

Review

Lignin – from natural adsorbent to activated carbon: A review

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Abstract

The present review compiles the work done over the last few decades on the use of lignin and lignin-based chars and activated carbons as adsorbents for the removal of substances from water and focuses on the utilisation of lignin as adsorbent, its conversion to chars and activated carbons and the use of these materials as adsorbents. Moreover, the review also examines the textural and surface chemical properties of lignin-based activated carbons. The work so far carried out indicates that lignin is relatively non-reactive and probably the component of lignocellulosic precursors primarily responsible for the microporosity of activated carbons. Under appropriate conditions of activation it is possible to obtain materials with surface areas and pore volumes approaching $2000 \text{ m}^2 \text{ g}^{-1}$ and $1 \text{ cm}^3 \text{ g}^{-1}$, respectively, and these materials have capacities for the aqueous phase adsorption of metallic pollutants that are comparable to those of commercial activated carbons. Relatively little work has so far been published and there is considerable scope for more detailed studies on the preparation, characterisation and adsorption applications of lignin-based activated carbons.

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1. Introduction

Lignin is the second most abundant natural raw material (Gosselink et al., 2004) and nature's most abundant aromatic (phenolic) polymer (Lora and Glasser, 2002), whose main function is to cement the cellulose fibres in plants. It is generally obtained from black liquor, a waste discharged from paper mills in large quantities, and which can pose a major problem of disposal (Mohan and Kartikeyan, 1997; Zhang and Chuang, 2001). On the other hand, as the production of lignin amounts to more than 50 million tons/year there has been increasing interest in the development of economically viable new applications and examples can be found on the web page of the International Lignin Institute (www.ili-lignin.com). Currently, much of the lignin produced by the paper industry is consumed as a fuel. Although there are some other marginal applications, such as an adhesive or tanning agent, no

major large scale application has so far been found (Gosselink et al., 2004). Another possible application for excess lignin is as a precursor for activated carbon (AC) production. In fact, as lignin has a high carbon content and a molecular structure similar to bituminous coal it ought to be an ideal precursor and the data that are currently available confirm that lignin is a particularly interesting material to use. However, until now no detailed review has appeared on the state of art of conversion of lignins into ACs and their use as adsorbents.

2. Lignin: origin, source and chemistry

2.1. Molecular structure

Lignin (Boeriu et al., 2004; Chakar and Ragauskas, 2004) is a natural polymeric product arising from an enzyme initiated dehydrogenative polymerisation of the three primary precursors shown in Fig. 1. It is an integral part of lignocellulosic materials with the relative amount present varying over the approximate range of 10–30%

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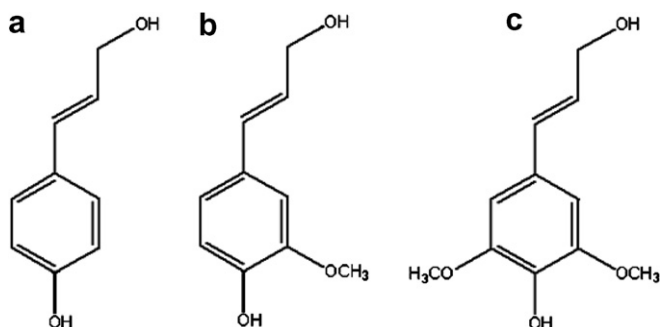


Fig. 1. Lignin precursors: (a) *p*-coumaryl alcohol, (b) coniferyl alcohol and (c) sinapyl alcohol.

although certain materials, such as coir (~45%), have much higher lignin content (Hon, 1996). Besides soft (25–31%) and hard (16–24%) wood other lignocellulosic materials which are sources of lignin include agricultural residues, other plant substances and cork (Hon, 1996; Carrott et al., 2006a,b). The lignin obtained from many of these precursors contains significant amounts, up to ~15%, of ash. This appears to be mainly silica, with lower amounts of sodium and calcium, and trace quantities of other metals (Khezami et al., 2005; Sharma et al., 2004; Rodríguez-Mirasol et al., 1993; Hayashi et al., 2000; Baklanova et al., 2003; Cagniant et al., 2003; Várhegyi et al., 1997; Fierro et al., 2005; Kuznetsov and Shchipko, 1995; Jakab et al., 1997; Ferdous et al., 2002) but can be readily removed by sulfuric acid washing.

Lignins may be divided into three broad classes, namely soft wood, hard wood and grass lignin, according to their composition in structural units (Adler, 1977; Roberts, 1996). A typical soft wood lignin, also called guaiacyl or coniferous lignin, is made up of coniferyl alcohol units. Soft wood lignins isolated by different methods and from different species are very similar in their structure and a

molecular model of a typical soft wood lignin molecule is shown in Fig. 2. The molecule shown has a molar mass of 1692, which is very close to the number average molar mass of alkali (Kraft) lignin commercialised by Aldrich. On the other hand, lignin is highly polydisperse and significant amounts of molecules up to 100 times larger are also present. Hard wood or dicotyledonous angiosperm lignin is made up of coniferyl and sinapyl alcohol units. Finally, grass, annual plant or monocotyledonous angiosperm lignin is made up of coniferyl, sinapyl and *p*-coumaryl units.

2.2. Isolation of lignins

Isolation of lignin (Hon, 1996) from lignocellulosic materials is generally difficult due to condensation and oxidation reactions which occur during the isolation process. The methods reported in the literature can be broadly divided into those that are based on the hydrolysis or solubilisation of cellulose and hemicelluloses by chemical reagents leaving lignin as an insoluble material, and those that are based on the dissolution or removal of lignin and yield solutions from which the product can be recovered by subsequent treatment. The isolation processes can be achieved using chemical and/or mechanical energy, although the former is preferred as damage to the fibres is minimised in this case. Commercial pulping and bleaching processes use acids, alkalis, organic solvents or biological agents which attack the lignin, causing its degradation and dissolution, thereby enabling separation of the cellulose fibres from the lignin.

