2</sub>	800	0.5-6	Stage 2	Turmuzi <i>et al.</i> 2004
Palm shell, coconut shell	850	1	CO <sub>2</sub>	700-900	1	Stage 2	Daud and Ali 2004
Corn cob	550	3	Air steam	350	0.08-1.33	Stage 2	El-Hendawy 2005
Pistachio shell	550	2	Steam	890	3	Stage 2	Wu <i>et al.</i> 2005
Apricot stone	-	-	Steam	650-800	1-4	Stage 1	Sentorun-Shalaby <i>et al.</i> 2006
Oil palm empty fruit bunch	-	-	Steam	300-800	0.5-6	Stage 1	Alam <i>et al.</i> 2007
Almond shell	600	-	N <sub>2</sub> /steam	850	-	Stage 2	Gonzalez <i>et al.</i> 2009
Walnut shell	600	-	N <sub>2</sub> /steam	850	-	Stage 2	Gonzalez <i>et al.</i> 2009
Almond tree pruning	600	-	N <sub>2</sub> /steam	850	-	Stage 2	Gonzalez <i>et al.</i> 2009
<i>M. oleifera</i> seed	-	-	Steam	800	-	Stage 1	Warhurst <i>et al.</i> 1997



The carbon yields of chemical activation are relatively higher (Sudaryanto *et al.* 2006; Mohanty *et al.* 2005). However, one disadvantage of chemical activation is that a further washing stage is required for complete removal of the chemical agent. Chemical activation by using phosphoric acid has been reported to be more suitable for producing fibrous activated carbons from cellulose fiber compared with physical activation by CO<sub>2</sub>. This is because it could create a highly porous structure, enabling a high adsorption capacity for micro pollutants such as phenol (Phan *et al.* 2006).

H<sub>3</sub>PO<sub>4</sub> acts as an acid catalyst to enhance bond cleavage of the lignocellulosic matrix as well as inducing the hydrolysis, condensation, and dehydration reactions. It promotes cross-linking reactions between phosphoric acid and the constituent biopolymers present inside the biomass. It can act as a template because the volume occupied by the acid inside the interior of the activated biomass is coincident with the micropore volume of the activated carbon derived (Zuo *et al.* 2009). Impregnation with ZnCl<sub>2</sub> causes degradation of the biomass and due to carbonization, it results in charring and aromatization of the carbon skeleton with a porous texture. Some of the previous studies reporting on the chemical activation of various agricultural byproducts are shown in Table 4.

KOH was found to be a better activating agent compared with ZnCl<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>, because KOH not only requires less energy than water vapor but it also has the least impact on the environment (Cao *et al.* 2006). KOH activation of peanut hull–produced activated carbon having a low surface area, similar to steam pyrolysis (Girgis *et al.* 2002). The activation step using KOH can be conducted in a glass reactor placed in a modified microwave oven using a frequency of 2.45 GHz (Foo and Hameed 2011). The specific surface areas of the two types of carbon derived from pistachio nutshells by KOH activation in a conventional electric oven and a modified microwave oven were very similar (700 and 796 m<sup>2</sup>/g). This suggested that the two methods (conventional and non-conventional) are effective for the preparation of activated carbon (Foo and Hameed 2011).

In general, chemical activation of the biomass with KOH and NaOH gives rise to carbons with high specific surface areas (>1000 m<sup>2</sup>/g). It is reported that the chemical activation costs can be reduced by using NaOH rather than KOH (Tongpoothorn *et al.* 2011; Vargas *et al.* 2011). It was reported earlier in the literature that a soft precursor such as rice husk activated with KOH had a surface area about 2551 m<sup>2</sup>/g within 60 min, whereas the surface area of the carbon became 2952 m<sup>2</sup>/g after NaOH activation for 90 min (Chen *et al.* 2011). It was concluded that intercalation of metallic sodium inside the carbon matrix is a comparatively slower process than potassium due to its higher boiling point (Qureshi 2008). Activated carbon was produced from red oak, walnut shell, and corncob using LiOH, NaOH, and KOH. It was found that the mass loss for activated carbon obtained by LiOH was highest. This made LiOH an unfavorable activation agent compared with KOH and NaOH (Leimkuehler 2010). However, these two alkalis are corrosive and deleterious chemicals. For this reason, recent studies have used K<sub>2</sub>CO<sub>3</sub> to yield activated carbon in one step. K<sub>2</sub>CO<sub>3</sub> is an environmentally safe reagent and is broadly used for food additives (Hayashi *et al.* 2002).

