JOURNAL OF MATERIALS SCIENCE 31 (1996) 199–203

Influence of resin content on the sorption properties of adsorbents produced from novolac–biomass composites

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Carbonaceous adsorbents produced from mixtures of novolac resin and olive stone biomass in various proportions were investigated with respect to their ability to adsorb toluene and cyclohexane from the vapour phase. The adsorption of toluene on all adsorbents was found to be higher than that of cyclohexane. The overall diffusion coefficient, *D*, of the adsorption process, the specific surface area and the pore volume of the adsorbents have been calculated. The results are discussed in terms of the size and shape of the pores, the polarity of the adsorbate and the dispersion forces between adsorbent and adsorbate. It is concluded that slit-shaped pores are also present in the adsorbents which are characteristic of carbon molecular sieves. Toluene can enter more pores than cyclohexane for the adsorbents used. The adsorbent derived from the mixture of novolac/biomass = 20/80 shows the highest adsorption (i.e. equilibrium uptake, diffusion coefficient, specific surface area and pore volume) of toluene and cyclohexane.

1. Introduction

Adsorbents are widely used in liquid- and gas-phase adsorption for water- and air-pollution control and in various separation and purification processes [1]. Activated carbons are the most suitable adsorbents for the removal of substances in low concentrations. Adsorbent resins produced from organic polymers, as well as zeolites, show advantages in the process of "solvent recycling" [2]. The effectiveness of the adsorbent in this process depends not only on the adsorption but also on the desorption ability of the adsorbent. However, activated carbon should also be connected in such processes in order to have very low vapour emissions [2].

Commercial activated carbons are produced primarily from carbonaceous materials like coal, wood, peat, coconut and petroleum coke, using a thermal or chemical activation process [1, 2]. Furthermore, commercial activated carbons are available which are produced by carbonization of typical synthetic polymers, such as macroreticular styrene/divinylbenzene copolymers, and they are used, for example, in drinking water treatment [1, 3]. Activated carbons show very high adsorption capacity (up to 0.85 $cm^3 g^{-1}$); however, they have a broad pore distribution with a high portion of meso- and macropores [4]. Carbon molecular sieves having high adsorption capacity (0.40 $cm^3 g^{-1}$) and 0.7–0.8 nm pores have been prepared by pyrolysis of polyvinylidene chloride (PVDC) [5]. By pyrolysis of Saran (copolymer consisting of 80–90% polyvinylidene chloride and various amounts of polyvinyl chloride and plasticizer) the carbonaceous residues have 0.6 nm pores with an adsorption capacity of 0.36 $cm^3 g^{-1}$ [6]. The pyrolysis residues of phenol-formaldehyde resin have pore diameters of 0.4 nm and a low adsorption capacity of 0.10 $cm^3 g^{-1}$ [4].

Carbon molecular sieves (CMS) have some advantages compared to zeolites [3, 7]. Zeolites are not stable in an acidic medium, whereas CMS are stable. Zeolites prefer to adsorb water and therefore their separation ability decreases strongly in the case of a humid gas mixture. CMS are less hydrophilic and their capacity and selectivity are relatively unaffected by the presence of water (vapour or liquid). CMS are more suitable than zeolites for the separation of mixtures of aromatic substances due to their slit-shaped pores. Zeolites have cylindrical pore openings and tend to adsorb linear molecules, while CMS tend to have selective adsorption capacities in the order planar > linear > branched [3]. However, polarity differences are also used for zeolites to separate aromatic from saturated paraffins and hydroaromatic compounds [8].

Polymeric carbon adsorbents have also been produced by using appropriate mixtures of novolac resin with olive stone biomass, which is an agricultural by-product produced in very large quantities in

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mediterranean and other countries [9–11]. The aim of this work was to investigate the sorption properties of such adsorbents produced by various proportions of novolac–biomass. The vapour phase adsorption of toluene and cyclohexane was investigated.