Alkaline pulping is currently the most widely used method and has two variations referred to as the kraft (or sulfate) and the soda process. Sodium hydroxide is the principal reagent in both, with sodium sulfide being an additional component in the kraft process. Acidic pulping by the sulfite process uses a combination of sulfur dioxide and water at high temperatures and pressures. Of the other methods, none has gained sufficient importance to be used on a commercial scale, although removal of lignin using organic solvents may be of some use (Roberts, 1996).

3. Lignin: as natural adsorbent

3.1. Pure lignin as adsorbent

Published studies, including the representative results given in Table 1, show that lignin can be a good adsorbent over a wide concentration range. However, there have been some significant differences between results reported by different authors and there has also been some debate over whether the uptake of adsorbates by lignin is a process of simple adsorption or a combination of processes.

The first publications were by Wedekind and Garee (1928a,b) who studied the uptake of hydrochloric and sulfurous acids, potassium and ammonium hydroxides and iodine in potassium iodide solution by hydrochloric acid

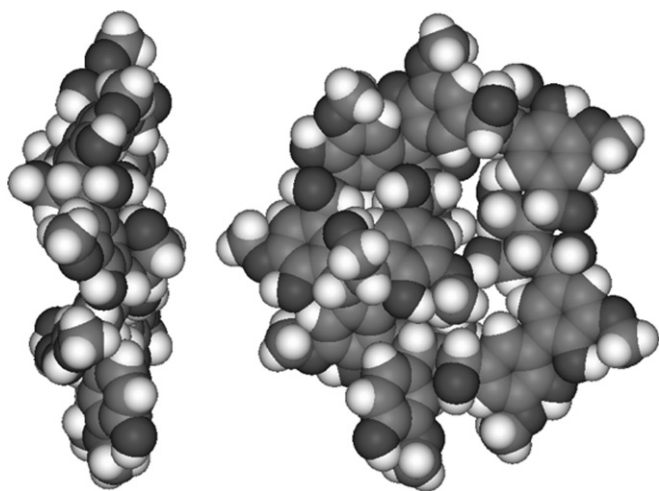


Fig. 2. Molecular model of lignin with molar mass of 1692, containing nine guaiacyl units. White = H; gray = C; black = O. Geometry optimised using DS Viewer Pro 6.0 (Accelrys Software Inc.).

Table 1
Reported sorption capacities (mg g^{-1}) for lignins

Reference	Type	Pb(II)	Cu(II)	Zn(II)	Cd(II)	Hg(II)	Cr(III)	Cr(VI)
Merdy et al. (2002)	Straw		4.2					
Acemioğlu et al. (2003)	Organosolv		~1.7					
Sciban and Klasnja (2004)	Kraft		~3.4					
Sciban and Klasnja (2004)	Hydrolysis		1.7					
Sciban and Klasnja (2004)	Amino		26.4					
Dizhbite et al. (1999)	Amino		26.4				11.5	
Dizhbite et al. (1999)	Hydrolysis		~1.7				~0.8	
Mohan et al. (2006)	Kraft		137		87			
Demirbas (2004)	Lignin (Beech)	8.2			6.7			
Demirbas (2004)	Lignin (Poplar)	9.0			7.5			
Basso et al. (2004)	Lignin ^b				48.3			
Lalvani et al. (2000)	Indulin AT						6.6	5.6
Bailey et al. (1999)	Sulfuric					150		
Srivastava et al. (1994)	Lignin ^a	1865		95				

^a Lignin extracted from black liquor.

^b Lignin from Aldrich Chemical Company.

lignins obtained from beech, oak and the Japanese root dioscorea-tokoro-makino. It was suggested that the uptake varies linearly with the solute/lignin ratio and that the process is partially reversible with the acids but irreversible with the hydroxides. It was also suggested that the assimilation of hydrochloric acid was caused by the formation of a solid solution rather than by adsorption whereas the uptake of potassium hydroxide or ammonium hydroxide involved a chemical combination between the base and the lignin. The authors also studied the sorption of dyes and it was observed that the dyes were completely taken up by the lignin. In this respect lignin differs widely from cellulose which does not permanently fix acid or basic dyes.

One of the most studied solutes is Cu(II). Its sorption on different types of lignin has been studied by Merdy et al. (2002), Acemioğlu et al. (2003), Sciban and Klasnja (2004) and Dizhbite et al. (1999), who all found low uptakes. On the other hand, Kokorevics (as reported by Sciban and Klasnja, 2004) and Dizhbite et al. (1999) using amine functionalised lignin reported significantly higher uptakes of 26.4 mg g^{-1} . Mohan et al. (2006), using Kraft lignin, reported even higher uptakes of 137 mg g^{-1} .

Similar differences have also been found with Cd(II). Cd(II) removal by modified lignin obtained from beech and poplar woods by alkali glycerol delignification was studied by Demirbas (2004), who reported low uptakes, whereas Mohan et al. (2006) and Basso et al. (2004) reported high values of 87 mg g^{-1} and 48.3 mg g^{-1} , respectively. In other studies by Masri et al., as reported by Bailey et al. (1999), a much higher uptake of 150 mg g^{-1} of Hg(II) by sulfuric acid lignin was found.

Much higher differences have been found with Pb(II). Lalvani et al. (1997) reported low values. On the other hand, Srivastava et al. (1994) using lignin extracted from black liquor reported the remarkably high uptake of 1865 mg g^{-1} . These authors also found that the sorption capacity increased with increasing pH and with temperature and suggested that the high adsorption capacity was

due to polyhydric phenols and other functional groups on the lignin surface.