**Table 4.** Chemical Activation of Lignocellulosic Biomass

Biomass	Carbonization Temperature (°C)	Carbonization Time (h)	Activating Agent	Activation Temperature (°C)	Activation Time (h)	Production Steps	Reference
Acorn, olive seed	400-800	1	H <sub>3</sub> PO <sub>4</sub>	-	-	Stage 1	Lafi 2001
Sugarcane bagasse	500	0.5	ZnCl <sub>2</sub>	-	-	Stage 1	Tsai <i>et al.</i> 2001
Rice straw	700-1000	1	KOH	600-950	1	Stages 1 and 2	Oh and Park 2002
Chickpea husk	500-900	1	K <sub>2</sub> CO <sub>3</sub>	-	-	Stage 1	Hayashi <i>et al.</i> 2002
Date pit	300-700	2	H <sub>3</sub> PO <sub>4</sub>	-	-	Stage 1	Girgis and El-Hendawy 2002
Palm shell	200-600	2	H <sub>3</sub> PO <sub>4</sub>	-	-	Stage 1	Guo and Lua 2003
Guava seed	200-750	1	ZnCl <sub>2</sub>	700	1	Stage 2	Rahman and Saad 2003
Pistachio nutshell	500	2	KOH	500-900	2	Stage 2	Lua and Yang 2004
Sago waste	105	3	H <sub>3</sub> SO <sub>4</sub>	-	0.75	Stage 1	Kadirvelu <i>et al.</i> 2004
Rubber wood sawdust	200	0.25	H <sub>3</sub> PO <sub>4</sub>	500	-	Stage 2	Srinivasakannan and Bakar 2004
Rice husk	450	-	KOH, NaOH	400	0.3-1	Stage 2	Guo <i>et al.</i> 2005
Olive-seed waste reduce	800	1	KOH	800-900	1-4	Stage 2	Stavropoulos and Zabaniotou 2005
Rubber wood sawdust	400	1	H <sub>3</sub> PO <sub>4</sub>	-	-	Stage 1	Kalavathy <i>et al.</i> 2005; Karthikeyan <i>et al.</i> 2005
<i>Tectona grandis</i> sawdust	300-600	1-3	ZnCl <sub>2</sub>	-	-	Stage 1	Mohanty <i>et al.</i> 2005
Pistachio shell	550/2	2	KOH	780	1	Stage 2	Wu <i>et al.</i> 2005
Corncob	450	4	KOH	850	1.2	Stage 2	Cao <i>et al.</i> 2006
Cassava peel	450-750	1-3	KOH	-	1	Stage 1	Sudaryanto <i>et al.</i> 2006

**Table 4.** Chemical Activation of Ligno-cellulosic Biomass (continued)

Biomass	Carbonization Temperature (°C)	Carbonization Time (h)	Activating Agent	Activation Temperature (°C)	Activation Time (h)	Production Steps	References
Olive stone, walnut shell	600	1	KOH	900	1	Stage 2	Martinez <i>et al.</i> 2006
Jute fiber	900	2	H <sub>3</sub> PO <sub>4</sub>	-	-	Stage 1	Phan <i>et al.</i> 2006
Coconut fiber	600	2	KOH, NaOH, CaCO <sub>3</sub> , H <sub>3</sub> PO <sub>4</sub> , ZnCl <sub>2</sub>	800	1	Stage 2	Radhika and Palanivelu 2006
Palm shell	600-1000	2	K <sub>2</sub> CO <sub>3</sub>	-	-	Stage 1	Adinata <i>et al.</i> 2007
Pecan shell	300-500	1	H <sub>3</sub> PO <sub>4</sub>	-	-	Stage 1	Guo and Rockstraw 2007
Olive kernel	270-600	-	KOH	800-900	1-4	Stage 2	Zabaniotou <i>et al.</i> 2008
Olive stone	700	1	ZnCl <sub>2</sub>	-	-	Stage 1	Spahis <i>et al.</i> 2008
Peach stone	500	2	H <sub>3</sub> PO <sub>4</sub>	-	-	Stage 1	Attia <i>et al.</i> 2008
Sunflower oil cake	600	0	H <sub>3</sub> SO <sub>4</sub>	-	-	Stage 1	Karagoz <i>et al.</i> 2008
Jute fiber	100	12	H <sub>3</sub> PO <sub>4</sub>	-	-	Stage 1	Senthilkumar <i>et al.</i> 2005
Corn cob	550	3	KOH	700	1	Stage 2	El-Hendawy 2005
Tea fruit peel	-	-	H <sub>3</sub> PO <sub>4</sub> , ZnCl <sub>2</sub>	500	40 min	Stage 1	Gao <i>et al.</i> 2013
<i>Acacia mangium</i> wood	-	-	KOH, CaO	500	2	Stage 1	Danish <i>et al.</i> 2011
Flamboyant ( <i>Delonix regia</i> ) pods	500	1.5	NaOH	700	1.5	Stage 2	Vargas <i>et al.</i> 2011

**Table 4.** Chemical Activation of Lignocellulosic Biomass (continued)

Biomass	Carbonization Temperature (°C)	Carbonization Time (h)	Activating Agent	Activation Temperature (°C)	Activation Time (h)	Production Steps	Reference
<i>Jatropha curcas</i>	400	1	NaOH	800	2	Stage 2	Tongpoothorn <i>et al.</i> 2011
Sea-buckthorn stones	-	-	ZnCl <sub>2</sub>	550	3	Stage 1	Mohammadi <i>et al.</i> 2010
Sea-buckthorn stones	-	-	H <sub>3</sub> PO <sub>4</sub>	550	3	Stage 1	Mohammadi <i>et al.</i> 2010
Palm shell	-	-	ZnCl <sub>2</sub>	500	2	Stage 1	Arami <i>et al.</i> 2010
Walnut shell	-	-	ZnCl <sub>2</sub>	450	1	Stage 1	Yang and Qiu 2010
<i>Euphorbia antiquorum</i> L.	400	-	H <sub>3</sub> PO <sub>4</sub>	800	10 min	Stage 2	Sivakumar and Palanisami 2009
<i>Thevetia peruviana</i>	400	30 min	KOH	800	10 min	Stage 2	Baseri <i>et al.</i> 2012
<i>Thevetia peruviana</i>	400	-	H <sub>3</sub> PO <sub>4</sub>	800	10 min	Stage 2	Baseri <i>et al.</i> 2012
<i>Enteromorpha prolifera</i>	-	-	ZnCl <sub>2</sub>	500	1	Stage 1	Li <i>et al.</i> 2010
Olive stone	-	-	ZnCl <sub>2</sub>	200-700	30-180 min	Stage 1	Yavuz <i>et al.</i> 2010
Tamarind wood	-	-	ZnCl <sub>2</sub>	439	40 min	Stage 1	Acharya <i>et al.</i> 2009
<i>Cunninghamia lanceolata</i>	-	-	H <sub>3</sub> PO <sub>4</sub>	475	90 min	Stage 1	Zuo <i>et al.</i> 2009
<i>Sargassum longifolium</i> , red Seaweed, <i>Hypnea valentiae</i>	-	-	ZnCl <sub>2</sub>	400-800	2	Stage 1	Aravindhan <i>et al.</i> 2009
Soybean oil cake	-	-	K <sub>2</sub> CO <sub>3</sub> , KOH	600, 800	1	Stage 1	Tay <i>et al.</i> 2009
Coffee endocarp	-	-	KOH	650, 750, 850	2	Stage 1	Nabais <i>et al.</i> 2008
<i>Artocarpus heterophyllus</i> peel	200	30	H <sub>3</sub> PO <sub>4</sub>	550	45 min	Stage 2	Prahas <i>et al.</i> 2008

