Production of Carbonaceous Adsorbents by Using Novolac-Resin and Cottonseed

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Synopsis

Mixtures of novolac resin with pressed cottonseed in different proportions after their curing as small cylinders, and also pressed cottonseed as powder were pyrolyzed until 1000°C. Some samples follow, as well as an activation process by steam between 700 and 950°C. The weight losses of the samples are much higher, up to 500°C, while small weight losses are observed over 800°C. The weight losses for the 100% pressed cottonseed during the carbonization are essentially higher than those of the specimens also containing novolac; indeed, for the total weight losses up to 1000°C an increasing linear dependence was found with increasing proportion of the cottonseed in its mixture with novolac. The shrinkage of the specimens also containing novolac follows in general a curve similar to that of the weight losses for the corresponding case. The specific surface areas of the carbonaceous materials produced show higher values with measuring by CO_2 than by N_2 due to the larger dimensions of the N_2 molecule as compared to the CO_2 molecule, so that N_2 areas are more sensitive to slight changes in aperture sizes of the porous materials produced. The specific surface areas of the materials that have also been activated indicate higher values in comparison with those without activation and also higher than activated carbon commercially available. The more increased and fine porous structure of the activated carbons as compared to those only pyrolyzed become also obvious from the corresponding photos obtained by the scanning electron microscope. These results are also in agreement with the discoloring ability of the produced adsorptive media for the methylene blue from aqueous solution, following the Freundlich equation for the adsorption.

INTRODUCTION

The production of products by using cheap raw materials is a requirement with an important meaning nowadays. Such raw materials are certainly some agricultural byproducts, from which other useful final products after appropriate treatment can be produced. Activated carbon derived from vegetable material can be used to remove color and odors or, in general, adsorb many organic materials.[1] Such agriculture byproducts that can be used as raw materials for the production of carbonaceous adsorptive media are, e.g., coconut hulls, olive stones, apricot stones, almond shells, etc.[2-5]

Besides, carbonaceous adsorptive media have been produced by combination of an agriculture byproduct (as olive stones) or typical raw material for production of activated carbon (as lignite) with polymer resins (as phenol–formaldehyde resin).[6-8] According to the ratio of both materials (e.g., lignite, novolac resin), samples as powder or a cylindrical form can be produced,

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which resemble lignite or novolac and therefore indicate the corresponding pore-volume distribution. The last mentioned are very different for the corresponding carbonaceous materials produced by pyrolysis until 1000°C of raw materials consisting of lignite only or of novolac only. Furthermore, by using novolac in comparison with lignite there is the advantage of having a binder, so that by combination of both materials various molded articles can be constructed.[7]

It has been found that carbonaceous adsorptive media can be derived from cottonseed and novolac resin.[9] The cottonseed is an agriculture byproduct as residual of the treatment to obtain the cotton, and it is produced in large amounts per year in certain countries. This study concerns the production of carbonaceous adsorptive media with a combination of cottonseed and novolac resin as raw materials, and also the characterization of the products derived, including their comparison to commercial adsorbent.

EXPERIMENTAL

Production Method

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).[10] The novolac produced was ground to powder, as also the hexamethylenetetramine ("hexa"), which was used as a curing medium in the ratio of novolac/"hexa" = 3.5 : 1 wt/wt.

The cottonseed used was pressed, ground, and sifted, and grains in a diameter less than 300 μm were obtained and homogenized. Then, cottonseed was mixed in different proportions with novolac in addition to an appropriate quantity of "hexa." The mixture, after being homogenized, was placed into small cylindrical molds (i.e., dimensions $\Phi 5 \times 15$ mm). The curing was performed by heating at 170°C for 30 min.

The specimens, after being removed from the molds, were put into a horizontal oven and were heated under N_2 atmosphere at an average heating rate of about 4°C/min until 1000°C, having a residence time of 10 min at this temperature. In the case of 100% cottonseed, the powder was directly carbonized. The weight losses during the thermal degradation of the samples were determined by weighing them before and after the carbonization process. The shrinkage of the specimens during their thermal degradation was also determined by measuring their length before and after the carbonization. Then, for some samples followed an activation process by using steam at a temperature between 700 and 950°C in a vertical oven. By weighing the sample before and after this process the burnoff was also determined.