2. Experimental procedure

2.1. Adsorbent preparation

Carbonaceous adsorbents were produced from novolac resin and biomass [9, 10]. The resin was prepared by polymerization of phenol and formaldehyde (in proportion 1.22: 1 mol: mol) with oxalic acid as catalyst (in proportion 1.5% wt/wt phenol) after which the resin was separated, dried and pulverized. Biomass consisted of the agricultural/industrial by-product that is left from olives after pressing and separation of the oil. It was dried, ground and sieved to yield grains with a diameter less than 300 μm. Hexamethylenetetramine (hexa) was used as the curing agent of novolac in the proportion 7: 2 wt novolac: wt hexa. Mixtures of biomass with novolac–hexa were formed into small cylinders after curing at 170 °C for 30 min. Carbonization of cured specimens was accomplished in a cylindrical tube oven under a continuous flow of nitrogen. The temperature of the oven was raised to 1000 °C at the rate of 4 °C $\min^{-1}$, after which the samples remained in the oven for a further 10 min and were subsequently cooled to room temperature and kept under vacuum.

2.2. Characterization by sorption

The adsorbents that were produced by carbonization of the cured material, were degassed prior to use under vacuum at 200 °C for 3 h. Toluene and cyclohexane, that were used for the vapour-phase adsorption were reagent grade. For the vapour-phase adsorption experiments a quartz spring apparatus, including a Griffin and George cathetometer, was used. This apparatus is described in detail elsewhere [12, 13]. All sorption experiments were conducted at 20 °C and a pressure of 0.1 relative to the saturation pressure of the vapour of this temperature.

3. Results

Table I shows the composition before the carbonization process and the form of the carbonaceous materials produced. For the adsorption experiments, the adsorbents were used in this form. Fig. 1 shows the weight loss and the shrinkage of the materials during the carbonization process up to 1000 °C. It is observed that the weight loss and the shrinkage decrease as the proportion in novolac increases. The plot of the change in weight and length versus the proportion of raw materials gives straight lines.

Figs 2 and 3 show the weight of the adsorbed vapour (toluene and cyclohexane, respectively) per unit weight of adsorbate (i.e. uptake) versus time, for the adsorbents of Table I. The curves show initially a strong increase up to about $t = 30$ min, after which they are gradually stabilized at about $t = 60$ min. The behaviour of all adsorbents against both adsorbates, toluene and cyclohexane, is qualitatively similar and toluene is adsorbed more strongly than cyclohexane by the same adsorbent. The following classification scheme might be applied:

Group 1: C0, C100

Group 2: C40, C50

Group 3: C20

If the particles can be approximated as uniformly porous spherical bodies of fixed size, then diffusion theory shows that diffusion-controlled uptake into an

TABLE I Compositions and form of materials

No	Symbol	Proportions of raw materials		Form of materials
		Novolac	Biomass	
1	C100	100	0	Granules
2	C50	50	50	Small cylinders
3	C40	40	60	Small cylinders
4	C20	20	80	Small cylinders
5	C0	0	100	Powder

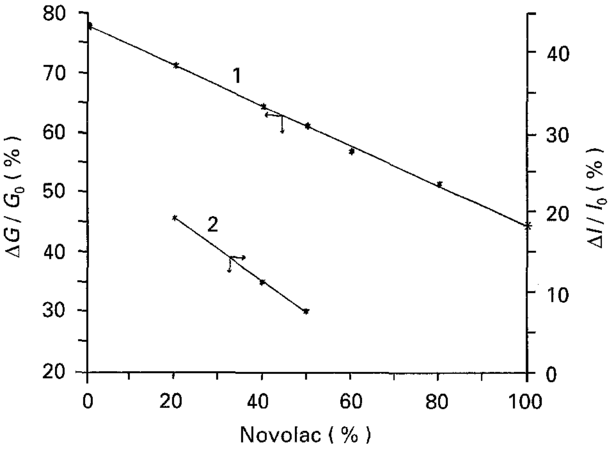

Figure 1 (1) Weight loss and (2) shrinkage versus novolac contained in the initial mixture.

