

# Activated Carbon from Lignocellulosic Biomass-Phenolic Resin

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## SYNOPSIS

Lignocellulosic biomass of agricultural/industrial by-products residues was taken after the pressing and extraction of olive-oil and lignin Klason and  $\alpha$ -cellulose were isolated. Also, phenol-formaldehyde was polymerized by using an acid catalyst. Various mixtures of lignocellulosic materials and novolac resin were cured with hexamethylenetetramine and then pyrolyzed up to 1000°C. The IR-Spectrum of the cured material consisted of 20% novolac and 80% cellulose is practically similar to that of 100% cellulose. The corresponding material with lignin Klason instead of cellulose has different IR-Spectrum compared to that of 100% lignin, because of additional reactions taken place between lignin and novolac under curing conditions. The weight losses, the shrinkages at the end of the pyrolysis, the specific surface area of the carbonaceous materials produced and their adsorption abilities of methylene blue and alizarin yellow from aqueous solutions were determined. The material consisted of 20% novolac and 80% cellulose or 80% lignin, appears as optimum characteristics of production process. The experimental results are also discussed under the aspect of sample shapes that influence the adsorption as well as the electron donor-acceptor (EDA) interactions between the functional groups of dyes and the carbonaceous materials. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Activated carbons are broadly used in different sectors of technique and they show continuously extension of their application fields. Activated carbon adsorption is used for removal of harmful substances from process solutions during treatment of polluted soils (e.g., broad spectrum of components of waste water like phenol, chlorobenzene, benzene).<sup>1</sup> Tungsten (VI) and molybdenum (VI) are strongly adsorbed by activated carbon from acid solution.<sup>2</sup> Protection against highly toxic, volatile liquids like perfluorobutene has been achieved by activated carbon vapor filters.<sup>3</sup> Adsorptive processes with activated carbons are used in new emission-poor systems and installations, e.g., for purification of air contained chlorhydrocarbons<sup>4</sup> or have been proposed for heat management (refrigeration, heat pump, etc.).<sup>5</sup>

Lignocellulosic materials, derived from residues of biomass or from by-products of agricultural industries, have been found to be of great interest as raw materials to produce other useful chemical products like liquid hydrocarbons.<sup>6</sup> Such natural polymers as lignocellulosic or their constituents, viz. cellulose and lignin, have nowadays considerable importance as polymeric raw materials combined or not with synthetic polymers like epoxy, phenolic resins, etc.<sup>7-10</sup> On the other hand, typical organic polymers like styrene/divinylbenzene copolymers can be transformed to activated carbon by appropriate carbonization. Such products have been commercially available for many years.<sup>11</sup> Furthermore, carbonaceous adsorbents have been prepared based on the combination of lignocellulosic materials (like olive stones and cottonseed) with resins (like phenol-formaldehyde resin).<sup>12-15</sup>

This article aims to investigate the role of cellulose and lignin, which are the main components of lignocellulosic materials, to produce activated carbons as previously described.

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## EXPERIMENTAL

### Production Method

Lignocellulosic biomass of agricultural/industrial by-products residues was taken after the pressing and extraction of olive-oil and lignin Klason and  $\alpha$ -cellulose were isolated.<sup>16,17</sup> Weak ether bonds of raw material were alkaline hydrolyzed with NaOH and Na<sub>2</sub>S in autoclave at 180°C, 9 atm for 1.5 h following precipitation and separation.  $\alpha$ -Cellulose (mentioned below as cellulose) was isolated from previous pulp by addition of 17% NaOH. Lignin Klason was obtained as residue by acid hydrolysis of polysaccharides with 72% H<sub>2</sub>SO<sub>4</sub>. Cellulose and lignin Klason were ground, sifted, and grains of diameter less than 300  $\mu$ m were obtained and homogenized separately.

Novolac resin was prepared by polymerization of phenol-formaldehyde (1.22:1 mol/mol) with oxalic acid as catalyst (1.5 wt/wt to phenol). Then, novolac was pulverized and mixed with hexamethylenetetramine ("hexa"), which is the curing medium, in a ratio of novolac:"hexa" = 3.5:1 wt/wt. Mixtures of cellulose or lignin with novolac-hexa were cured at 170°C for 30 min and then pyrolyzed under N<sub>2</sub> stream up to 1000°C, according to the method previously described.<sup>12-15</sup>

Fourier Transform Infrared (FTIR)-Spectroscopy of raw and cured materials was performed in "NIC" equipment, Nicolet Analytical Instruments 60 SX, by using KBr-tablets. Weight losses of ma-

terials during their thermal degradation were determined by weighing them before and after carbonization process. Shrinkages of materials during their thermal degradation were also determined by measuring their length before and after carbonization.