Characterization of the Carbonaceous Materials Produced

The *specific surface area* of the samples after their thermal degradation was measured according to DIN 66 132. As gas for the measurements N_2 and CO_2 were used, and the measurements were done at -196 and -79°C correspondingly.

TABLE I
Composition of the Raw Materials and Conditions Used
for the Production of Carbonaceous Materials

Run	Novolac/pres. cottonseed	Carbonization (maximum temperature)	Activation
1	0/100	1000°C	—
2	20/80	1000°C	—
3	20/80	1000°C	930°C, by steam burnoff 63%
4	Commercial activated carbon		

The *structure* of the samples after their thermal degradation was examined with the aid of the scanning electron microscope of type Cambridge Stereoscan S-150.

The *discoloring ability* of the samples after their thermal degradation was also examined for the dye of methylene blue from its aqueous solution (initial concentration 0.0320 g/L). This dye is used to inhibit polymerization, on the one hand,[11] and has also been used broadly in the past for the evaluation of activated carbons.[12] For this determination a certain amount of a carbonaceous material as powder was mixed with a definite amount of an aqueous solution of the dye at 25°C under continuous stir by using a magnetic stirrer. By obtaining liquid samples at different time intervals and after removal of the solid components from the samples, the color of the pure liquid was colorimetrically determined (by using a calibration scale or with the aid of the Colourimeter Lovibond Tintometer Model E).

RESULTS

Table 1 shows the composition and the proportions of the raw materials used, as also the maximum temperature for the carbonization and activation process of the carbonaceous materials produced (case nos. 1–3). In comparison with these cases one case of commercial activated carbon is also examined.

Figure 1 shows the weight losses of samples during their carbonization up to 1000°C. In all cases the weight losses are very high until 500°C, while generally small weight losses are observed over 800°C. The weight losses of the 100% pressed cottonseed at the separate stages of the thermal degradation are essentially higher than those of the samples that also contained novolac. The total progress of the curves are almost the same, and they have an appropriate displacement to higher weight losses with an increasing amount of cottonseed.

Figure 2 presents the weight losses of samples heated until 1000°C according to an increasing ratio of pressed cottonseed/novolac, which results in a linear dependence. Figure 3 indicates the change of the length (shrinkage) of molded specimens up to 1000°C. The more important shrinkage is observed up to 800°C, while over 800°C small shrinkage of the specimens takes place.