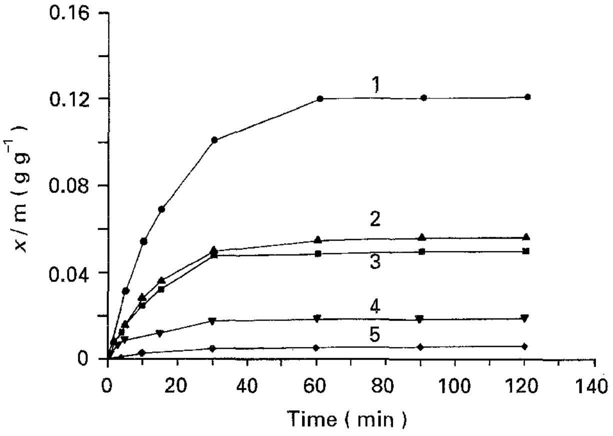

Figure 2 Adsorption of toluene versus time x, adsorbed amount of vapour; m amount of carbonaceous adsorbent. 1, C20; 2, C40; 3, C50; 4, C0; 5, C100 (see Table I).

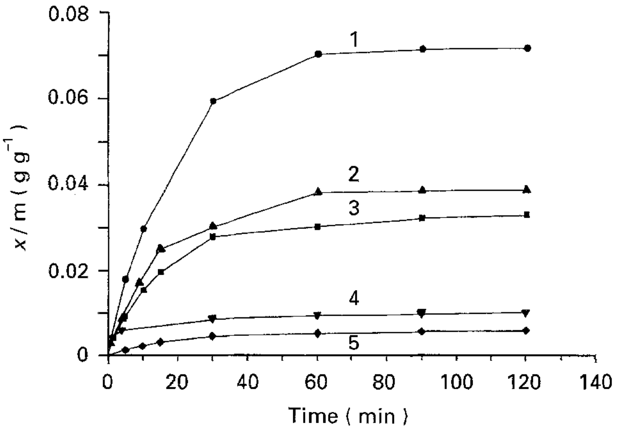

Figure 3 Adsorption of cyclohexane versus time: x, adsorbed amount of vapour; m, amount of carbonaceous adsorbent. 1, C20; 2, C40; 3, C50; 4, C0; 5, C100 (see Table I).

TABLE II Diffusion coefficients according to the diffusion equation 1

Adsorbent	vapour	Diffusion coefficients D/a^2 (10^{-5} s^{-1})	Radius, (mm)	D (10^{-6} cm^{2}s^{-1})
C0	Toluene	15	1.2	2.2
C20		3.1		0.5
C40		4.3		0.6
C50		3.9		0.6
C100		2.7		0.4
C0	Cyclo-hexane	6.3	1.2	0.9
C20		3.1		0.5
C40		4.3		0.6
C50		4.3		0.6
C100		2.0		0.3

initially empty solid from a gas phase at fixed pressure can be approximated at small times by the equation [14,15]

$$\frac{Q_t - Q_0}{Q_\infty - Q_0} = \frac{6}{\pi^{\frac{1}{2}}}\left(\frac{Dt}{a^2}\right)^{\frac{1}{2}} \qquad (1)$$

where Q_t, Q_0, Q_∞, are the amounts adsorbed at time t, when $t = 0$, and at equilibrium ($t \to \infty$), respectively. D is the diffusion coefficient, assumed to be independent of concentration, and a is the effective radius of the particle.

The calculation of D depends on the parameter a which is difficult to determine (Table II). Different considerations concerning the type and the values of the parameter a have been reported in the literature. In many cases of carbonaceous adsorbents, the parameter a can be set equal to the particle radius, r [8,15,16].

Figs 4 and 5 show the ratio of the vapour uptake at time t divided by the corresponding equilibrium value, against the square root of the time. The adsorbents C0 and C100 show the fastest and slowest rate of adsorption, respectively, and all other adsorbents have an intermediate rate. A similar behaviour is observed in the adsorption of cyclohexane.