It has been observed that sometimes a one-step process for producing activated carbon is not efficient. In a one-step process, enough activating agent may not be able to penetrate inside the biomass and break down the cross-linkages or react with the resultant carbon sufficiently to generate abundant pores. In this context, if the chemical activating agent is added with the previously carbonized materials or char containing a certain amount of porosity, that would facilitate the activating agent to diffuse into the pores and react with the carbon easily. Therefore, it can be concluded that addition of the activating agent after the raw material is carbonized would be better (Cao *et al.* 2006).

#### *Physiochemical activation*

The majority of the research conducted by previous researchers used either the physical or the chemical activation method alone. This yielded activated carbons either having low surface area and/or being mainly microporous in nature (Daud and Ali 2004; Stavropoulos and Zabanjotou 2005; Sudaryanto *et al.* 2006; Lua *et al.* 2006). In the case of the physiochemical activation method, physical and chemical activations are performed simultaneously after carbonization of the precursors. The combination of the chemical and physical activating agent can produce activated carbon having specific surface properties (Khalili *et al.* 2000). Table 5 lists some of the biomass types that were used to prepare activated carbon by the physiochemical activation method.

The physiochemical activation method has been employed by Hu and Srinivasan (2001) to obtain high surface area, granular, mesoporous activated carbons with mesopore volume above 70%. Several activating agents, mainly phosphoric acid, zinc chloride, and alkaline metal compounds have been used previously. However, the use of zinc chloride is not preferable because the activated carbon produced by zinc chloride cannot be used in pharmaceutical and food industries as it may contaminate the product due to the liberation of toxic zinc (Srinivasakannan and Bakar 2004). El-Hendawy (2005) described KOH as more efficient on the precursor than char where the porosity is not very prominent. Corn cob fiber can strongly adsorb KOH during impregnation, while in carbonization, KOH shows a very limited effect on the produced carbon. The strongly adsorbed KOH does not disappear by washing with distilled water and still remains on the surface, causing partial blockage of the existing pores. Therefore, activation with KOH may need subsequent gasification with CO<sub>2</sub> or steam. The combined activation procedure will impinge on the pore cavity, thus leading to a well-developed porous structure (El-Hendawy 2005). Tseng *et al.* (2006) found that KOH activation alone could only produce a microporous type of activated carbon. However, the process of KOH impregnation along with CO<sub>2</sub> gasification had produced activated carbon having a higher ratio of macropores and mesopores. This improves mass transfer within the activated carbon matrix.

#### **Application of Carbon Materials as Adsorbent**

The performance of activated carbons derived from different lignocellulosic residues for the removal of a specific pollutant from waste water depends on the surface chemistry and textural properties (Elizalde-González and Hernández-Montoya 2008). Surface areas, pore size distribution, functional groups, and various other physiochemical parameters play significant roles in the adsorption process of a given pollutant.

**Table 5.** Physiochemical Activation of Lignocellulosic Biomass

Biomass	Carbonization Temperature (°C)	Carbonization Time (h)	Activating Agent	Activation Temperature (°C)	Activation Time (h)	Production Steps	Reference
Date stone	-	-	HNO <sub>3</sub> /steam	600	-	Stage 1	Hazourli <i>et al.</i> 2009
Date stone	-	-	H <sub>3</sub> PO <sub>4</sub> /steam	600	-	Stage 1	Hazourli <i>et al.</i> 2009
Olive stone	-	-	CaCl <sub>2</sub> /CO <sub>2</sub>	800	-	Stage 1	Juarez-Galan <i>et al.</i> 2009
Pistachio shell	-	-	Steam	450	1.5	Stage 1	Wu <i>et al.</i> 2005
Sugarcane bagasse	-	-	H <sub>2</sub> SO <sub>4</sub> /air	160	-	Stage 1	
Coconut shell	500	3	ZnCl <sub>2</sub> /steam	900	0.5	Stage 2	Azevedo <i>et al.</i> 2007
Coconut shell and palm seed	-	-	ZnCl <sub>2</sub> /CO <sub>2</sub>	800	2-3	Stage 1	Hu and Srinivasan 2001
Coir pith	-	-	H <sub>2</sub> SO <sub>4</sub> /CO <sub>2</sub>	900	0.5	Stage 1	Santhy and Selvapathy 2006
Rice husk	-	-	ZnCl <sub>2</sub> /CO <sub>2</sub>	600	1	Stage 1	Yalcin and Sevinc 2000
Corn cob	450	1.5	KOH/CO <sub>2</sub>	780	1	Stage 2	Tseng <i>et al.</i> 2006
Rattan sawdust	700	1	KOH/CO <sub>2</sub>	750	2	Stage 2	Hameed <i>et al.</i> 2007b
Kenaf core	400	2	KOH/CO <sub>2</sub>			Stage 2	Chowdhury <i>et al.</i> 2012b

Until recently, different types of kinetics, isotherms, and thermodynamics characterization have been performed to study the sorption process of priority water pollutants using lignocellulosic-based activated carbons. Most of these studies were conducted under batch conditions. However, a limited number of studies using dynamic conditions (*i.e.* packed bed columns) have been reported.