Table II summarizes the results of the determination of the specific surface area of samples after their thermal treatment by using CO_2 or N_2. In the cases of only pyrolyzed samples (case nos. 1 and 2) the specific surface areas by
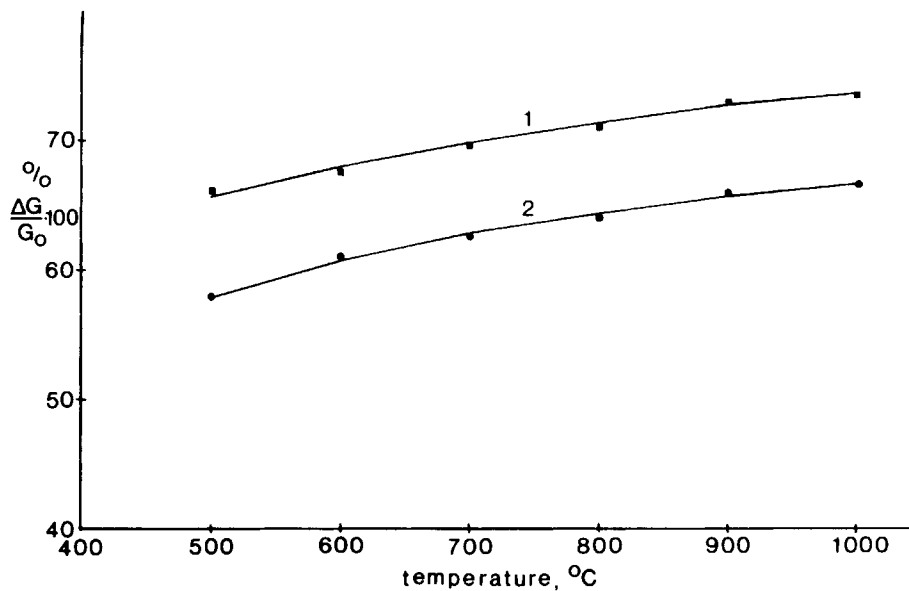
Fig. 1.   Weight losses of samples during their thermal degradation: (1) 100% pressed cotton-seed; (2) 20% novolac–80% pressed cottonseed. (The weight losses include ~ 8% initial moisture of the pressed cottonseed.) ΔG = weight losses, G_0 = initial weight.
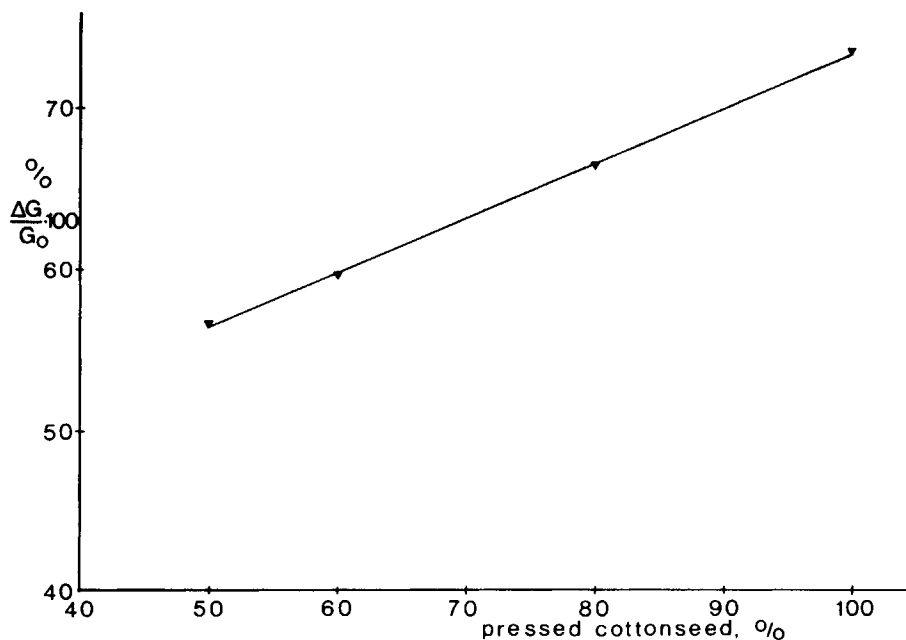