### Characterization of Carbonaceous Materials

The specific surface area of materials after their thermal degradation was measured according to DIN 66132 with CO<sub>2</sub> as gas at -79°C. The discoloring abilities of materials were also determined by using methylene blue and alizarin yellow R in aqueous solutions (initial concentration 0.0320 g/L for both dyes). Certain amount of adsorptive material was mixed with known amount of aqueous solution of dye at 25°C without stirring. The proportions of weight of adsorptive material to volume of initial solution of dye, were: 0.5 g/L, 2 g/L, 10 g/L. The color of solution for different time intervals was determined by colorimetric calibration scale or by Colourimeter Lovibond Tintometer Model E. The measurements error was ca.  $\pm$  2%.

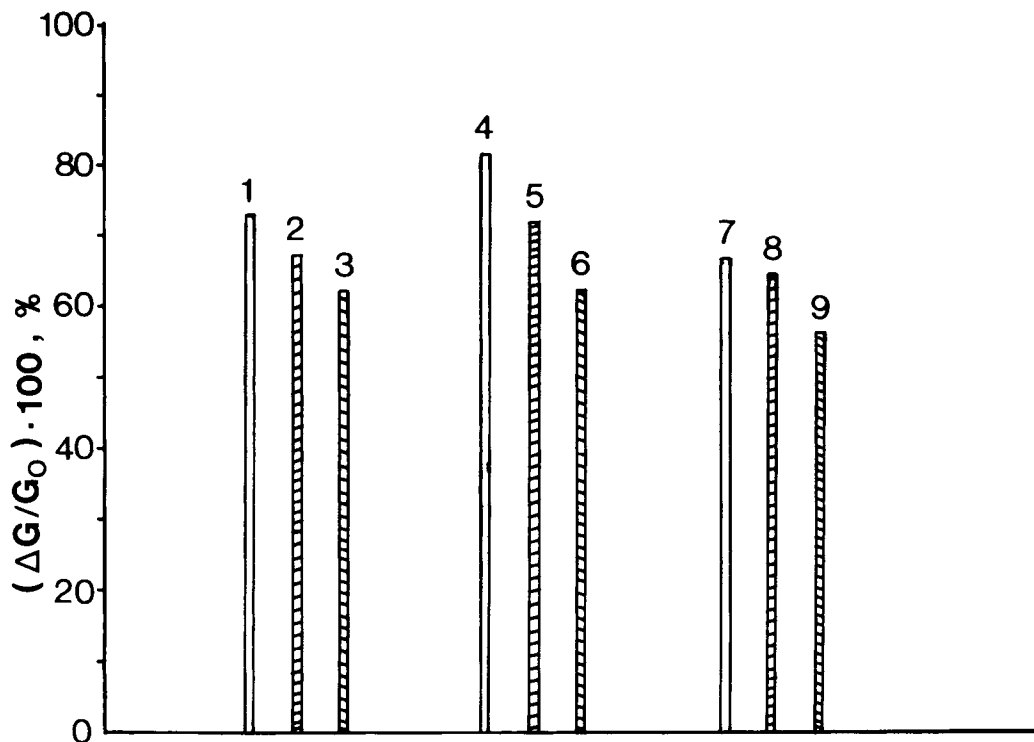
## RESULTS

Table I refers to the composition and the proportion of raw materials used for the production of carbonaceous materials as well as to their specific surface area. For initial proportion of raw materials 20/80