## **Removal of Inorganic Contaminants**

### *Removal of cations*

Among various pollutants present in surface water, inorganic species of heavy metals and metalloids are of major concern as they are difficult to remove. Such difficulty can be attributed to their smaller ionic size, bio magnification in the food chain, complex state of existence, very low concentrations in high volume, and competition with non-toxic inorganic species (Wojnarovits *et al.* 2010; Tajar *et al.* 2009).

It was reported that polar or acidic oxygen functional groups on the surface of activated carbons play a fundamental role in the sorption of metal (Basso *et al.* 2002). The functional groups present in activated carbon include carbonyls, phenols, lactones, and carboxylic acids (Basso *et al.* 2002). It was concluded that the higher the content of the functional groups, the greater the sorption capacity exhibited by the activated carbon. Activated carbons with sulfur functional groups are suitable for the removal of some heavy metals such as cadmium (Tajar *et al.* 2009). The cation exchange capacity of activated carbons can be enhanced via chemical activation (Puziy *et al.* 2005). The activated carbons prepared from phosphoric acid activation may show a considerable cation-exchange capacity. Some literature has stated that the cation-exchange properties of activated carbons are dominated by the presence of carboxylate, phenolic, phosphorous, and thiol-containing surface groups (Adil 2006; SenGupta 2002; Dastgheib, and Rockstraw 2001). Dastgheib and Rockstraw (2001) reported that an ion-exchange and surface complexation with oxygen- and phosphorus-containing groups on pecan-shell activated carbon may be involved in the adsorption of copper from water.

Lead has been classified as a serious hazardous heavy metal because it can diffuse inside the soft tissues and form metallothionein. The toxicity symptoms are brain damage, uncoordinated body movement, convulsions, loss of appetite, and after a certain time coma and death. It is one of the most widely used metals in piping, accumulators, lead chambers, anti-knock substances, soldering, and colored pigments. It was reported that several metal-processing industries release lead with organic chelating agents citric and tartaric acid. In this regard, rubber wood sawdust-based steam pyrolyzed carbon was used to adsorb lead in a multi-component system of lead with citric acid (Sreejalekshmi *et al.* 2009). The adsorbed citric acid introduces a  $-\text{COOH}$  group onto the surface of the carbon, creating more sorption sites for lead. Cadmium is also considered a serious water pollutant in several countries. Even at very low concentrations, it is highly toxic to the aquatic environment and to human health (Wang *et al.* 2011). Different activating salts ( $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{K}_2\text{CO}_3$ ) were employed for activated carbon obtained from coconut shells for adsorption of cadmium ions (Gimba *et al.* 2009).  $\text{H}_3\text{PO}_4$  acid activated *Arundo donax* plant canes-based carbon was used for the removal of cadmium and nickel ions (Basso *et al.* 2002). *Spartina alterniflora* plant (Wang *et al.* 2011) activated carbon can be used for preparing adsorbents for cadmium removal. Molybdenum is also the most concentrated trace metal in seawater, which exhibits stability and weak adsorption behavior (Bostick *et al.* 2003). It can be readily accumulated by forage plants, and

consequently consumed by the grazing ruminant animals. It was observed that zinc chloride-treated activated carbon developed from coir pith was an effective adsorbent for the removal of molybdate ions (Namasivayam and Sangeetha 2006b). The study showed that addition of perchlorate, thiocyanate, sulphate, and chloride reduced the removal whereas phosphate hardly influenced the removal of molybdate ions from aqueous solution. Copper has been removed by pecan shell (Dastgheib and Rockstraw 2001), fruit stones (Puziy *et al.* 2005), kenaf fiber (Chowdhury *et al.* 2012c), olive-waste (Baccar *et al.* 2009), and coconut palm-based activated carbon (de Lima *et al.* 2011). Arsenic (III) was removed from synthetic and industrial waste water by using copper-impregnated, coconut-husk carbon where maximum removal percentage was observed at pH 12 (Manju *et al.* 1998). Maximum monolayer sorption capacity was found to be 146.30 mg/g which increased with the increase of temperature. Table 6 summarizes different types of lignocellulosic precursors that have been used for the preparation of activated carbons for heavy metal removal.