Fig. 2.   Weight losses of samples heated until 1000°C according to the proportion of pressed cottonseed in mixture with novolac. (The weight losses include ~ 8% initial moisture of the pressed cottonseed.) ΔG = weight losses, G_0 = initial weight.
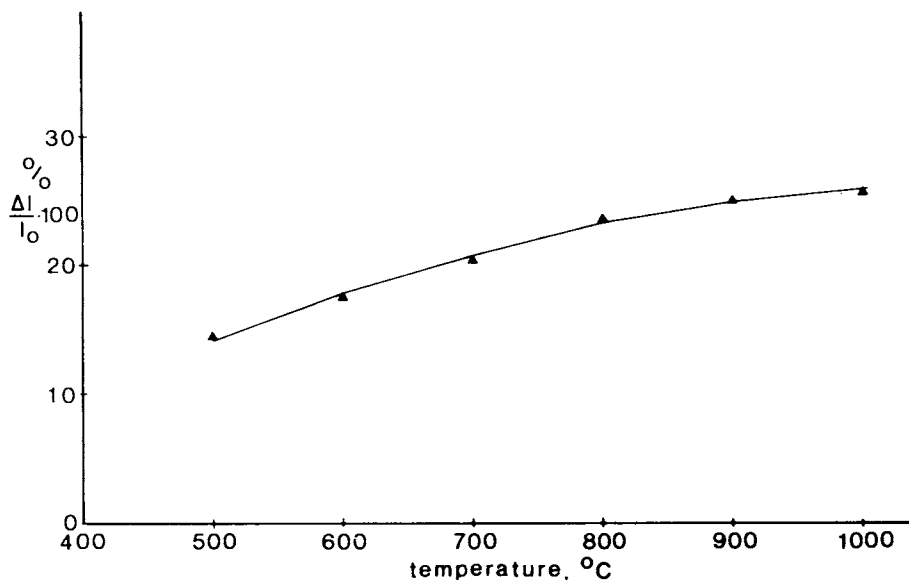
Fig. 3.   Change of the length (shrinkage) of molded specimens during their thermal degradation (20% novolac–80% pressed cottonseed). Δl = change of the length, l_0 = initial length.
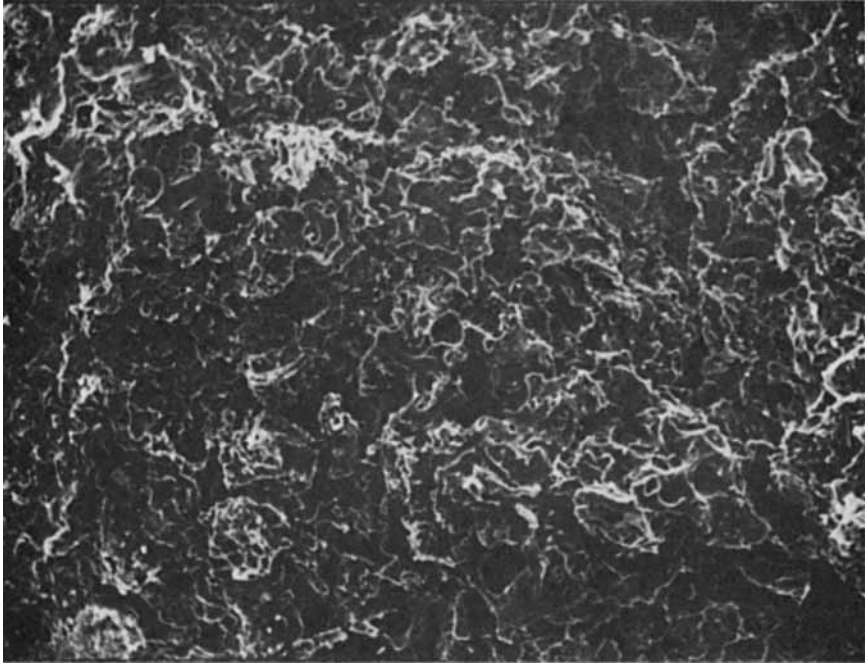
using CO_2 and also N_2 are lower than 100 m^2/g. On the contrary, in case no. 3, in which after the pyrolysis activation by steam has also been performed, the sample has high values of specific surface areas measured by CO_2 and also N_2, and both of them really exceed the corresponding values of the commercial activated carbon (case no. 4). Generally, it is also observed that the value of the specific surface area is higher by using CO_2 than N_2.

From Figures 4 and 5 can be seen the structure of different samples with the aid of scanning electron microscope. The activated case (Fig. 5) has a finer porous structure in comparison with the appropriate pyrolyzed case (Fig. 4).
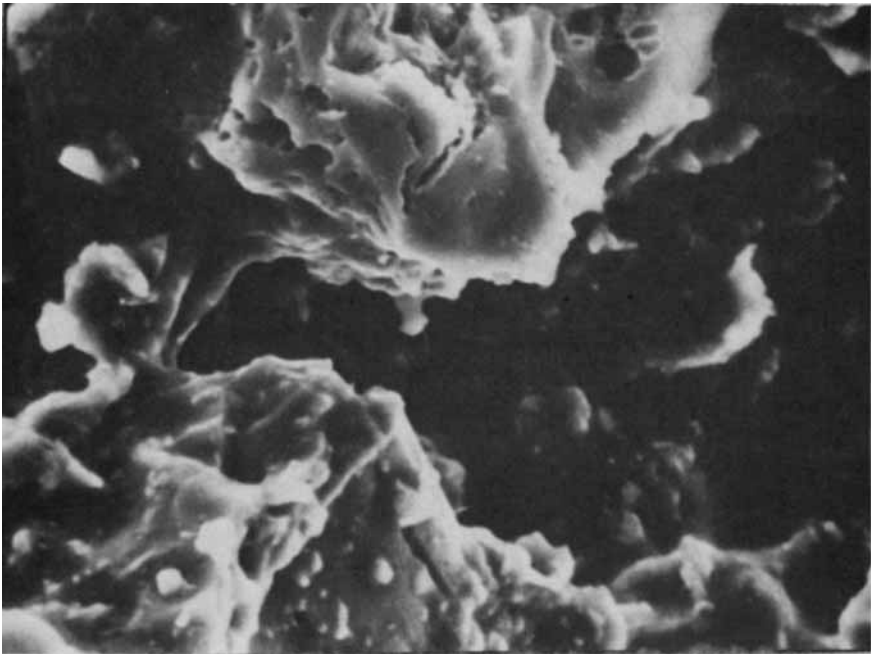
Figures 6–8 present the results of the discoloring of aqueous solution of the methylene blue by using various carbonaceous materials as adsorptive media. In all four cases (Figs. 6 and 7) the same curve of adsorption–time is observed, i.e., high adsorption appears initially, then an intermediate interval of decreasing rate, and finally the equilibrium stage is approached.