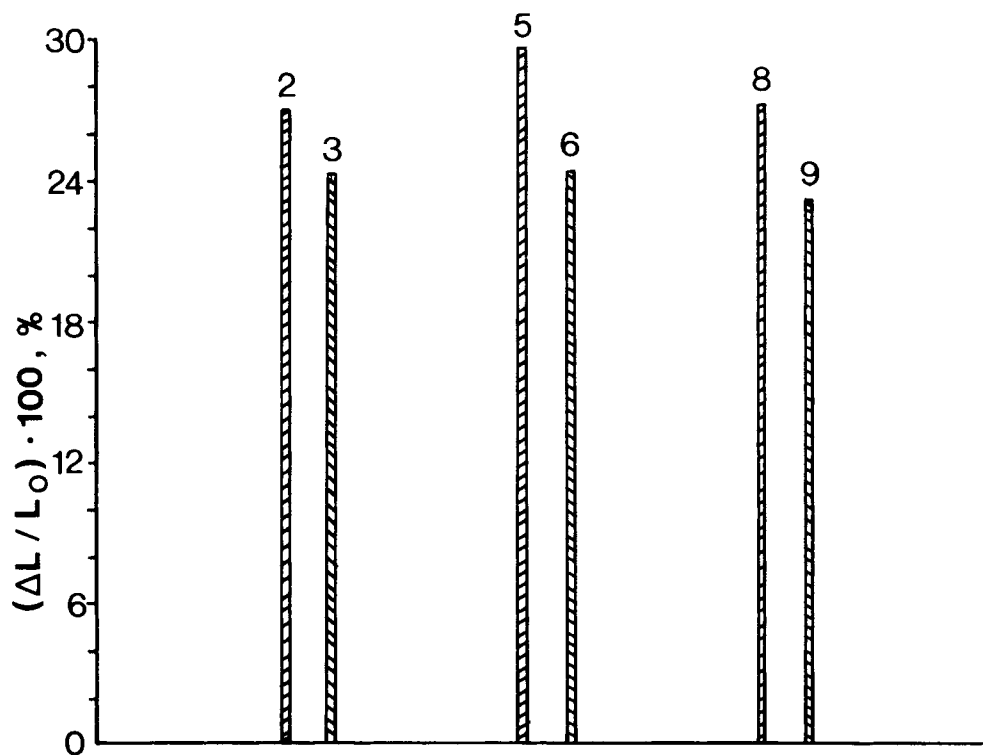
**Table I** Composition of Raw Materials for the Production of Carbonaceous Materials and Their Specific Surface Area (Curing with "Hexa" at 170°C and Pyrolysis Up to 1000°C)

No.	Raw Materials				Specific Surface Area by CO <sub>2</sub> (m <sup>2</sup> /g)
	Pressed and Extracted Olive Stones (%)	Cellulose (%)	Lignin Klason (%)	Novolac (%)	
1	100				
2	80			20	500
3	60			40	350
4		100			
5		80		20	800
6		60		40	600
7			100		
8			80	20	450
9			60	40	120

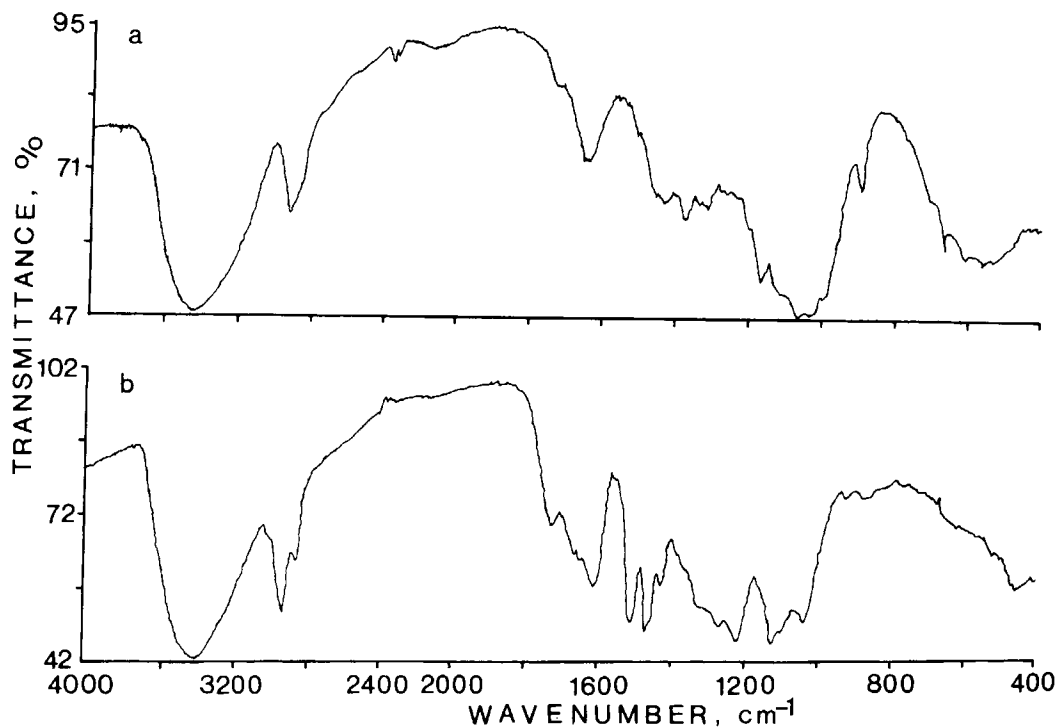
Shape of samples for measurements of specific surface area: small cylinders