**Table 6.** Application of Activated Carbons Obtained from Lignocellulosic Biomass for Removal of Heavy Metal

Lignocellulosic Biomass	Pollutant	Activating Agent	Reference
Mangosteen fruit shell	Lead	KOH, CO <sub>2</sub>	Chowdhury <i>et al.</i> 2012a
Kenaf core	Copper	KOH, CO <sub>2</sub>	Chowdhury <i>et al.</i> 2012b
<i>Spartina alterniflora</i> plant	Cadmium	H <sub>3</sub> PO <sub>4</sub>	Wang <i>et al.</i> 2011
Coconut palm	Copper, cadmium, chromium	H <sub>2</sub> O, O <sub>2</sub>	de Lima <i>et al.</i> 2011
Pecan nutshell	Lead	H <sub>3</sub> PO <sub>4</sub>	Hernandez-Montoya <i>et al.</i> 2011
Oak cup pulps	Chromium	H <sub>3</sub> PO <sub>4</sub> , ZnCl <sub>2</sub>	Timur <i>et al.</i> 2010
Nutshell	Cadmium	H <sub>3</sub> PO <sub>4</sub> , SO <sub>2</sub>	Tajar <i>et al.</i> 2009
Maize stalk	Lead	KOH	El-Hendawy 2009
Coconut shell	Lead, copper, mercury	K <sub>2</sub> CO <sub>3</sub> , FeCl <sub>2</sub> , ZnCl <sub>2</sub> , CaCl <sub>2</sub>	Gimba <i>et al.</i> 2009
African palm pit	Lead	HNO <sub>3</sub>	Giraldo and Moreno-Piraján 2008
Cane sugar bagasse	Lead	HNO <sub>3</sub>	Giraldo and Moreno-Piraján 2008
Grape seed	Copper	ZnCl <sub>2</sub>	Ozçimen and Ersoy-Mericboyu 2009
Chestnut shell	Copper	ZnCl <sub>2</sub>	Ozçimen and Ersoy-Mericboyu 2009
<i>Pinus sylvestris</i> sawdust	Chromium	HCl, NaOH, H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub>	Alvarez <i>et al.</i> 2007
Apricot and peach stone	Copper	H <sub>3</sub> PO <sub>4</sub> , air	Puziy <i>et al.</i> 2007
Coir pith	Nickel, mercury, chromium	ZnCl <sub>2</sub>	Namasivayam and Sangeetha 2006a
<i>Arundo donax</i> plant canes	Cadmium, nickel	H <sub>3</sub> PO <sub>4</sub> , CO <sub>2</sub> , air	Basso <i>et al.</i> 2002
Pecan shell	Copper	H <sub>3</sub> PO <sub>4</sub> , air	Dastgheib and Rockstraw 2001



Chromium is a mutagen and potentially carcinogenic heavy metal. Previous research reported that chromium can be removed by using activated carbons derived from *Pinus sylvestris* sawdust (Álvarez *et al.* 2007). The sawdust was activated by using HCl, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, AlCl<sub>3</sub>, and NaOH, and it was observed that H<sub>3</sub>PO<sub>4</sub> acid-activated sawdust showed the maximum uptake for chromium. Oak cups pulp was activated using H<sub>3</sub>PO<sub>4</sub> and ZnCl<sub>2</sub> (Timur *et al.* 2010) to remove the chromium. *Terminalia arjuna* nut and *Casurina equisetifolia* leaves were activated by ZnCl<sub>2</sub> to adsorb chromium. Nickel and mercury were removed using ZnCl<sub>2</sub>-activated coir-pith carbon (Namasivayam and Sangeetha 2006a).

### Removal of anions

The sorption performance of thiocyanate ions was investigated on ZnCl<sub>2</sub>-activated coir-pith carbon (Namasivayam and Sangeetha 2005). The influence of different process parameters such as contact time, thiocyanate concentration, adsorbent dose, pH, and temperature was studied. Experimental data followed both Langmuir and Freundlich isotherms and the sorption kinetics obeyed the second-order kinetic model. Maximum monolayer adsorption capacity was found to be 16.2 mg/g. The presence of different concentrations of vanadate, nitrate, molybdate, selenite, and perchlorate reduced the removal percentage of thiocyanate, whereas phosphate, sulfate, and chloride had an insignificant influence on the removal of thiocyanate.

ZnCl<sub>2</sub>-activated carbon developed from coir pith was used for the removal of sulfate from aqueous solution, and adsorption was found to be at maximum in the pH range 3.0 to 9.0 (Namasivayam and Sangeetha 2008). The addition of other anions—perchlorate, chloride, molybdate, nitrate, and phosphate—reduced the removal of sulfate. Experiments with synthetic ground water showed that the percent removal of sulfate anion by ZnCl<sub>2</sub>-activated carbon is higher compared with synthetic sulfate solutions due to the presence of calcium in the ground water.

The presence of fluoride anions in drinking water is detrimental, as concentrations higher than 1.5 mg/L are the principal cause of dental fluorosis and may cause bone fluorosis in children. Fluoride can interact with some bivalent ions such as calcium (Hernández-Montoya *et al.* 2011). It exhibits a strong affinity towards multivalent metal ions, e.g., Al<sup>3+</sup>, Fe<sup>3+</sup>, and Zr<sup>4+</sup> (Alagumuthu and Rajan 2010). In this regard cashew nutshells were impregnated with zirconium oxy chloride before carbonization (Alagumuthu and Rajan 2010). The researchers concluded that the fluoride ions were attracted by chloride and hydroxide species present over the carbon, and the sorption took place by both electrostatic interaction and chemisorption mechanisms. Activated carbons obtained from pecan nutshells and eggshell wastes can be used for fluoride ions removal from water (Hernández-Montoya *et al.* 2012). The presence of calcium-containing species over the surface of carbon played a significant role in the uptake of fluoride ions.

### Removal of Organic Pollutants

Oxygen-containing functional groups predominate in the sorption process of phenol and its derivatives (Tamir *et al.* 2010). Most of the studies indicated that N and O heteroatoms are playing a vital role in phenol adsorption (Nabais *et al.* 2009). Some research concluded that phenol adsorption onto activated carbon takes place by a complex mechanism of electrostatic and dispersion interactions (Nabais *et al.* 2009). The sorption process has been related to the electrostatic force of attraction between dyes and

activated carbon and also in some cases through intermediate complex formation (Timur *et al.* 2010). The literature indicates that several mechanisms including ion-dipole forces, ion exchange, and hydrogen bonding are responsible for the sorption of dyes.