TABLE II
Specific Surface Area of Different Carbonaceous
Materials by Using CO_2 or N_2

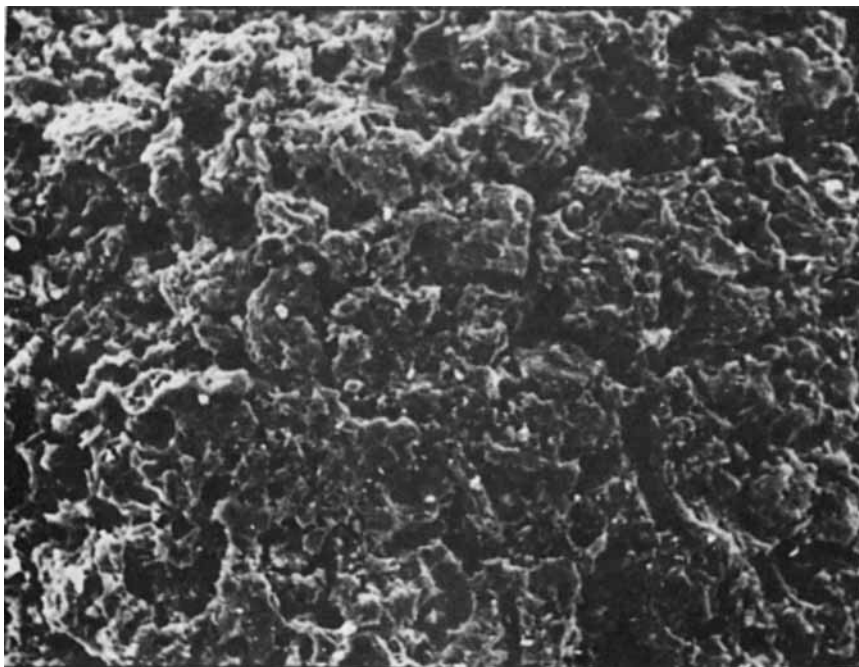| Run	Specific surface area by CO_2 (m^2/g)	Specific surface area by N_2 (m^2/g)	Shape of samples
1	< 100	< 100	Powder
2	< 100	< 100	Small cylinders
3	900	850	Small cylinders
4	600	~ 500	Powder

(a)