Kraft pine lignin powder was used as adsorbent by Crist et al. (2002, 2003) for removing a wide variety of metal ions and the results showed that the uptake of metals is accompanied by a release of protons or existing metals from the lignin. The binding strength was found to be in the order $\text{Pb(II)} > \text{Cu(II)} > \text{Zn(II)} > \text{Cd(II)} > \text{Ca(II)} > \text{Sr(II)}$. For proton displacement, only more tightly bound metals (Pb(II), Cu(II), Zn(II), Cd(II)) can compete with protons for anion binding sites at low pH, but at high pH, uptake of Ca(II), Sr(II) and Li(I) can also occur. It can be seen from Table 1 that in other studies where different metal ions have been compared the uptake also varies in the same order as the binding strength. This indicates that in spite of the differences in absolute values of uptake reported by different authors, there is a greater consistency in relative uptake values. The results in the Table also suggest the additional order $\text{Pb(II)} > \text{Cu(II)} > \text{Cr(III)} > \text{Cr(VI)}$.

Overall, the results presented in Table 1 suggest that, with the exception of a few results (Sciban and Klasnja, 2004; Dizhbite et al., 1999; Mohan et al., 2006; Bailey et al., 1999; Srivastava et al., 1994), the adsorption capacities of unactivated lignin are comparatively low and that in general lignin is inferior to activated carbon for aqueous phase metal ion removal.

Besides the sorption of metals, lignin has also been used to remove other materials such as dyes, bile acids, cholesterol, surfactants, pesticides and phenols (Dizhbite et al., 1999; Ludvík and Zuman, 2000; Allen et al., 2005; Van Beinum et al., 2006). For example, Dizhbite et al. (1999) studied acid hydrolysis lignins and their nitrogen derivatives for the removal of organic pollutants, bile acids and cholesterol. The materials were found to exhibit good sorption capacity towards phenols and nitrogen containing aromatic compounds. Further, it was suggested that amination of lignocellulosic materials enhances bile acid sorption capacity. Adsorption of two cationic surfactants,

cetylpyridinium chloride and cetyltrimethylammonium chloride, was studied by Agarwal et al. (1999). The authors studied the effect of various parameters such as temperature, pH, concentration and particle size of lignin.

3.2. Lignocellulosic materials as sorbents

An extremely large number of studies on the use of lignocellulosic materials as adsorbents has been published. However, in most of the published work, the composition is not specified and there is no attempt to relate the adsorptive properties to the amount of lignin or cellulose present. Discussion of this work is beyond the scope of this review. Nevertheless, it is worthwhile pointing out that it suggests that lignin is the main component responsible for adsorption by wood and other lignocellulosic materials (Basso et al., 2002, 2004; Dupont and Guillon, 2003).

4. Lignin: as precursor for chars and activated carbons

4.1. Activated carbon

Activated carbons (ACs) are the oldest adsorbents known (Hassler, 1963). ACs have a very porous structure with a large internal surface area ranging from 500 to 2000 m² g⁻¹ and owing to this possess good adsorption capacities towards various substances. They have found application in removing a wide variety of pollutants including both organic and inorganic substances from the liquid or gaseous phases (Gabaldón et al., 2000; Carrott et al., 1991, 2005, 2006a,b; Walker and Weatherley, 1999; Hu et al., 1998; Urano et al., 1991; LeCloirec et al., 1997; Pirbazari et al., 1992; Malhas et al., 2002; Lalezary et al., 1986; McKay et al., 1985). ACs are available in two main forms: powdered activated carbon (PAC) and, in particular, granular activated carbon (GAC). PAC is comprised of fine particles, less than about 0.2 mm in diameter, and thus presents large external surface area and small diffusional resistance. Hence, the rate of adsorption is very high. GAC on the other hand is comprised of larger carbon particles, up to about 5 mm in diameter, with smaller external surface areas compared to PAC. These are generally preferred for the adsorption of gases and vapours and for use in fixed bed filtration systems due to the fact that the granular form is more adaptable to continuous contacting. In addition, GAC can be regenerated, whereas this is often impossible with PAC due to the difficulty of separating the powdered adsorbent from the fluid. Various materials like coal, coconut shells, lignite, wood and peat are commonly used for the preparation of ACs (Mattson and Mark, 1971). A wide variety of other materials have also been used by many workers as source materials (Kennedy et al., 2004; Aygün et al., 2003; Márquez-Montesinos et al., 2001; Razvigorova et al., 1998; Juang et al., 2000; Warhurst et al., 1997; Carrott et al., 2003; Gupta and Ali, 2002) and two basic activation methods have been used.

4.1.1. Physical activation

Physical activation is a process in which the precursor is developed into AC using gases and is generally carried out in a two-step process. Carbonisation is the first stage and involves the formation of a char, which is normally non-porous, by pyrolysis of the precursor at temperatures in the range 600–900 °C in an inert, usually nitrogen, atmosphere. Activation is the second stage and involves contacting the char with an oxidising gas, such as CO₂ or steam, in the temperature range 600–1200 °C, which results in the removal of the more disorganised carbon and the formation of a well developed micropore structure.

4.1.2. Chemical activation

Chemical activation involves impregnation with chemicals such as H₃PO₄, KOH or NaOH followed by heating under a nitrogen flow at temperatures in the range 450–900 °C, depending on the impregnant used. Carbonisation and activation proceed simultaneously and the method often leads to materials with higher micropore volumes and wider micropore sizes and these materials are therefore generally preferred for liquid phase applications.

4.2. Lignocellulosic precursors

A summary of some relevant published data for the properties of chars and ACs made from different lignocellulosic precursors is given in Table 2. Most authors have reached fairly similar conclusions from their work although, as we will point out below, there have also been some conflicting views.

Gergova et al. (1994) in their study of the production of ACs from agricultural by-products suggested that the microstructure is strongly dependent on the original plant texture of the corresponding raw material, that is, on the lignin and cellulose content. Furthermore, from their studies on hydrolytic lignin and crystalline cellulose it was suggested that lignin char has more total pore volume as compared to cellulose char. Results obtained by Órfão et al. (1999) have also shown that suitable chars can be made from lignocellulosic materials. It was suggested that lignin is the main component responsible for most of the char produced. Further, Zanzi et al. (2002) in their study on the pyrolysis of agricultural residues at high temperature also noted that higher lignin content results in higher char yield. A similar observation was made by González et al. (2003) in their study on the pyrolysis of cherry stones, and it was suggested that lignin is the main source of char formation, while hemicellulose and cellulose are the volatile fractions.