#### *Removal of phenolic compounds*

Phenols and their derivatives are considered priority pollutants by the U.S. EPA and other environmental protection agencies. The process effluents from steel industries, gasoline, plastic, pesticides, and pharmaceuticals introduce phenol into water bodies (Timur *et al.* 2010). The Environmental Protection Agency (EPA) has set a limit of 0.1 mg/L of phenol in waste effluents. Considering its high toxicity, the World Health Organization (WHO) has set a limit of 0.001 mg/L of phenol concentration in potable water. Table 7 is a summary of lignocellulosic biomass that so far has been employed to produce activated carbon for removal of phenolic compounds from waste water.

**Table 7.** Application of Activated Carbons Obtained from Lignocellulosic Biomass for Removal of Phenolic Compounds

Lignocellulosic Biomass	Pollutant	Activating Agent	Reference
Vine shoot	Phenol, p-nitrophenol	HNO <sub>3</sub> and CO <sub>2</sub>	Mourao <i>et al.</i> 2011
Almond shell	Phenol, p-nitrophenol	HNO <sub>3</sub> and CO <sub>2</sub>	Mourao <i>et al.</i> 2011
Pecan nutshell	Phenol	H <sub>3</sub> PO <sub>4</sub>	Bello-Huitle <i>et al.</i> 2010
Oak cup pulps	Phenol	H <sub>3</sub> PO <sub>4</sub> and ZnCl <sub>2</sub>	Timur <i>et al.</i> 2010
Castile nutshells	Phenol	H <sub>3</sub> PO <sub>4</sub>	Bello-Huitle <i>et al.</i> 2010
Kenaf	Phenol	HNO <sub>3</sub> and CO <sub>2</sub>	Nabais <i>et al.</i> 2009
Rapeseed	Phenol	HNO <sub>3</sub> and CO <sub>2</sub>	Nabais <i>et al.</i> 2009
Palm fiber	2, 4, 6 –tri chlorophenol	CO <sub>2</sub> , KOH	Tan 2008
Palm shell	2, 4, 6 –tri chlorophenol	CO <sub>2</sub> , KOH	Tan 2008
Empty fruit bunch	2, 4, 6 –tri chlorophenol	CO <sub>2</sub> , KOH	Tan 2008
Coconut husk	2, 4, 6 –tri chlorophenol	CO <sub>2</sub> , KOH	Tan 2008
Oil palm empty fruit bunch	2,4- dichlorophenol	N <sub>2</sub>	Zahangir <i>et al.</i> 2007
Cedar wood	p-nitrophenol	H <sub>2</sub> SO <sub>4</sub> and CO <sub>2</sub>	Cuerda-Correa <i>et al.</i> 2006
Coir pith	Phenol	ZnCl <sub>2</sub>	Namasivayam and Sangeetha 2006a
Fir wood	Phenol, p-cresol	KOH and CO <sub>2</sub>	Wu and Tseng 2006
<i>Eucalyptus grandis</i>	Phenol	N <sub>2</sub>	Tancredi <i>et al.</i> 2004

Carbon-oxygen groups of activated carbon act as electron donors, and aromatic rings of phenol act as acceptors during the sorption process of phenolic compounds. In another study it was reported that acidic carbon-oxygen functional groups, which evolve CO<sub>2</sub>, suppress the removal of phenolic compounds, whereas the nonacidic surface groups producing CO enhance the sorption efficiencies of phenolic compounds (Bansal *et al.*

2002). It was suggested that the interaction between  $\pi$  electron systems of activated carbon and aromatic rings has a strong influence on the sorption of phenol and chlorophenols (Jung *et al.* 2001). Recent research indicated that  $\text{ZnCl}_2$ -activated oak cups pulp carbon showed better sorption capacities than  $\text{H}_3\text{PO}_4$ -activated carbon (Timur *et al.* 2010). Pecan and castile nutshells were chemically activated, and the researchers concluded that pecan nutshells were better precursors for phenol uptake (Bello-Huitle *et al.* 2010). Batch experiments were conducted for phenol sorption using microporous activated carbons derived from kenaf and rapeseed (Nabais *et al.* 2009). Oil palm empty fruit bunches were activated for removal of phenolic compounds (Alam *et al.* 2007). Based on the findings, it was concluded that smaller amounts of acidic functional groups will initiate more removal efficiencies for phenolic compounds.

### *Removal of dyes*

Dyes in waste effluent are another serious problem due to their persistent and carcinogenic nature. They can affect aquatic flora and fauna to a great extent. Several industries such as textile, food coloring, cosmetics, carpet industries, along with pulp and paper industries utilize large quantities of dyes. Most dyes used in textile industries are stable in light. They are not biologically degradable and are resistant to aerobic digestion. The dye effluents exhibit toxic effects on microbial populations and can be carcinogenic to mammals. Dyes used in industrial processes can be divided into five classes: acid, basic, direct, disperse, and reactive. Recently  $\text{HNO}_3$  acid-activated *Luffa egyptiaca* plant was used to prepare activated carbon for the removal of direct blue 106 (El-Ashtoukhy 2009). Equilibrium studies were performed at 25 °C and for different pH conditions. Results showed that the maximum adsorption was obtained at pH 2. Another sea plant, namely *P. oceanica* (L.), was activated by  $\text{ZnCl}_2$  to produce activated carbon for methylene blue adsorption, and the sorption capacity observed was 280 mg/g (Dural *et al.* 2011). *Euphorbia rigida*-based activated carbon absorbed 114.45 mg/g of methylene blue from aqueous solution. Bamboo wastes have been widely used for the synthesis of activated carbons for dye removal (Ahmad and Hameed 2010; Chan *et al.* 2008; Chan *et al.* 2009). Elizalde-González *et al.* (2007) reported the adsorption of several basic, acid, and reactive dyes from aqueous solutions by avocado-activated carbons impregnated with  $\text{H}_3\text{PO}_4$ . Anthraquinone dyes (acid blue 80 and acid green 27) were removed by using activated carbons obtained from seeds of mango, guava, and orange (Elizalde-González and Hernández-Montoya 2008). Despite negligible surface area, orange seed-based activated carbon was more efficient for the removal of acid green 27, whereas mango seed-based activated carbon was more effective for the removal of acid blue 80. Pecan and castile nutshells were activated by  $\text{H}_3\text{PO}_4$  for the removal of methylene blue dye from water, and the sorption capacity of pecan nutshells-based activated carbon was higher than that obtained for castile nutshells (Bello-Huitle *et al.* 2010). Hernández-Montoya *et al.* (2011) have reported the preparation of activated carbons for sorption studies of acid blue 25 using pecan nutshells-based carbon and calcium solution extracted from eggshell wastes. Results obtained from these studies suggested that not only the surface area but also the porosity of these activated carbons play an important role in the removal process of the dyes. Based on the findings it was concluded that the interaction between the functional groups of activated carbons and these dyes were very important in the adsorption process. Table 8 is a summary of the lignocellulosic residues that were used to prepare activated carbon for removal of several types of dyes.