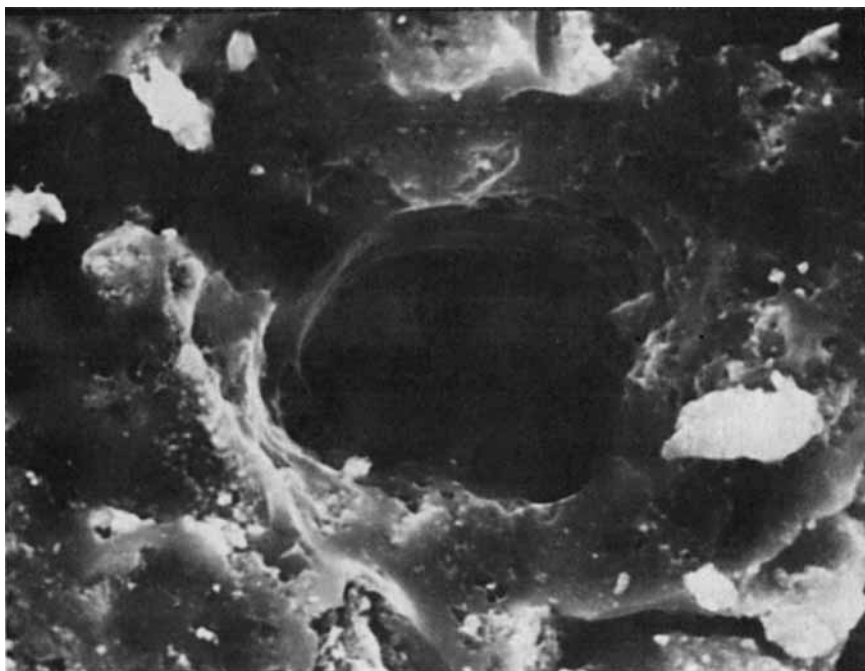(b)

Fig. 4. Photographs by using the scanning electron microscope (case no. 2, Table I): (a) magnification ×83; (b) magnification ×1050.

(a)

(b)

Fig. 5.   Photographs by using the scanning electron microscope (case no. 3, Table I): (a) magnification ×83; (b) magnification ×1050.
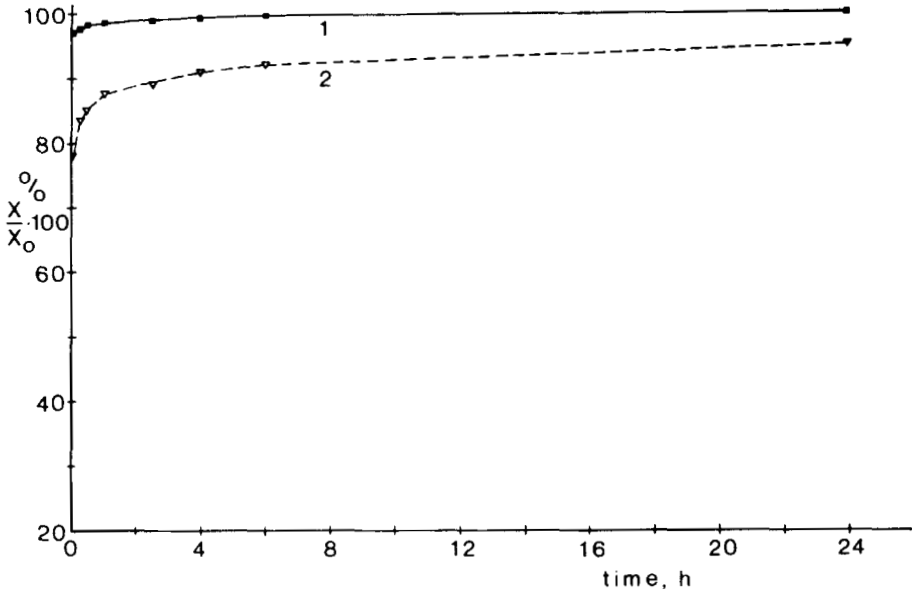
Fig. 6. Adsorption of methylene blue from aqueous solution on carbonaceous materials (see Table I): (1) 100% pressed cottonseed; (2) 20% novolac–80% pressed cottonseed. X = adsorbed amount of methylene blue, X_0 = initial amount of methylene blue in the solution before the adsorption, m = amount used of carbonaceous material = 1 g/100 mL of solution.
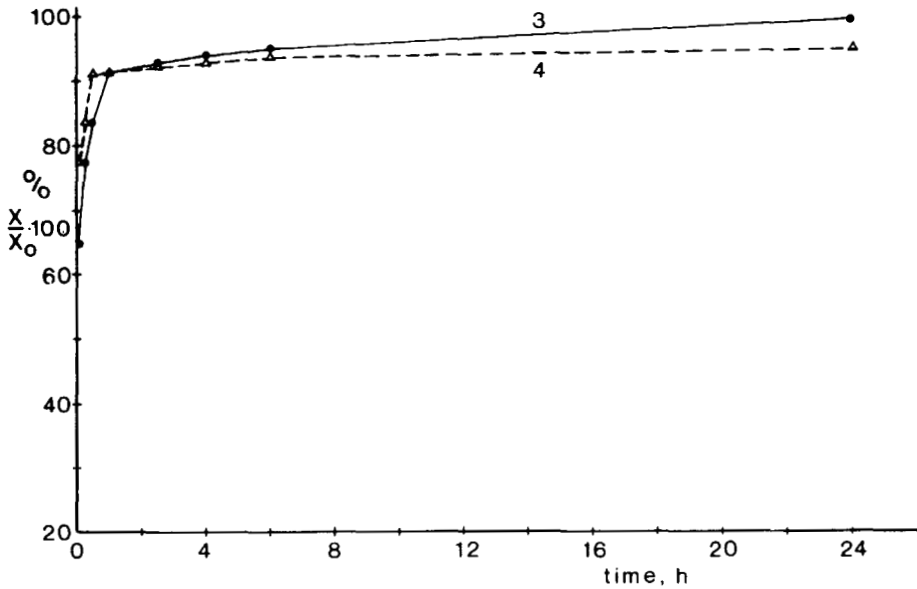