Reed and Williams (2004) studied five types of biomass and also concluded that the characteristics of ACs are influenced by their feedstock. Table 2 shows that, out of the five materials used, the one with higher lignin content produces a higher amount of char which in turn produces the highest amount of AC. Furthermore, the BET surface area was found to be comparable and with highest micropore surface

Table 2
Characteristics of the biomass, and surface area and porosity of the activated carbons derived from them

Reference		Carbon (%)	Lignin (%)	Cellulose (%)	Char yield (%)	BET surface area char (m ² /g)	BET surface area activated carbon (m ² /g)	Micropore surface area (m ² /g)
Reed and Williams (2004)	Hemp	41.2	3.3	67.0	28.5	–	877	555
	Flax	43.3	2.5	56.5	25.1	–	776	436
	Jute	44.1	11.8	64.4	24.6	–	840	396
	Coir	46.6	41–45	36–43	34.4	–	822	685
	Abaca	43.7	5.1	63.2	28.6	–	860	587
Daud and Ali (2004)	Palm shell	50.0 ^a	53.4	29.7	–	–	260	–
	Coconut shell	48.6 ^a	30.1	19.8	–	–	183	–
Zanzi et al. (2002)	Olive waste	50.9 ^b	28.0	44.8	17.5 ^b	3.1	–	–
	Untreated	45.6 ^b	21.7	43.6	13.2 ^b	68.7	–	–
	wheat straw							
	Wood birch	48.6 ^b	21.0	42.6	5.6 ^b	0.7	–	–

^a By elemental analysis.

^b Moisture and ash free.

area, for the coir, having highest lignin content. Studies were made to compare the pore development in ACs produced under identical conditions from palm shell and coconut shell by Daud and Ali (2004). It was suggested that the activation rate is higher and it is easier to activate the char (carbonised in nitrogen) having more cellulosic content than having high lignin content. Moreover, the surface area and the porosity of the material produced with high lignin content, i.e., palm shell based carbons, were found to be more as compared to coconut shell based ACs. Studies by Sharma et al. (2004) on the characterisation of lignin chars also suggested that lignin chars have low reactivity, compared to those from other biomass constituents, owing to its highly cross-linked nature. Lignin has been found to be effective in creating pores, as evident from the work by Kennedy et al. (2004) who prepared AC composites from rice husk by chemical activation using phosphoric acid. It was suggested that during activation, the opening of pores on the surface of the rice husk is due to the extraction of substances, by dissolution of lignins and other mineral components from the husk during the impregnation process, and this creation of pores is responsible for the increase in surface area and porosity.

Jagtoyen and Derbyshire (1998) while producing ACs from yellow poplar and white oak using chemical activation found that activation of lignin produces mostly micropores, while activation of cellulose produces a mixture of pore size. On the other hand, they also suggested, in contradiction to the other authors already referred to, that the acid attacks lignin and hemicellulose first, possibly because of easier access to amorphous lignin polymers than to crystalline cellulose. Khezami et al. (2005) produced ACs from powdered wood components (cellulose, lignin and xylan). In agreement with other authors, it was suggested that all the basic components of wood are able to yield activated chars. However, contrary to other authors, it was suggested that these activated chars have similar characteristics and that the microporosity is due to cellulose and not due to lignins and hemicellulose.

Some authors have reported moderately high values, in the range of 385–465 m² g⁻¹, for the surface area of chars (Baklanova et al., 2003). However, most authors have found much lower values. From the experimental results of Khezami et al. (2005) it was suggested that the surface area of the char produced from lignin is less than 10 m² g⁻¹. Previous studies by Sharma et al. (2004) on the characterisation of lignin chars also reported low surface area values of 5 m² g⁻¹. Rodríguez-Mirasol et al. (1993) reported surface area of 23 m² g⁻¹, while Wu and Iisa (1998) observed surface area of 14.5 m² g⁻¹ for the char produced by partial pyrolysis of a black liquor at a temperature of 950 °C. Similarly, Hayashi et al. (2000), reported surface areas of carbonised samples ranging from 10 to 50 m² g⁻¹. Higher values are obviously possible after activation.

4.3. Activated carbon from lignin

As lignin is rich in carbon content and has a proven ability for sorption (Dizhbite et al., 1999; Demirbas, 2004; Basso et al., 2004; Lalvani et al., 2000; Srivastava et al., 1994; Ludvík and Zuman, 2000; Allen et al., 2005) it is a good choice for the production of ACs. A brief summary of the work published and which is discussed in subsequent paragraphs is presented in Table 3.

4.3.1. Physical activation

Among the earlier efforts, Bagno et al. (1978) designed and constructed a pilot plant to produce char and AC from a hydrolysis kraft chemical recovery. The char was converted to GAC which was comparable to commercial products. Eucalyptus kraft lignin was investigated as a precursor for production of ACs by Rodríguez-Mirasol et al. (1993). It was found that activation of the material at 850 °C for 20 h in CO₂ could produce ACs having an appreciable surface area of 1853 m² g⁻¹ with a micropore volume of 0.57 cm³ g⁻¹. It was also suggested that increase of microporosity and widening of micropore size distribu-