**Table 8.** Application of Activated Carbons Obtained from Lignocellulosic Biomass for Removal of Dyes

Lignocellulosic Biomass	Pollutant	Activating Agent	Reference
<i>Pisum sativum</i>	Methylene blue	ZnCl <sub>2</sub>	Geçgel <i>et al.</i> 2013
Corn husk	Methylene blue	ZnCl <sub>2</sub>	Khodaie <i>et al.</i> 2013
Tea peel fruit residues	Methylene blue	ZnCl <sub>2</sub> , H <sub>3</sub> PO <sub>4</sub>	Gao <i>et al.</i> 2013
<i>P. oceanica</i> (L.) dead leaves	Methylene blue	ZnCl <sub>2</sub>	Dural <i>et al.</i> 2011
Pecan nutshell	Acid blue 25	H <sub>3</sub> PO <sub>4</sub> and CaCl <sub>2</sub> solution	Hernández-Montoya <i>et al.</i> 2011
Castile nutshell	Methylene blue	H <sub>3</sub> PO <sub>4</sub>	Bello-Huitle <i>et al.</i> 2010
Oak cups pulp	Basic red 18, Methylene blue, acid red 111	H <sub>3</sub> PO <sub>4</sub> and ZnCl <sub>2</sub>	Timur <i>et al.</i> 2010
Pecan nutshell	Methylene blue	H <sub>3</sub> PO <sub>4</sub>	Bello-Huitle <i>et al.</i> 2010
Coconut shell	Indigo blue	FeCl <sub>3</sub> , ZnCl <sub>2</sub> , CaCl <sub>2</sub> , K <sub>2</sub> CO <sub>3</sub>	Gimba <i>et al.</i> 2009
Bamboo	Acid yellow 117	H <sub>3</sub> PO <sub>4</sub>	Chan <i>et al.</i> 2009
<i>Luffa egypitiaca</i> plant	Direct blue	HNO <sub>3</sub> , H <sub>3</sub> PO <sub>4</sub> and ZnCl <sub>2</sub>	El-Ashtoukhy 2009
Bamboo	Acid blue 25	H <sub>3</sub> PO <sub>4</sub>	Chan <i>et al.</i> 2008
Bamboo	Methylene blue	KOH, CO <sub>2</sub>	Hameed <i>et al.</i> 2007a
Rattan sawdust	Methylene blue	KOH, CO <sub>2</sub>	Hameed <i>et al.</i> 2007b
Durian shell	Methylene blue	KOH	Chandra <i>et al.</i> 2007
Fir wood	Acid Blue 74, Methylene blue	KOH, CO <sub>2</sub>	Wu and Tseng 2006
Coconut flower	Reactive red	ZnCl <sub>2</sub>	Senthilkumar <i>et al.</i> 2006
Jute fiber	Reactive red	ZnCl <sub>2</sub>	Senthilkumar <i>et al.</i> 2006
Olive seed waste	Methylene blue	KOH, CO <sub>2</sub>	Stavropoulos and Zabaniotou 2005
Jute fiber	Methylene blue	H <sub>3</sub> PO <sub>4</sub> , hot air	Senthilkumar <i>et al.</i> 2005

### Removal of pesticides

Leaching of pesticides applied to agricultural land is one of the main reasons for pollution of aqueous effluents. Pesticides and their degradation products are considered as potential hazards for aquatic ecosystems and human health due to their carcinogenicity and mutagenicity. Activated carbon prepared by steam activation of rape seed stalks, soya stalks, corncob, and olive kernels was used to remove bromopropylate pesticides from water, and the removal efficiencies observed were 90% to 100% (Ioannidou *et al.* 2010). Oil palm fronds- and banana stalk-activated carbon were prepared by KOH impregnation and CO<sub>2</sub> gasification to remove bentazon from waste water (Salman and Hameed 2010; Salman *et al.* 2011). 2,4-dichlorophenoxyacetic acid pesticides were also removed by banana stalk-activated carbon. In this study, the removal efficiency of bentazon and 2,4-

dichlorophenoxyacetic acid pesticides was 96.5% from 25 mg/L solution and 98.4% from 50 mg/L solution, respectively (Salman *et al.* 2011).

#### *Removal of pharmaceutical compounds*

The removal of acetaminophen (*i.e.*, paracetamol) from aqueous solution using an activated carbon from peach stones was reported (Cabrita *et al.* 2010). The prepared carbon contained a pyrone and/or chromene-like structure that was characterized by a high content of oxygen functional groups. The prepared carbon showed better performance than that obtained from commercial activated carbon and plastic wastes. This study concluded that the sorption was dominated by a complex process dependent on the physicochemical properties of the activated carbon.