Fig. 7. Adsorption of methylene blue from aqueous solution on carbonaceous materials (see Table I): (3) 20% novolac–80% pressed cottonseed; (4) commercial activated carbon. X = adsorbed amount of methylene blue, X_0 = initial amount of methylene blue in the solution before the adsorption, m = amount used of carbonaceous material = 20 mg/100 mL of solution.
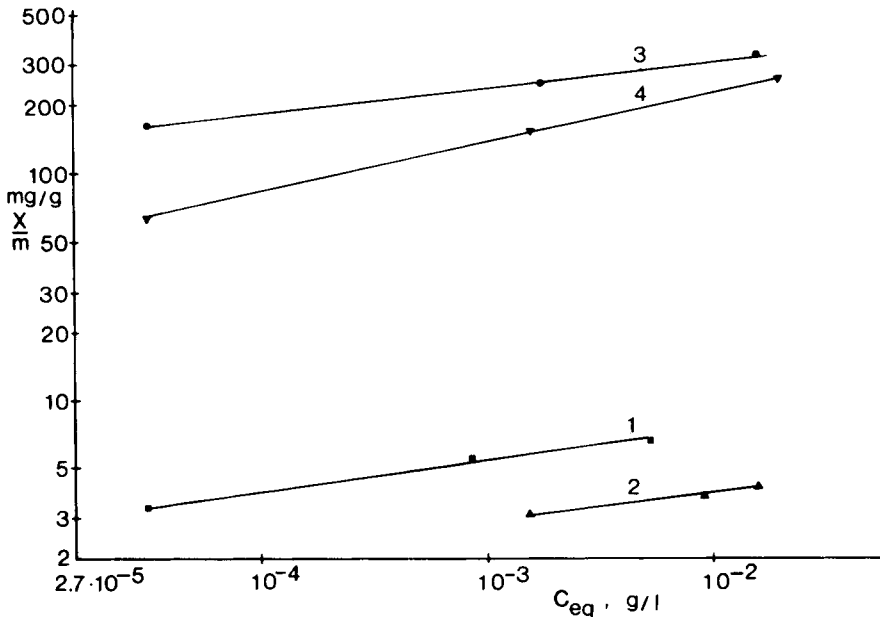
Fig. 8. Adsorption of methylene blue from aqueous solution on carbonaceous materials (see Table I) according to the Freundlich equation. X/m = adsorbed amount of methylene blue per weight unit of the carbonaceous material used; C_{eq} = concentration at the equilibrium of the adsorbed substance (methylene blue) from the solution.

The cases of Figure 7 have greater adsorption ability than those of Figure 6, since it must be taken into consideration that, in the last-mentioned cases, a 50 times greater amount of the carbonaceous material in the initial solution of the dye is used. Besides, there is found a greater adsorption ability in case no. 3 (Table 1), which has been prepared in the laboratory, as compared to the case no. 4, supplied commercially.