Table 3
Physical and chemical activation of lignins

Reference	Lignin used	Activation	Conditions	Surface area (m ² /g)	Micropore volume (cm ³ /g)
Khezami et al. (2005)	Indulin C ^a	Physical: carbonisation – N ₂	C (300 °C, 1 h)	<10	<0.01
Rodríguez-Mirasol et al. (1993)	Kraft lignin	Physical: carbonisation – N ₂ Activation – CO ₂	C (350 °C, 2 h) + A(800 °C + 40 h), C (350 °C, 2 h) + A(850 °C + 20 h)	1613 1853	0.47 0.57
Hayashi et al. (2000)	Lignin ^b	Physical: carbonisation – N ₂	C (500–900 °C)	10–50	–
Baklanova et al. (2003)	Hydrolytic lignin	Physical: carbonisation – Ar activation – steam	C (600 °C, 2 h) + steam (800 °C),	865	0.365
Kuznetsov and Shchipko (1995)	Hydrolytic lignin	Physical: pyrolysis (fluidised bed) – air (with Al–Cu–Cr catalyst) activation-steam	Temp: pyrolysis – 700 °C, steam activation – 780 °C	769	–
Gergova et al. (1994)	Hydrolytic lignin	Physical: steam activation	700 °C, 2 h	–	0.33
Khezami et al. (2005)	Indulin C ^a	Chemical: carbonised then activated with KOH	Lignin:KOH :: 4:1 (700 °C, 1 h)	514	0.214
Hayashi et al. (2000)	Lignin ^b	Chemical: ZnCl ₂ , H ₃ PO ₄ , K ₂ CO ₃ , Na ₂ CO ₃ , KOH, NaOH	Impregnation ratio 1 for all	~800–2000	–
Gonzalez-Serrano et al. (1997)	Kraft lignin	Chemical: ZnCl ₂	Lignin:ZnCl ₂ :: 1:2.3 (500 °C, 1 h)	~1800	1.039
Gonzalez-Serrano et al. (2004)	Kraft lignin	Chemical: H ₃ PO ₄	Lignin:H ₃ PO ₄ :: 1:2 (427 °C, 2 h)	1459	0.82
Zou and Han (2001)	Hydrolysis lignin	Chemical: carbonised then activated with KOH	Lignin:KOH :: 1:4 (850 °C, 15 min)	2753	1.37
Fierro et al. (2003b)	Kraft lignin	Chemical: H ₃ PO ₄	Lignin:H ₃ PO ₄ :: 1:1.4 (600 °C, 1 h)	1370	0.78

C – carbonisation, A – activation.

^a From black liquors of kraft pulping.

^b From strong black liquor of kraft pulping, acidulated with CO₂ to obtain the lignin.

tion takes place as activation time proceeds. Although the authors obtained appreciable surface areas the activation times were very long, confirming the low reactivity of lignin already mentioned in the previous section.

Hydrolytic lignin was used as starting material for the preparation of ACs by Baklanova et al. (2003). Influence of carbonisation temperature showed that increase in temperature only caused slight changes in the BET surface area and micropore volume and that the average micropore width decreased with the carbonisation temperature. The authors suggested that carbonisation temperatures of 600–700 °C could be used for producing microporous char materials with a minimum average size of micropores using argon. Furthermore, they observed that steam activation of the carbonised samples produced ACs having surface area as high as 865 m² g⁻¹, with a corresponding micropore volume of 0.37 cm³ g⁻¹.

The effect of thermal and steam treatment on the structural formation of carbons from cotton lignin was studied by Perezdrienko et al. (2001). It was suggested that the carbons obtained from cotton lignin and other materials (fruit kernels, saw dust, peat, nut shells etc.) showed high activity for the extraction of precious metals from process solutions. It was further noted that changing the carbonisation temperature from 400 to 800 °C makes the concentration of the surface acidic centres lower. The activation of carbonised carbons with superheated steam at 800 °C is

accompanied by additional formation of carboxyl groups up to 40% combustion loss. Further, it was suggested that lignin carbons containing only acidic functional groups, or those containing both acidic and basic centres simultaneously, could be prepared by varying the combustion loss in activation of lignin carbon.

4.3.2. Chemical activation

High surface area ACs were prepared from lignin precipitated from kraft black liquors by Gonzalez-Serrano et al. (1997) using chemical activation by ZnCl₂. It was found that the surface area increased with increasing temperature from 350 to 500 °C, but then decreased and was found to be a maximum for an impregnation ratio of lignin to ZnCl₂ of 1:2.3. Furthermore, it was found that the microporosity also increased up to 500 °C. However, it was suggested that ACs with a porous structure suitable for gas phase applications could be prepared using a temperature as low as 400 °C. Although these authors obtained good materials from lignins, it should be pointed out that the use of ZnCl₂ is nowadays not recommended due to the toxicity of zinc. The same authors (Gonzalez-Serrano et al., 2004) also used H₃PO₄ as activating agent and, as can be seen from Table 3, the carbons prepared from pyrolysis of the H₃PO₄ impregnated lignin also had high surface areas and well developed porosity. It was found that increasing the temperature of activation from 350 to

427 °C increased the surface area from $\sim 1000 \text{ m}^2 \text{ g}^{-1}$ to $\sim 1500 \text{ m}^2 \text{ g}^{-1}$. An impregnation ratio of $\text{H}_3\text{PO}_4/\text{lignin} = 2$ and an activation temperature around 427 °C were recommended as the best combination of operating conditions to prepare ACs for aqueous phase applications.

Activating agents such as ZnCl_2 , H_3PO_4 and some alkali metal compounds in a ratio of 1:1 were tried by Hayashi et al. (2000). The surface areas of the ACs produced, was found to be in the range of $800\text{--}2000 \text{ m}^2 \text{ g}^{-1}$ for the temperature range 500–900 °C. It was suggested that a carbonisation temperature of 600 °C for ZnCl_2 and H_3PO_4 produces activated carbons having nearly the same surface areas as those of commercial ACs. However, for alkali metal activation, a carbonisation temperature of 800 °C was found to be best for achieving maximum surface area. It is interesting to note that ACs prepared using K_2CO_3 showed surface areas as high as $2000 \text{ m}^2 \text{ g}^{-1}$. However, Na_2CO_3 was the only material which showed comparatively poor surface area ($<1000 \text{ m}^2 \text{ g}^{-1}$) as compared to the commercial ACs (1267 and $1089 \text{ m}^2 \text{ g}^{-1}$) used by the workers.

ACs were prepared from Chinese hydrolysis lignin by Zou and Han (2001) using chemical activation. It was suggested that carbonisation is a necessary step in order to obtain high surface areas since it creates new cross-links within the lignin, producing a material with low volatility and strongly favouring an increase in the amount of aromatics produced in the cross-linking reaction with KOH.