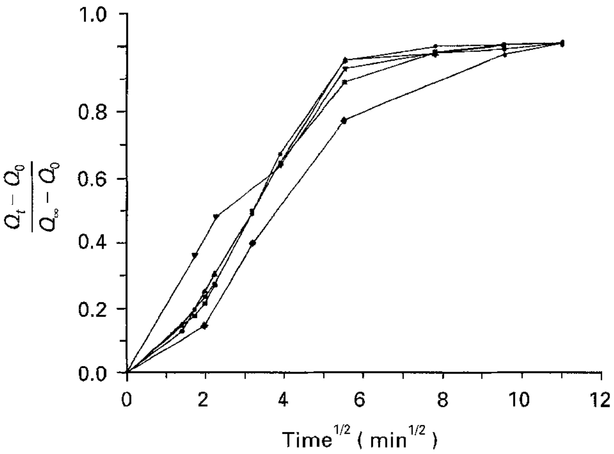

Figure 4 Ratio $(Q_t - Q_0)/(Q_\infty - Q_0)$ versus the square root of time for the adsorption of toluene. (●) C20, (▲) C40, (■) C50, (▼) C0, (◆) C100 (see Table I).

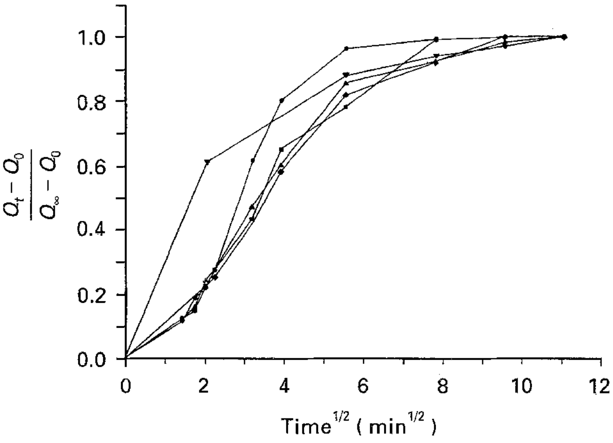

Figure 5 Ratio $(Q_t - Q_0)/(Q_\infty - Q_0)$ versus the square root of time for the adsorption of cyclohexane. (●) C20, (▲) C40, (■) C50, (▼) C0, (◆) C100 (see Table I).

The slopes of the initial parts of the curves of Figs 4 and 5 allow the calculation of the quantity D/a^2. Then, the diffusion coefficients, D, are calculated by using the above equation using the particle radius, r, in place of the parameter a. The particle radius, r, is the radius of a sphere having an external surface equal to that of the cylindrical samples used. From the values of D/a^2 and D it is observed that 100% biomass has the highest diffusion coefficient, 100% novolac has the lowest, and the mixtures of novolac–biomass have intermediate values in both adsorbates.

The specific surface area, A_p (m^2 g^{-1}), can be calculated from [17]

$$A_p = (X_m/M)\, a_m\, L \times 10^{-20} \qquad (2)$$

where X_m is the monolayer capacity in grams of adsorbate per gram of solid (obtained from the equilibrium value of adsorption), M is the molecular weight of the adsorbate (i.e. toluene or cyclohexane), a_m is the average area occupied by a molecule of adsorbate in the completed monolayer, and L is the Avogadro constant. According to Mikhail and Robens [18], the values of a_m are 0.38 and 0.46 nm^2 for cyclohexane and toluene, respectively.