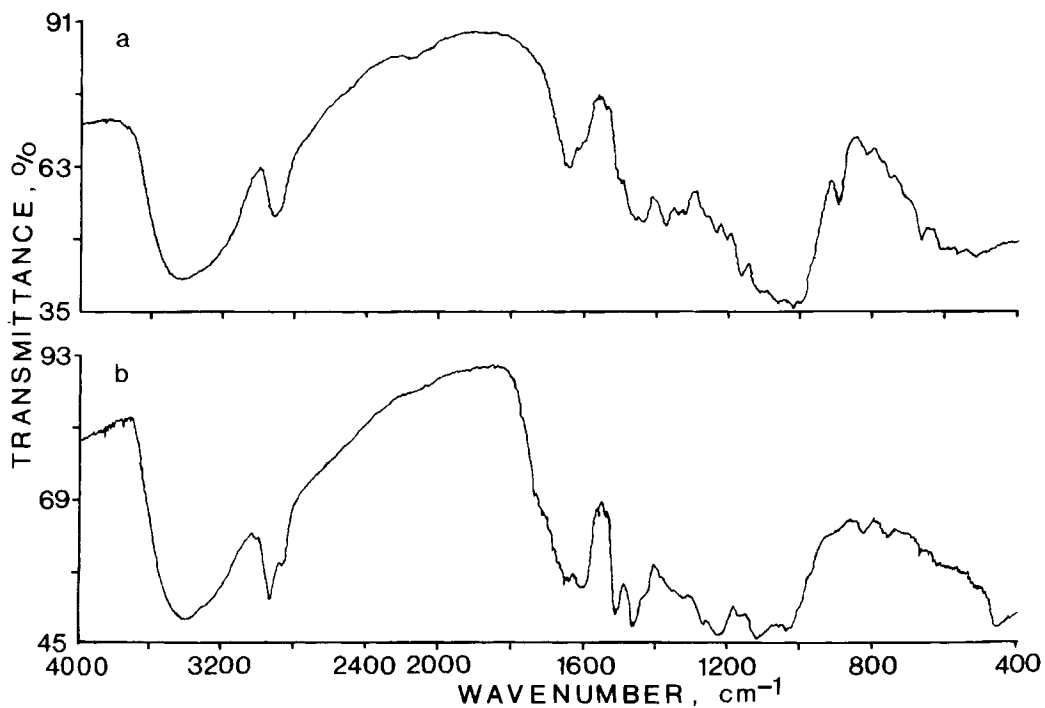
**Figure 1** Weight losses of materials thermally degraded up to 1000°C (for symbols 1-9, see Table I).



**Figure 2** Change of length (shrinkage) of molded specimens thermally degraded up to 1000°C (for symbols 2, 3, 5, 6, 8, and 9, see Table I).



**Figure 3** IR-Spectra. (a) No. 4 (see Table I): 100% cellulose (without curing and pyrolysis). (b) No. 7 (see Table I): 100% lignin Klason (without curing and pyrolysis).



**Figure 4** IR-Spectra. (a) No. 5 (see Table I): novolac/cellulose = 20/80 cured with "hexa" (without pyrolysis). (b) No. 8 (see Table I): novolac/lignin Klason = 20/80 cured with "hexa" (without pyrolysis).

(i.e., 80% pressed and extracted olive stones or cellulose or lignin Klason), the specific surface areas are higher than that of 40/60. For the same initial proportion 20/80 or 40/60, the specific surface areas follow the order: cellulose > olive stones > lignin Klason.

Figure 1 shows weight losses of materials because of their thermal degradation up to 1000°C. Weight losses are increased with the proportion of pressed and extracted olive stones or cellulose or lignin Klason (and by decreasing proportion of novolac). For the same initial proportion 20/80 or 40/60, the weight losses are increased according to the order: cellulose > olive stones > lignin Klason.