Fierro et al. (2003b) prepared ACs from lignin by chemical activation using phosphoric acid. Various parameters like effect of impregnation ratio (acid/lignin = 0.7–1.75), carbonisation temperature (400–650 °C) and impregnation time (1–48 h) were studied. It was suggested that the porosity in ACs from cellulosic materials is also due to phosphoric-lignin interactions and that a great part of the microporosity in ACs prepared from lignocellulosic materials comes from lignin; the optimum temperature for porosity development in lignin-derived ACs was suggested to be 600 °C. Furthermore, they suggested that the acid/lignin ratio strongly affects the pore structure and char yield. The effect of impregnation time is more important at high carbonisation temperatures due to decomposition of phosphate and polyphosphate bridges cross-linking parts of the carbon structure.

5. Characterisation studies

5.1. Surface functional groups

5.1.1. FTIR

It is well known that activated carbons have a wide variety of surface functional groups and that the nature of these groups depends on the precursor and method of activation.

Perezdrienko et al. (2001) studied the IR spectra of ACs prepared from cotton hydrolytic lignin prepared at different carbonisation temperatures. The spectra of samples

carbonised at 400 °C were found to have a set of absorption bands in the interval $3600\text{--}430 \text{ cm}^{-1}$ whose intensity markedly decreased with increasing carbonisation temperature over the range 400–800 °C. The bands observed were $3500\text{--}3330$, 2860 , 2800 , $1790\text{--}1625$, $1440\text{--}1413$, $1200\text{--}1070 \text{ cm}^{-1}$, in the range $900\text{--}675 \text{ cm}^{-1}$ and a few others. Analysis of the IR spectra of the carbonised lignin indicated a gradual decrease in the intensity of vibrations of the hydroxyl-containing groups with increase in the carbonisation temperature. It was suggested that with increasing activation time, up to a 50% combustion loss, a part of the alcoholic hydroxyls undergoes deeper oxidation to carboxyls and aldehydes which follows from the gradual increase in the intensity of the absorption bands at $1700\text{--}1720 \text{ cm}^{-1}$, related to (C=O) stretching vibrations, and a decrease in the intensity of absorption bands at $3330\text{--}3350 \text{ cm}^{-1}$, associated with stretching vibrations of the (O–H) bond. Cagniant et al. (2003) also discussed IR peaks observed in lignin samples and suggested a large band near 3400 cm^{-1} assigned to OH groups, a carbonyl band around 1706 cm^{-1} and bands around 1600 , 1510 , 1460 and 1426 cm^{-1} assigned to aromatic skeleton vibrations. However, the main band at 1600 cm^{-1} was suggested to be due to phenolic groups, bands at 1269 and 1325 cm^{-1} were guaiacyl (mixed with ester bands) and syringyl propane units, respectively, and the strong band observed around 1210 cm^{-1} was assigned to C–O stretching in aryl ethers. Further, during their study on ammoxidation of lignins in gaseous air and ammonia, to obtain ACs containing nitrogen surface functions, it was suggested that during heating in air changes occur with the disappearance of some bands (1702 cm^{-1}) showing that the structure of the lignin is somewhat destroyed.

From the FTIR spectra of raw lignin studied in the range of $4000\text{--}600 \text{ cm}^{-1}$ Sharma et al. (2004), suggested that the band at 3419 cm^{-1} could be identified as corresponding to OH, while those at 2844 cm^{-1} due to methoxyl groups, aliphatic CH at $3000\text{--}2860 \text{ cm}^{-1}$, aromatic CH groups at 3064 cm^{-1} and aromatic ring modes at 1513 and 1597 cm^{-1} . It has been noted that the band at 1368 cm^{-1} could be due to both OH in-plane bending and CH bending and the weak band at 667 cm^{-1} for the out-of plane OH bend. The band at 2843 cm^{-1} was suggested to be due to the symmetric CH_3 stretch of the methoxyl group and the band at 1033 cm^{-1} due to the C–O stretch in O– CH_3 and C–OH, and the sulfonic acid at about 1200 cm^{-1} . The bands for the hydroxyl group above 3000 cm^{-1} were suggested to be due to alcoholic or phenolic components. The bands of the carbonyl groups appeared in the range between 1660 and 1725 cm^{-1} . The authors suggested that the exact position of the bands was dependent on whether the C=O groups were in conjunction with the aromatic ring (below 1700 cm^{-1}) or not (above 1700 cm^{-1}). The most characteristic bands of lignin were suggested to be at 1513 and 1597 cm^{-1} (aromatic ring vibrations) and between 1470 and 1460 cm^{-1} (CH deformation and aromatic ring vibrations). Further, according

to the authors the higher intensity of the band observed at 1513 cm^{-1} compared to that at 1597 cm^{-1} suggested the lignin to be from the softwood. It was observed that at $550\text{ }^\circ\text{C}$ most IR bands, except those due to aromatic CH and OH stretches disappeared resulting in mainly aromatic char. FTIR analyses of thermally treated lignins have been studied by other workers (Braun et al., 2005) too.

5.1.2. TPD

Gonzalez-Serrano et al. (2004) using temperature programmed desorption (TPD), and from the CO and CO₂ evolved, characterised the groups present on ACs from lignin. According to these workers, increasing the activation temperature from 425 to $600\text{ }^\circ\text{C}$ and increasing the impregnation ratio, decreases the presence of oxygen acidic groups (carboxylic, lactonic) on the surface of the resulting carbons. The relative amount of these groups in all cases was fairly low and they were absent in the AC prepared at the highest activation temperature investigated ($600\text{ }^\circ\text{C}$) as no CO₂ was detected for this sample. On the other hand, the workers observed that the amount of carbon–oxygen surface groups (carbonyl, ether, quinone) evolving as CO compares favourably with that reported for many other ACs including carbons surface modified by oxidation. With increase in the activation temperature, the total amount of carbon–oxygen surface groups also increased and the same trend was observed with regard to the impregnation ratio although in this case the effect was not so significant. From the nature of the evolved gas, H₂O, CO and CO₂, and the temperature at which they were formed, Khezami et al. (2005) using TPD suggested that the prominent groups present on lignin ACs were phenol, carbonyl, ether, carboxylic acid, lactone and carboxylic anhydrides.