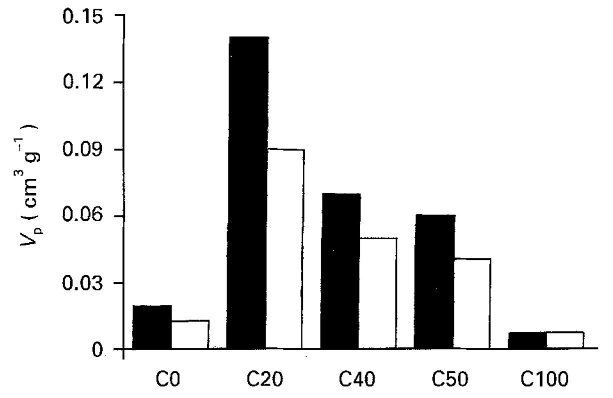

Figure 6 Pore volume, V_p, for the adsorption of toluene (black) and cyclohexane (white); for the indicated adsorbents, see Table I.

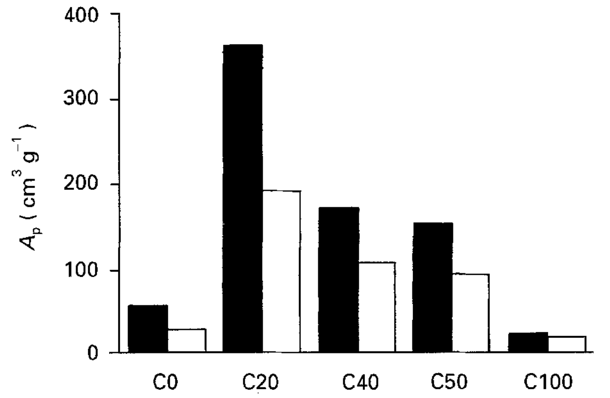

Figure 7 Specific surface area, A_p, for the adsorption of toluene (black) and cyclohexane (white); for the indicated adsorbents, see Table I).

Assuming that the volume of adsorbed vapour of the liquid fills all the pores with a diameter greater than the molecular diameter of the adsorbate molecule, then the pore volume (cm^3 g^{-1}) can be calculated from the vapour-phase adsorption according to

$$V_p = X_m/\rho \qquad (3)$$

where ρ is the density of the adsorbate.

Figs 6 and 7 show the results of the specific surface area, A_p, and the pore volume, V_p, for the adsorption of toluene and cyclohexane. C20 shows the highest values, C40, C50 show intermediate values and C0, C100 the lowest values for A_p and V_p. All materials show higher values of A_p and V_p for toluene than for cyclohexane.

4. Discussion

It is apparent from Figs 2 and 3 that the relative order of the adsorbents with respect to increasing vapour uptake is the same in both cases: C20 ≫ C40, C50 ≫ C0, C100. It is obvious that the pyrolysis residues of the mixtures of novolac with biomass had different porous systems from those of 100% biomass (C0) and 100% novolac (C100). Thus, the pyrolysis reactions of the mixtures differ from those of their simple components. Indeed, it has been observed [19], that the mixtures of novolac/biomass = 20/80 up to 75/25 pyrolysed up to ~600 °C show lower weight loss than that expected by the rule of mixtures due to additional cross-linkages of lignin contained in the biomass with the hexa. This stabilization effect vanished during pyrolysis at higher temperatures because of the breaking of other chemical bonds, for example, cross-linkages. Therefore, the weight loss at 1000 °C follows a linear relationship with increased novolac content (Fig. 1). The porous structure of the residues obtained from the mixtures favours the adsorption of toluene and cyclohexane compared to that of the simple components. The proportion of novolac/biomass = 20/80 (C20) seems to have the best porous structure with respect to the adsorption of toluene and cyclohexane.

From Figs 2 and 3 it is observed that all adsorbents containing biomass show a selectivity in toluene uptake with respect to cyclohexane. The uptake of toluene on the adsorbent C100 is only slightly higher than that of cyclohexane; however, in both cases, the adsorption is very low. This is an indication that the pore structure of the adsorbent derived from 100% novolac (C100) differs from that of the adsorbents derived from biomass alone, or from the mixtures of novolac–biomass. This is also consistent with the values of the diffusion coefficient, D, which are the highest for 100% biomass (C0), the lowest for 100% novolac (C100) and their mixtures have intermediate values. The adsorption of an adsorbate on an adsorbent depends on many parameters, such as the pore size of the adsorbent and their distribution, the shape of the pores, the molecular size and the shape of the adsorbate, the polarity of the adsorbent and the adsorbate, etc. Generally, it is difficult to evaluate the importance of these parameters, and especially for carbonaceous adsorbents which generally, opposite to other adsorbents like zeolites, do not have a uniform pore structure.