According to Figure 2, increased changes of length (shrinkages) up to 1000°C are observed by increasing the proportion of olive stones or cellulose or lignin Klason (and by decreasing proportion of novolac). For the same initial proportion 20/80 or 40/60, the shrinkages are increased according to the order: cellulose > olive stones > lignin Klason.

Figures 3 and 4 represent the IR-Spectra of raw

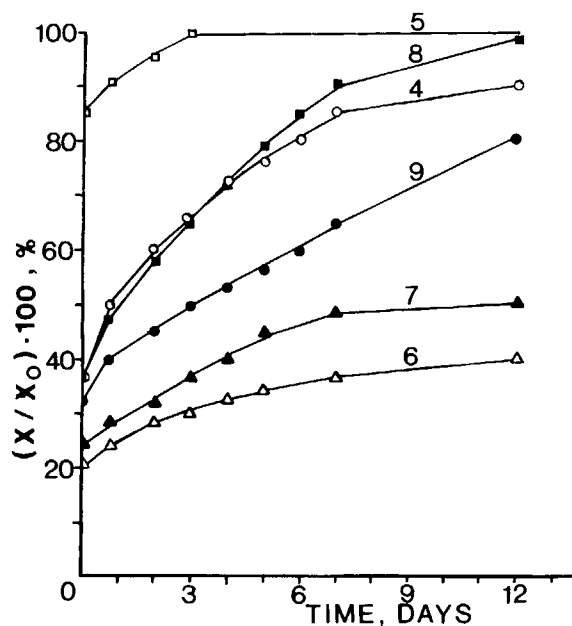
materials used for the production of activated carbons; the bands can be interpreted according to ref. 18, and the results are summarized in Table II. Various overlapping bands are mainly in the "finger"-print region (under 1500 cm<sup>-1</sup>). Cellulose and lignin Klason show different IR-Spectra; cured material of 20% novolac-80% cellulose show practically similar IR-Spectrum compared to 100% cellulose, while the IR-Spectrum of cured material of 20% novolac-80% lignin Klason has some important differences compared with that of 100% lignin Klason. These differences are mainly: at 1715 cm<sup>-1</sup> and 1410 cm<sup>-1</sup> (there is no absorption band for 80% lignin Klason), at 1640 cm<sup>-1</sup> (due to novolac), at 815 cm<sup>-1</sup>, and 750 cm<sup>-1</sup> (which are not present in 100% lignin Klason). According to these characteristics, it can be concluded that the combination of 20% novolac-80% lignin Klason leads to an increase of benzene rings due to additional reactions taking place between lignin and novolac under curing conditions.

Figures 5-8 represent the adsorption of methylene blue and alizarin yellow from aqueous solutions on

**Table II Description of IR-Bands for Various Materials Produced**

Group	Band (Peak), cm <sup>-1</sup>			
	Description in Table I			
	No. 4 (Fig. 3a)	No. 7 (Fig. 3b)	No. 5 (Fig. 4a)	No. 8 (Fig. 4b)
OH	3.420	3.420	3.420	3.420
CH <sub>2</sub> , CH <sub>3</sub>	2.930	2.930	2.930	2.930
C—O—CH <sub>3</sub>		n 2.854		n 2.854
COOH (C=O)		v 1.715		
C=C without conjugation (1680-1620 cm <sup>-1</sup> ) or aromatic ring	1.650		1.650	1.640
Aromatic ring		1.600		1.600
		1.510		1.510
CH <sub>2</sub> , CH <sub>3</sub>	1.420	1.465	1.420	1.465
COOH (combination vibrations)		1.410		
CH <sub>3</sub>	1.378		1.378	
OH	1.320		1.320	
Bands possibly due to syringyl vibrations		1.320		1.320
		1.270		1.270
		1.130		1.130
CH (bending)		1.240		1.240
CO—O— or OH asymmetric ring	1.165		1.165 (1.110)	(1.110)
C—O	1.060		1.060	
Guaiacyl band possibly		1.040		1.040
Ring (asymmetric)	900		900	
Ring (two neighbor H of substitutes of benzene ring)				815
Ring (three neighbor H of substitutes of benzene ring)				750
Ring	700		700	

Symbols: n, negligible; v, very low intensity.