5.2. Pore size distribution

Rodríguez-Mirasol et al. (1993) suggested that microporosity and widening of micropore size distribution take place as physical activation in CO₂ proceeds. However, it was observed that AC from kraft lignin also has a well developed meso- and macroporosity. It was further observed that with change of activation temperature from 800 to $850\text{ }^\circ\text{C}$, there was no relevant effect on porosity and the porous structure is essentially determined by burn-off. At low burn-off limited degree of mesoporosity was observed, while at high activation degrees, macroporosity was also observed and became significant. Gonzalez-Serrano et al. (1997) obtained ACs having micropore volumes as high as $\sim 1\text{ cm}^3\text{ g}^{-1}$ on chemical activation of lignin with ZnCl₂. The porosity was found to increase with increase of activation temperature up to $500\text{ }^\circ\text{C}$ then decreased significantly at $600\text{ }^\circ\text{C}$. With increase of impregnation ratio of ZnCl₂ to lignin (from 0.4 to 2.3), the porosity was found to have an increasing trend with widening of pores as the temperature increased up to $500\text{ }^\circ\text{C}$. However, the mesopore size distribution remained essentially within

the low mesopore range (below $\sim 5\text{ nm}$ diameter) even at high impregnation ratios. Similarly, Hayashi et al. (2000), showed that the pore volumes of ACs prepared by ZnCl₂ and H₃PO₄ activation increased with an increase in temperature over the range 500 – $600\text{ }^\circ\text{C}$, and then decreased with an increase in temperature over the range of 600 – $900\text{ }^\circ\text{C}$. It was suggested that above $600\text{ }^\circ\text{C}$, the carbon structure shrinks resulting in decrease of surface area and pore volume. The pore volumes of the ACs prepared by alkali metal compound activation increased with carbonisation temperatures up to about $800\text{ }^\circ\text{C}$ which was suggested to be due to pore enlargement up to this temperature. However, the authors suggested that above $800\text{ }^\circ\text{C}$, the excess enlargement induces combination of pores, resulting in an increase in mesopores for all alkali metal salts, and a decrease of micropore volume, and of surface area. Baklanova et al. (2003) prepared ACs from lignin by carbonisation and further activation in steam and found that the surface area and microporosity increased nearly linearly with burn-off. It is further observed that above 60% burn-off the average width of the micropores increased and also the mesoporosity became prominent.

Porosity of lignin ACs obtained by chemical activation using phosphoric acid has also been explained by Fierro et al. (2003b). It was suggested that low impregnation ratios promote the creation of micropores whereas acid/lignin ratios equal to or higher than 1.0 slightly affect the pore size distribution. Increasing impregnation times reduce the BET surface area and the total pore volume. Moreover, impregnation times also affect the pore size distribution of the activated carbons. Further, Gonzalez-Serrano et al. (2004) observed that all ACs produced in the range 350 – $600\text{ }^\circ\text{C}$ showed fairly high values of micropore volume and its variation was the same as that of surface area. However, the same behaviour was also observed for the mesopore volume. It was suggested that increasing the activation temperature and impregnation ratio leads to widening of the pore size distribution with a higher relative contribution of mesoporosity.

5.3. Fractal dimension

Fractal dimensions, which are a measure of the roughness of a surface, were estimated by Hayashi et al. (2002) by applying the FHH (Frenkel-Halsey-Hill) equation to N₂ adsorption isotherms determined on ACs prepared from lignin by chemical activation with KOH, NaOH, ZnCl₂ and H₃PO₄. The results showed that for ZnCl₂ and H₃PO₄ activation the change in fractal dimension is insignificant over the temperature range 500 – $900\text{ }^\circ\text{C}$ indicating development of pores to be complete. However, the decrease in surface area observed above 873 K was suggested to be due to thermal shrinkage. On the other hand, it was observed that the fractal dimension of the AC prepared by KOH and NaOH activation increased between 773 and 873 K , and decreased with an increase of carbonisation temperature above 973 K . This was suggested to be

due to new pore development between 500 and 800 °C by the activation. However, the excess activation lead to the collapse of the walls of the smaller pores which then combined to form larger pores. Therefore, both the specific surface area and the fractal dimension decreased for temperatures above 800 °C.

5.4. Pyrolysis

A continuous distribution type model for lignin decomposition has been proposed by Caballero et al. (1995). Taking into account that the different fractions decomposed at different temperatures, a new kinetic model was proposed for satisfactorily correlating the experimental results obtained in the pyrolysis of kraft lignin. The model is based on a function of distribution of solid decomposition. It was suggested that using this model, it is possible to derive correlations between the kinetic parameters, the pre-exponential factor and the activation energy by considering operating temperature for the fractions. Várhegyi et al. (1997), while studying the pyrolysis of lignin suggested that the thermal decomposition of lignins occurs in a broad temperature range resulting in 30–50% char with significant amount of low molecular mass volatiles, in addition to the monomeric and oligomeric products. It was suggested that the low molecular mass products are formed by the cleavage of functional groups. Further, the lignins contain various oxygen functionalities having different thermal stability and the scission of the functional groups takes place at different temperatures. At higher temperatures, complex char forming reactions occur involving the complete rearrangement of the carbon skeleton and the release of gaseous products. The presence of cations (Na^+ , NH_4^+ , Ca^{2+}) has a significant effect on the course of decomposition. Sodium enhances the formation of char and gaseous products. The experimental results showed that in comparison to the sharper derivative thermogravimetry (DTG) peaks of cellulose and hemicelluloses, lignins result in wide, flat DTG peaks. On their experiments on milled wood lignins, a formal approximation by a pseudo-first-order reaction gave extremely low 'activation energies' in the range of 34–65 kJ mol⁻¹. The corresponding pre-exponential factors were also very low ($10^{0.3}$ – 10^3).