#### **Regeneration of Activated Carbon**

For the feasibility of the process, regeneration of the prepared activated carbon materials is extremely important. The efficiency of the desorbing agents depends on the types of carbon, the concentration of the adsorbed species, the types of adsorbate, and the operating conditions, including concentration of the eluting solution, temperature, contact time, and sorbent dosage employed for the desorption process. The common techniques used for regeneration are solvent regeneration, bio-regeneration, and thermal volatilization. In the case of thermal regeneration, about 5% to 10% of the carbon is lost by attrition and burnoff during each cycle. Moreover, it has the disadvantage of high energy consumption (Hamdaoui *et al.* 2005). The bio-regeneration method is not efficient as most biological activities are slow. It produces a lot of sludge which is non-biodegradable (Hamdaoui *et al.* 2005). Thus, solvent regeneration, in which carbon loss by attrition is negligible, is considered the most attractive technique.

Previous studies indicated that copper-loaded pecan-shell activated carbon was successfully carried out using 10% HCl solution, and about 98% of copper can be desorbed using HCl, whereas distilled water was proven inefficient for desorbing copper (Dastgheib and Rockstraw 2001), which showed that copper was chemically attached over the prepared carbon. Similarly, 90% of cadmium and nickel ions were recovered from *Arundo donax* plant canes-based activated carbon by using HCl (Basso *et al.* 2002). HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> acid-eluting media were used for desorption of cadmium from nutshell-based carbon (Tajar *et al.* 2009). Chromium desorption from *Pinus sylvestris* sawdust-based carbon was carried out with H<sub>2</sub>SO<sub>4</sub> acid (Álvarez *et al.* 2007). After the first regeneration cycle, the sorption performance was reduced successfully. Desorption of molybdate from ZnCl<sub>2</sub> activated coir-pith carbon was insignificant at pH 2.0, which was due to the addition of Cl<sup>-</sup> ions in the form of HCl. Desorption was high at pH > 9.0, and in the pH range 4.0 to 9.0 desorption was negligible for all the concentrations of molybdate under investigation. The findings indicated that the molybdate ions that were adsorbed by the ion exchange mechanism were desorbed and the rest of the molybdate ions that were attached by surface complex formation did not desorb (Namasivayam and Sangeetha 2006). Copper-impregnated coconut-husk carbon loaded with As (III) was regenerated using 30% H<sub>2</sub>O<sub>2</sub> in 0.5 M HNO<sub>3</sub> (Manju *et al.* 1998). After two cycles, the adsorption capacity was decreased from 88.6 to 81.6 % (Manju *et al.* 1998). The study indicated that desorption of As(III) by 30% H<sub>2</sub>O<sub>2</sub> in 0.5 M HNO<sub>3</sub> was due to the formation of H<sub>3</sub>AsO<sub>3</sub> (As(III) species) which is neutral. Another species present was

H<sub>3</sub>AsO<sub>4</sub> (As(V) species), and this was not attracted by the positive surface of the prepared carbon.

In acidic conditions due to the addition of HCl, about 58% to 74% at pH 2, and in basic conditions at pH 11 about 83% to 97% of sulfate was desorbed from coir-pith carbon (Namasivayam and Sangeetha 2008). A similar trend was followed for thiocyanate also where basic pH favours the desorption process (Namasivayam and Sangeetha 2005). HCl and NaOH were used for desorption of fluoride from the adsorbent of zirconium-impregnated cashew nutshell (Alagumuthu and Rajan 2010); 95% of fluoride can be recovered by using a NaOH solution.

Ethanol desorption was carried out successfully to desorb 2,4,6-trichlorophenol and methylene blue from coconut husk, oil palm shell, oil palm empty fruit bunch, and palm fiber-based activated carbon (Tan 2008). The study indicated that about 75.10% and 99.64% methylene blue and 2,4,6-trichloro phenol can be desorbed from coconut-husk activated carbon. The higher removal efficiency of 2,4,6-trichloro phenol was due to its higher solubility and smaller size than the methylene blue molecule.

## CLOSING STATEMENTS

This review has undertaken to enlist the wide range of lignocellulosic biomass which has been employed to prepare carbonaceous adsorbent materials for waste water treatment. Until now the conversion of biomass to carbon has mostly been carried out by the chemical activation of the precursors. The physical activation method yielded carbon with relatively less surface area, but this method does not need additional washing steps and is less corrosive than the chemical method. It is observed that activated carbons with improved adsorption properties can be prepared to remove organic and inorganic pollutants effectively by using the appropriate lignocellulosic precursors and by optimizing the production conditions of carbonization and activation. The literature review revealed that still there is a strong need to carry out extensive research on lignocellulosic biomass based on the following aspects:

1. In order to promote large-scale utilization of biomass-based carbon, special emphasis should be given to the optimization of synthesis conditions.
2. Suitable methodology must be developed to prepare activated carbon from lignocellulosic biomass. The systems need to be efficient enough to remove some large molecular weight organic compounds such as herbicides, pesticides, surfactants, and insecticides from waste effluents.
3. Production costs should be taken into consideration for the economical feasibility of the process.
4. The surface of the prepared activated carbon derived from biomass can be modified by different types of acidic oxidizing agents or bases for targeted pollutant materials.
5. The development of an effective regeneration technique needs to be prioritized in future research to reduce the expenses of waste water treatment. However, a small amount of research has been carried out on the regeneration of activated carbons. From this perspective, further research should be performed to develop effective

regeneration procedures as well as safe disposal of the pollutant-loaded activated carbons used for aqueous phase application.

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