**Figure 5** Adsorption of methylene blue from aqueous solution on pulverized carbonaceous materials.  $X$ : adsorbed amount of methylene blue;  $X_0$ : initial amount of methylene blue in solution before adsorption;  $m$ : amount of carbonaceous material = 0.5 g/L of solution (for symbols 4–9, see Table I).

carbonaceous materials (pulverized or having diameter of "grains"  $d < 63 \mu\text{m}$ ) with various proportions of dye and solution, without stirring.

The adsorption (Figs. 5 and 6 for pulverized materials) is increased according to the order: No. 5 > 8 > 4 > 9 > 7, 6, or 6, 7.

The materials having proportion of 20/80 reveal higher adsorption than 100% cellulose or lignin Klason. By increasing proportion of carbonaceous materials to volume of solution (viz. 2 g/L instead of 0.5 g/L), the rate of adsorption of dye increases. The amount of this increase differs significantly, considering different materials due to various porous structures that differently affect the filling of pores.

The materials of Figures 7 and 8 have diameter of "grains"  $d < 63 \mu\text{m}$ , whereas materials of Figures 5 and 6 are powders. Figure 7 cannot be directly correlated to Figures 5 and 6 because of different sample shapes resulting in different accessibilities of dyes (different diffusion, etc). According to Figures 7 and 8 (diameter of "grains"  $d < 63 \mu\text{m}$ ), the adsorption of methylene blue or alizarin yellow follows the order: No. 8 > 5 > 6 > 9.

## DISCUSSION

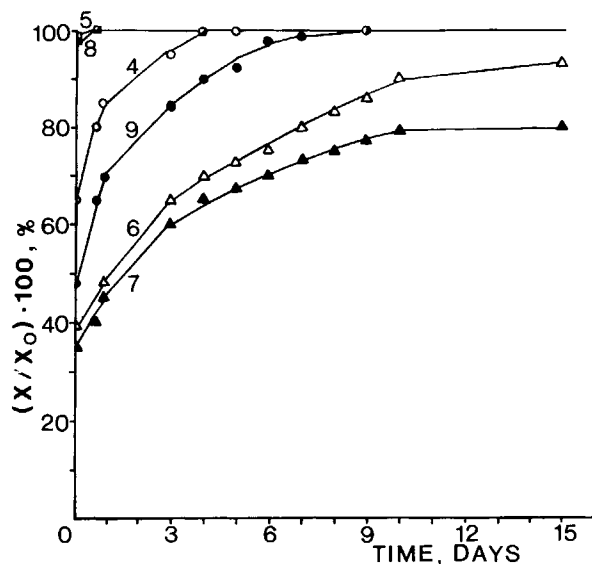
Two main groups of materials were prepared with various combinations of cellulose-novolac and lig-

nin-novolac. Also, combinations of novolac with olive stones will be discussed.

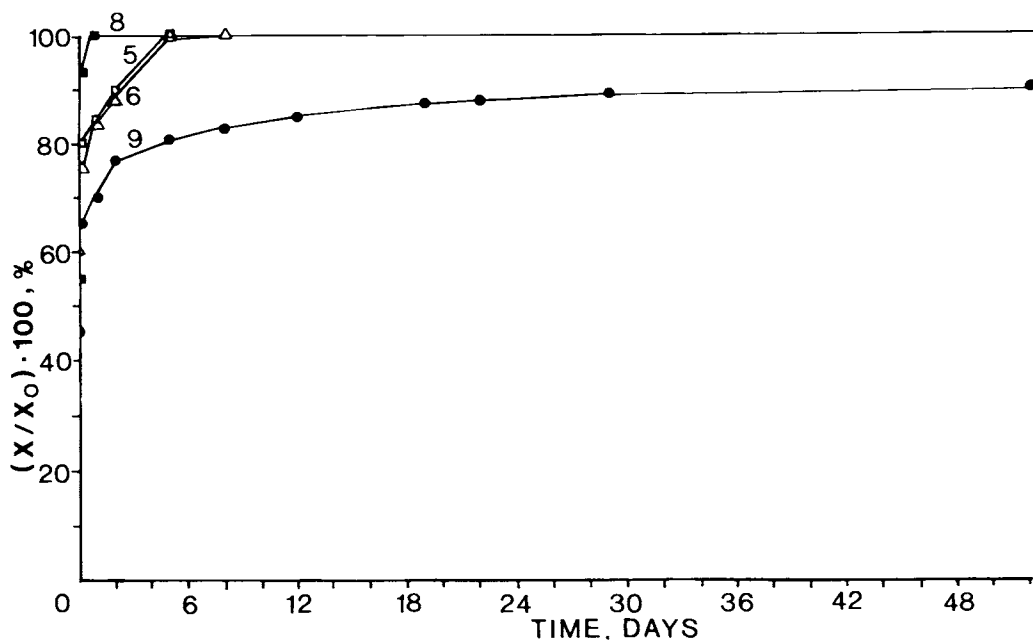
Similar relations of weight losses, shrinkages during pyrolysis, and specific surface area of carbonaceous materials are observed for each group of materials: No. 2 > 3, 5 > 6, 8 > 9 (see symbols in Table I).