Sharma et al. (2004) studied the effect of temperature on char yield and found that the char yield decreased rapidly with increasing temperature to ~62% from 150 to 400 °C, followed by a gradual decrease to 40% at 750 °C. The char yield decreased rapidly in the oxidising atmosphere (15% at 550 °C). It was suggested that the high char yields obtained were due to the presence of inorganic components such as potassium and sodium, and the removal of these inorganic components decreased the char yield. The surface area of the char formed was found to have a maximum of 5 m² g⁻¹ at temperatures in the range 350–400 °C. The results suggested that either the lignin chars are not microporous or that the pores within these chars are extremely small and dead-ended, preventing any access to the adsorb-

ing gas. The microporous samples with open pores are expected to have high surface areas. It was also suggested that the low areas could also be due to the formation of a plastic-like char as a result of the melting of lignin indicated by SEM results.

Pyrolysis of Kraft lignin impregnated with orthophosphoric acid and the effect of various parameters including heat treatment temperature up to 650 °C, impregnation time, inclusion of isothermal periods, acid to lignin mass ratio and gaseous atmosphere, on both the char yield and the rate of mass loss was studied thermogravimetrically by Fierro et al. (2005). It was found that lignin and orthophosphoric acid react completely in less than 1 h when mixed and longer impregnation times do not have any influence on char yield. It was found that the decomposition of pure lignin showed two maxima in the mass loss corresponding to evolution of moisture at 92 °C and to lignin decomposition in a broad temperature range from 150 to 650 °C, respectively. It was suggested that with addition of orthophosphoric acid, lignin dehydration proceeded to a larger extent and decomposition occurred in a narrower temperature range and at lower temperatures with higher char yields. It is interesting to note that the same authors also developed a kinetic model (Montané et al., 2005) for the pyrolysis at low heating rates of lignin activated with phosphoric acid. Beside these, various other workers (Kuznetsov and Shchipko, 1995; Jakab et al., 1997; Ferdous et al., 2002; Li and Van Heiningen, 1991; Kuroda et al., 2002) have also studied the pyrolysis of lignins.

6. Adsorption studies

Zou and Han (2001) prepared ACs from lignin, which they suggested has an adsorption capacity as high as 604 mg g⁻¹ for methylene blue. Further, in their studies on the production and characterisation of ACs from kraft lignin, Fierro et al. (2003a), prepared materials with various pore size distributions, surface areas and surface acidic groups and used them for the removal of Cu(II). The results obtained by them showed the significant importance of carbonisation temperature on the adsorption capacity for removal of copper. The maximum adsorption was found to be for the carbons prepared at a carbonisation temperature between 450 and 550 °C. It was found that on increasing the temperature acidic groups were degraded but increasing mesoporosity and surface area favoured diffusion and adsorption. Increasing the acid/lignin ratio did not influence significantly the adsorption capacity of the ACs once lignin had completely reacted with phosphoric acid.

The removal of carbon monoxide by oxidised active lignin carbon as adsorbent-catalyst, at moderate temperatures (20–80 °C) was studied by Grigor'ev et al. (2003). The authors suggested that the removal of CO can be made by these materials and further suggested that the regeneration could be done by passing air at a linear velocity of 0.15–0.30 m s⁻¹ at 180 °C. Further, it was proposed that

the sorption capacity of ACs can be increased by using a mixture of oxidising agents and by increasing the concentration of active centres. It was suggested that use of lignin ACs is advantageous due to lower energy expenditure during a regeneration stage, which is carried out at lower temperature (<180 °C). ACs developed by Gonzalez-Serrano et al. (2004) from kraft lignin by chemical activation with H₃PO₄ were found to have high surface areas with well developed micro and mesoporosity making them good adsorbents for aqueous phase applications. Maximum adsorption capacities of 227.3, 476.2 and 92.6 mg g⁻¹ for the toxic pollutants phenol, 2,4,5-trichlorophenol and Cr(VI), respectively were observed. The adsorption was found to be comparable with that reported for other ACs. ACs produced from kraft lignin from black liquor was used by Khezami et al. (2005) for the removal of methylene blue and phenol. The material so developed was able to remove 32.47 and 27.13 mg g⁻¹ of methylene blue and phenol, respectively.

7. Future directions

A certain amount of work has already been carried out on the production of ACs from lignin, as well as on the sorption of inorganic and organic substances on lignin and lignin-derived ACs. Although the amount of published work is still comparatively small, the results so far obtained are promising and there is clearly a need for more detailed systematic studies.

The comparatively low reactivity of lignin, in comparison with cellulose, appears to be established and this supports the view held by most workers that lignin is the component of wood and other lignocellulosic precursors which is primarily responsible for the microporosity. It has also been shown that it is possible to prepare ACs from lignin which have very high surface areas and pore volumes and which are comparable to the best commercial ACs. Pure lignin, when compared with lignin-based ACs, has lower adsorption capacity.

It is known that the adsorption capacity of ACs can be modified by controlling the conditions of activation or by post-activation surface treatments. However, the adaptation of general principles obtained with other materials to the specific case of lignin is still at an early stage. In the case of pure lignin, knowledge of its surface chemistry and the effects of surface treatment is scarce. The large differences found in adsorption capacities for different metals indicate that this may have a fundamental influence on the performance of lignin-based adsorbents. In addition, with both pure lignin and lignin-derived ACs there is little information on the relationship between adsorptive properties and molecular structure (coumaryl, coniferyl or sinapyl; functionalised; mean molar mass; reticulation; etc.). This also may be of fundamental importance as the porosity and surface chemistry, which determine the adsorptive properties, will be influenced by these factors. Finally, information on economic aspects related to, for example,

conversion of lignin into AC, or comparative costs of lignin or AC use and reuse, are not readily available in the open literature.

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