The adsorption of different substances like dyes and phenol on activated carbons follows the Freundlich equation or the Langmuir equation.[13,14] The experimental isothermal data of both above-mentioned carbonaceous materials have been proven according to these equations. The result is that the Freundlich equation is valid:

$$\frac{X}{m} = K \cdot C_{eq}^{1/n} \tag{1}$$

where X/m = adsorbed amount (e.g., of the dye) per weight unit of the adsorptive medium, C_{eq} = concentration at the equilibrium of the adsorbed substance from the solution, and K, n = empirical constants.

The constants of eq. (1) can be determined from the graphic expression of $X/m - C_{eq}$ in double-logarithm paper. Figure 8 represents the corresponding straight lines for the examined cases. The result is that case no. 3 has the greatest adsorption ability, consisting of carbonaceous material prepared in laboratory, and it exceeds case no. 4 supplied commercially. Besides, the

adsorption in case no. 1 (100% pressed cottonseed) exceeds those of case no. 2 (20% novolac–80% pressed cottonseed).

DISCUSSION

Pressed cottonseed as powder, and also molded specimens, produced with a combination of novolac/pressed cottonseed = 20/80, have been pyrolyzed up to 1000°C. It was found out lower weight losses for the samples also contained novolac (Fig. 1). The behavior of these specimens must be attributed to the systems of aromatic rings, which are stable during the thermal degradation as compared to other chemical substances.[15] Further, from Figure 3 there is established an almost similar progress for the decrease of the length in relation to the decrease of weight (Fig. 1) during the thermal degradation of the samples, which leads to the conclusion that this shrinkage must be due to the decreasing of the mass. So, an extra shrinkage cannot be observed, which could be attributed to other factors like crosslinking reactions or condensations of aromatic compounds to form polycyclic aromatic systems, which occur over approximately 700°C.[15] Worth mentioning is also the conclusion coming on the basis of Figure 2, i.e., there is an increasing linear dependence of the weight losses during the pyrolysis with an increasing percent of pressed cottonseed in the initial mixture of the raw materials. This information is useful for the plan of a production proceedings by choice of the appropriate proportion in order for the weight losses to be optimized in relation, of course, to the adsorption properties of the carbonaceous material.

During the activation by steam there is surely an extra weight loss, but an increasing porous structure is simultaneously created as compared to the corresponding cases of only pyrolyzed samples, as a result of using scanning electron microscopy (Figs. 4 and 5). This conclusion is also found out from the measurements of the specific surface area by using CO_2 or N_2 in the case of samples of only pyrolyzed or pyrolyzed and then activated (Table II, compare case no. 2 with no. 3).

Different values of the specific surface area by using CO_2 or N_2 (which are higher by using CO_2), have similarly been observed for carbonaceous materials derived from the pyrolysis of other organic materials, such as chars of lignite or anthracite[16] or materials containing thermosetting polymers (such as polyfurfuryl alcohol).[17] Since the minimum dimension of an N_2 molecule (0.365 nm) is larger than that of a CO_2 molecule (0.33 nm), N_2 areas are more sensitive to slight changes in aperture sizes, which have highly microporous materials like coals and chars.[16] From investigations based on the above-mentioned materials it has been concluded that the N_2 surface area is a measure of transitional and macroporosity, whereas adsorption of CO_2 measures essentially the total surface area of microporous coals and chars.[18] For the cases produced (Table I) and on the basis of the values of the specific surface area by using CO_2 or N_2 (Table II) it is found that by activation (case no. 3) an increasing porous structure is created, containing not only transitional pores and macropores but also micropores.

The activated sample after its pyrolysis as compared to that supplied commercially (Tables I and II, compare case no. 3 with no. 4) has higher values of specific surface area measured by N_2 or by CO_2; methylene blue also

has a higher adsorption ability (Figs. 7 and 8). That means that the porous structure has been increased by activation, so that more pores are accessible for the adsorption of a gas (CO_2, N_2) or a dye from its aqueous solution.

In conclusion, carbonaceous adsorptive media with a combination of raw materials novolac and pressed cottonseed can be produced. The use of novolac as compared to 100% pressed cottonseed has some advantages, such as lower weight losses during the thermal degradation of the initial material, and also the facility to mold various shapes of specimens because the resin acts as a binder.

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