Important deviations in the molecular diameters of the adsorbate are described in the literature. For example, the molecular diameter of benzene is given as 0.451, 0.680 and 0.592 nm calculated from Van der Waals co-volume, bond lengths and liquid density, respectively [18]. As the critical diameter of benzene, the value of 0.37 nm × 0.70 nm is often used in the literature [6–8, 20], for cyclohexane the value of 0.48 nm × 0.68 nm [7, 20] and for toluene the value of 0.66 nm [15]. Cyclic compounds, like benzene and cyclohexane which have planar and large molecules are more suitable to be adsorbed into slit-shaped pores [6, 7]. Carbon molecular sieves (0.6 nm molecular sieve), which adsorb both benzene and cyclohexane to a greater extent than neopentane (its critical diameter is 0.62 nm), lead to the suggestion that they have slit-like pores and/or pore constrictions of less than ~0.57 nm thick and greater than ~0.70 nm wide [6]. On the other hand, the adsorption of nitrogen is referred to pores > 0.43 nm, the adsorption of neopentane to pores > 0.62 nm and such molecules can enter into round-shaped pores or also into slit-shaped pores if the pore dimensions are at least as large as the minimum molecular diameter [7]. Carbon molecular sieves prepared by the pyrolysis of polyvinylbenzene, polyfurfurylalcohol, polycrylonitrile, etc., should have slit-shaped pores which give them their molecular sieve properties [3]. Based on the hypothesis that micropores consist of slit cracks with approximately parallel walls, it has been considered that active carbons are formed of stacks of parallel carbonized layers separated by more than 0.336 nm and with a diameter close to 4.0 nm, bounded with hydrogen or other functional groups. Macropores are the interstices between these particles, micropores being closed fissures smaller than 1.0 nm wide between carbonized layers within the particles. Thus, flat or linear molecules penetrate active carbons very easily. This model, with slight differences, has been also proposed for the polymeric carbons. Polymeric carbons suitably activated are effective adsorbents in which the whole of the internal surface is available to small adsorbed molecules [21].

The adsorbates used differ not only in their molecular diameter but also in the shape of their molecules and the polarity. Both toluene and cyclohexane have flat molecules but cyclohexane occurs in two different conformations, i.e. arm-chair and boat forms, the former being more stable [22]. On the other hand, the dipole moment of the toluene is 1.13 10^{-30} C.m. and that of the cyclohexane in zero [23]. The dispersion forces between the aromatic π-electron system of toluene and the π band of the graphite-like planes of the carbon are also responsible for adsorption [24]. Furthermore, the adsorption of linear molecules like pentane on the adsorbents used in lower than that of the toluene and cyclohexane [25]. The selective adsorption capacity follows the order planar $>$ linear molecules, which is also observed in carbon molecular sieves [3]. For the adsorbent consisting of 100% novolac (C100), the low uptake of toluene and cyclohexane can be explained by the small pore diameters (0.4 nm) of the pyrolysis residues of phenol-formaldehyde resin [4] which cannot be filled with both adsorbates having larger molecules.

In conclusion, the adsorbents used also seem to contain slit-shaped pores which are characteristic for carbon molecular sieves. Toluene can enter into more pores than the cyclohexane for the adsorbents used. The adsorbent derived from the mixture of novolac/biomass = 20/80 shows the highest adsorption (with respect to equilibrium, diffusion coefficient, specific surface area and pore volume) for toluene and cyclohexane.

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Received 27 May 1994
and accepted 17 March 1995