Generally, the formation of pores is caused due to weight losses during the pyrolysis of a substance, while the shrinkages could diminish pores extent. Comparing materials with 20% and 40% of novolac content, it is observed that although the weight losses of the first case are not significantly higher than those of the second case (Fig. 1), the specific surface area is much higher for the first than for the second (Table I). On the other hand, the shrinkages of the first case are obviously higher than that of the second one (Fig. 2), so that a reduction of the pores could be expected. However, the fact that the specific surface area of the first case is much higher than that of the second case, leads to the conclusion that low or no reduction of pores occurs and that shrinkages take place only due to the reduction of geometrical characteristics of the materials.

One hundred percent cellulose can be clearly distinguished from 100% lignin Klason by IR-Spectra. Cured material of 20% novolac–80% cellulose shows similar IR-Spectrum compared to 100% cellulose. However, IR-Spectrum of cured 20% novolac–80%



**Figure 6** Adsorption of methylene blue from aqueous solution on pulverized carbonaceous materials.  $X$ : adsorbed amount of methylene blue;  $X_0$ : initial amount of methylene blue in solution before adsorption;  $m$ : amount of carbonaceous material = 2 g/L of solution (for symbols 4–9, see Table I).



**Figure 7** Adsorption of methylene blue from aqueous solution on carbonaceous materials (having diameter of "grains"  $d < 63 \mu\text{m}$ .  $X$ : adsorbed amount of methylene blue;  $X_0$ : initial amount of methylene blue in solution before adsorption;  $m$ : amount of carbonaceous material = 10 g/L of solution (for symbols 5, 6, 8, and 9, see Table I).

lignin Klason differs considerably from that of lignin Klason because of additional reactions taken place between lignin and novolac under curing conditions.

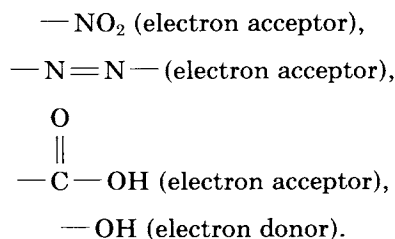
The discoloring abilities of carbonaceous materials cannot be directly correlated to weight losses, e.g., material No.5 (consisted of 20% novolac) indicates the highest adsorption of dye (higher than No. 4, which is consisted of 100% cellulose and reveals the highest weight losses (see Figs. 5, 6, and 1). Materials containing 20% novolac adsorb better than the corresponding materials containing 40% novolac (e.g., see Figs. 5 and 6, cases No. 5 > 6 and No. 8 > 9). This behavior can be attributed to the formation of pores in materials containing 20% novolac, which have better accessibilities with both dyes molecules.

The presence of cellulose (100% or 80%) in initial mixture is more favorable than the presence of lignin (100% or 80%) for pulverized samples (see Figs. 5 and 6, case No. 5 > 8, 4 > 7). For samples having diameter of "grains"  $d < 63 \mu\text{m}$ , the presence of 80% lignin in initial mixture is more favorable than the presence of 80% cellulose (see Figs. 7 and 8, case No. 8 > 5). According to that mentioned above, the accessibilities of pores of carbonaceous material produced from 80% cellulose are low for large molecules of dyes, viz. methylene blue, alizarin yellow. This is due to diffusion difficulties, although accessibilities for small gas molecules  $\text{CO}_2$  are higher as,

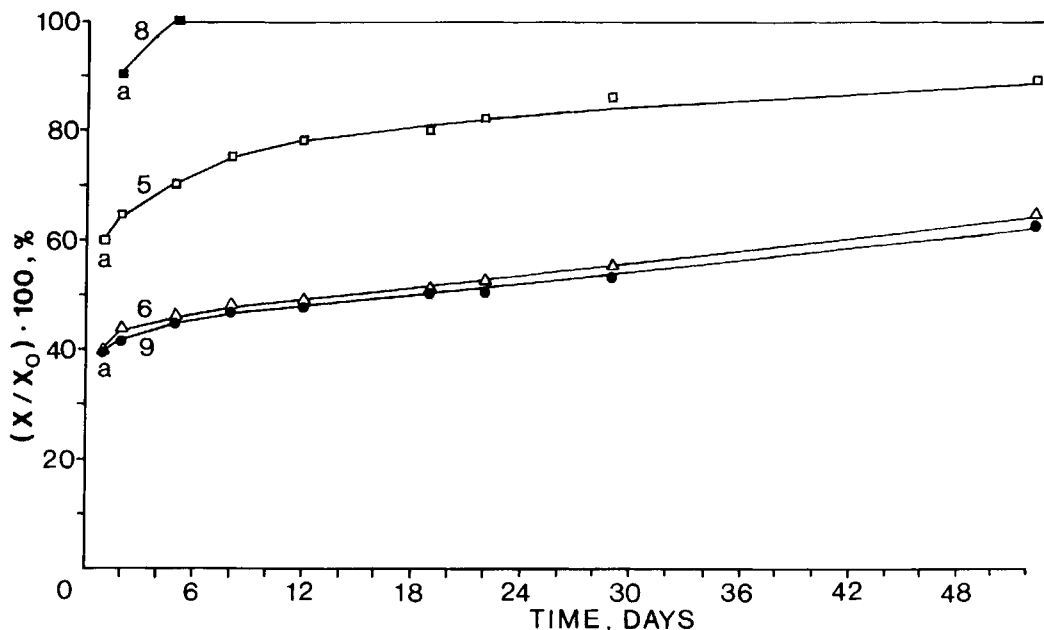
it resulted from the high specific surface areas of these materials (see Table I, case No. 5, 8).

It is remarkable, that the adsorption of methylene blue and alizarin yellow under same conditions (like shape of samples, etc.) follows the order (Fig. 7 and 8): No. 8 > 5 > 6 > 9.

In order to explain the similar behavior of both dyes, the molecular structures of these dyes must be taken into consideration. The molecule of methylene blue<sup>19</sup> involves an organic cation, which consists of the functional part of the dye and includes the following groups:  $\text{S}^+$  (electron donor),  $\text{N}^+(\text{CH}_3)_2$ , twice (electron donor). The molecule of alizarin yellow (19) contains:



On the other hand, the surface of carbonaceous materials (like charcoal) may contain basic or acid groups.<sup>20</sup> The adsorption of a dye (methylene blue, alizarin yellow) into carbonaceous material is influenced not only from pore sizes of carbonaceous ma-



**Figure 8** Adsorption of alizarin yellow from aqueous solution on carbonaceous materials (having diameter of "grains"  $d < 63 \mu\text{m}$ ).  $X$ : adsorbed amount of alizarin yellow;  $X_0$ : initial amount of alizarin yellow in solution before adsorption;  $m$ : amount of carbonaceous material = 10 g/L of solution (for symbols 5, 6, 8, and 9, see Table I).

terial but also from electron donor-acceptor (EDA) interactions between the functional groups of dye and carbonaceous material. The adsorbance of methylene blue indicates presence of electron acceptor groups contained in carbonaceous material. Adsorbance of alizarin yellow indicates the presence of electron donor groups. According to what has been already mentioned, the surface of carbonaceous materials contains both basic and acid groups.

## CONCLUSIONS

For lignocellulosic material (like olive stones) used as raw material for the production of activated carbons, higher amount of cellulose instead of lignin is more preferable under the aspects of increased specific surface area and increased adsorption of dyes. Simultaneously, higher weight losses take place during carbonization process. However, usage of lignin, especially in combination with novolac, lead to carbonaceous materials having good characteristics as adsorptive media and to low weight losses during carbonization. Particularly, the materials consisted of 20% novolac and 80% cellulose or 80% lignin reveal optimum characteristics of production process and of carbonaceous materials that are suitable as adsorptive media.

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