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Characterization of Inorganic Carbon-Supported Microfiltration and Ultrafiltration Membranes by Aqueous Phenol Adsorption

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ABSTRACT

The adsorption of phenol on inorganic carbon-supported microfiltration and ultrafiltration membranes has been determined. Using the statistical Student's *t*-test, it has been shown that phenol adsorption data are well fitted to the Langmuir and BET isotherm equations. It was thus concluded that the adsorption of phenol was monomolecular and that the specific surface area (*SSA*) calculated from these data was essential. M1 and M2 ultrafiltration membranes were found to have a higher *SSA* than microfiltration M14 and carbon support membranes. Assuming that a simple model of the porous structure consisted of a packed bed of spherical particles, it was possible to determine an apparent average pore diameter from *SSA* data using the Carman–Kozeny equation. The *SSA* determined from phenol adsorption was found to be close to that measured from mercury porosimetry for the microfiltration membrane and carbon support. Such a result is due to the fact that there is a common basis between the Carman–Kozeny equation employed in the adsorption method and the determination of the ratio $4V/A$ (V = total porous volume, A = total pore area) in the mercury porosimetry method (as both methods consider a constant volume/surface ratio of the pores along the microporous membrane thickness).

Key Words. Inorganic membranes; Phenol adsorption; Specific surface area; Membrane support characterization

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INTRODUCTION

The specific surface area (*SSA*) of adsorbents is conventionally evaluated by measurements of the monolayer capacity of the adsorbent for a selected solute, with a well-defined molecular cross-sectional area. Monolayer capacity may be found by using either the Langmuir or BET equation to fit the equilibrium adsorption data. The usual method employed for the determination of *SSA* is the low temperature adsorption of N_2 with a fitting using the BET equation (1). However, some works show that a discrepancy exists between *SSA* determined from the N_2–BET method and from adsorption in solution (2).

According to previous works, phenol is a suitable solute for *SSA* determination. It fulfills the requirements suggested by Giles (3) for the evaluation of *SSA*. Phenol was used to determine the *SSA* of active carbons and carbon blacks (4–8).

The main purpose of the present paper is to investigate aqueous phase phenol adsorption in order to evaluate the *SSA* of inorganic (mineral) carbon-supported ultra- and microfiltration membranes and also to look for correlations between data calculated from adsorption and mercury porosimetry. It appears possible to draw interesting conclusions about the structure of the membrane support on the basis of the evaluation by phenol adsorption of the specific surface area of inorganic membranes.

Former results regarding phenol adsorption on inorganic Carbosep membranes used in the present work were not available, so an exact comparison with the literature was not possible. However, results on phenol adsorption are available for carbonaceous adsorbents like carbon blacks and activated carbons (4–6). Similar interactions may be expected between phenol and carbon adsorbents as those observed for phenol and Carbosep membrane support. For the objectives of the present study, one of the most important issues is to discover whether phenol adsorption is monomolecular and reversible because some important conclusions will be drawn from these assumptions. Available data (4, 6) show that a rather wide plateau exists on a phenol adsorption isotherm (most often in the 80–300 mmol/L range). Numerical values of the amount adsorbed on this plateau differ for various adsorbents, but the abovementioned range is generally observed. Puri et al. (6) also found that adsorption of phenol is generally reversible, with only a minor participation of nonreversible phenol bonding to some adsorbents. On analysis of phenol adsorption in the literature (6), phenol adsorption isotherms (after reaching a long plateau) are seen to start to rise rapidly, which may be attributed to multilayer or aggregate adsorption.

The study of membrane structure properties with an aqueous phase adsorption is a quite simple technique. Its operating procedures are also easy in comparison with a computer-driven mercury porosimeter (which is frequently used for micro- and ultrafiltration membranes).

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MATERIALS AND METHODS

Materials

The water used during experiments was deionized, distilled, and passed through a Millipore Q System (Millipore, Molsheim, France). Phenol (pro analysis) was purchased from Merck (Germany). Three types of Carbosep tubular mineral membranes (Tech-Sep, 01703 Miribel, France) were used: M1 and M2 ultrafiltration membranes, M14 microfiltration membranes, and carbon supports with no internal selective layer. The membrane was mainly composed of a zirconium oxide layer bound to the carbon support. Their characteristics are given in Table 1. Each membrane of 6-mm inner diameter, 2 mm thickness and 1.2-m length was cut into pieces 4.5 cm long. After cutting, they were thoroughly washed by tap water and distilled water to remove dust and then boiled in distilled water for 1 hour and kept in distilled water for around 24 hours before use. A given membrane piece was only used once in adsorption measurements. All adsorption measurements were repeated 3–5 times, and average values were used for graphic representation and calculations. The following phenol solutions were used for the adsorption experiments: 0.001, 0.0025, 0.005, 0.0075, and 0.01 mol/L.

Methods

Phenol Adsorption Experiments

Adsorption was carried out using a static method in which a 4.5-cm long piece of membrane was soaked in a sealed glass tube; 5 mL of a phenol solution was added to the tube and the tube was sealed. Adsorption time was 24 hours during which all tubes were immersed in a thermostating bath at 22°C

TABLE 1
Characteristics of the Membranes Used

	Membrane M1	Membrane M2	Membrane M14	Carbon support
Membrane selective layer thickness (μm)	13–15 μm[a]	13–15 μm[a]	13–15 μm[a]	—
Average membrane porosity (ε)	—[d]	—[d]	0.15–0.2[b]	0.15–0.2[b]
Average membrane pore diameter d_p (μm) or membrane molecular weight cutoff (Dalton)	150,000 Da (0.016 μm[c])	15,000 Da (0.0042 μm[c])	0.1–0.2 μm[b]	0.1–0.2 μm[b]

[a] From W. Naceur, S. Elmaleh, and A. Grasmick, *First International Conference on Inorganic Membranes* (*ICIM*), July 3–6, 1989, Montpellier, France, p. 141.
[b] Measured by mercury porosimetry (Micromeritics 9320, USA).
[c] Calculated by using the equation MW (Da) = $30d_p$ (Å)$^{5/3}$.
[d] Not available.

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and gently shaken. Phenol concentration after adsorption was determined spectrophotometrically by measuring the absorbance at 254 nm using a Kontron UVIKON 830 spectrophotometer (Switzerland) and compared to the absorbance of phenol standards of known concentration.

Modeling of Adsorption Isotherms

Langmuir Model. The classical Langmuir theory for gas adsorption can be applied to adsorption from solution if the solution is sufficiently dilute. This isotherm can be written in a linearized form as follows:

$$\frac{1}{a} = \frac{1}{Ka_{\mathrm{m}}c} + \frac{1}{a_{\mathrm{m}}} \tag{1}$$

where a is the adsorbed amount, c is the solution concentration, a_{m} is the Langmuir monolayer capacity, and K is a binding constant. The value of a_{m} corresponds to the plateau value of this isotherm. The two constants a_{m} and K can be determined by a least-squares fitting of data $1/a$ vs $1/c$. Using the adsorption data presented in Fig. 1, both constants have been determined for all the membranes studied.

BET Model. Brunauer, Emmet, and Teller (1) extended the Langmuir mechanism to second and higher molecular layers in the case of gas adsorp-

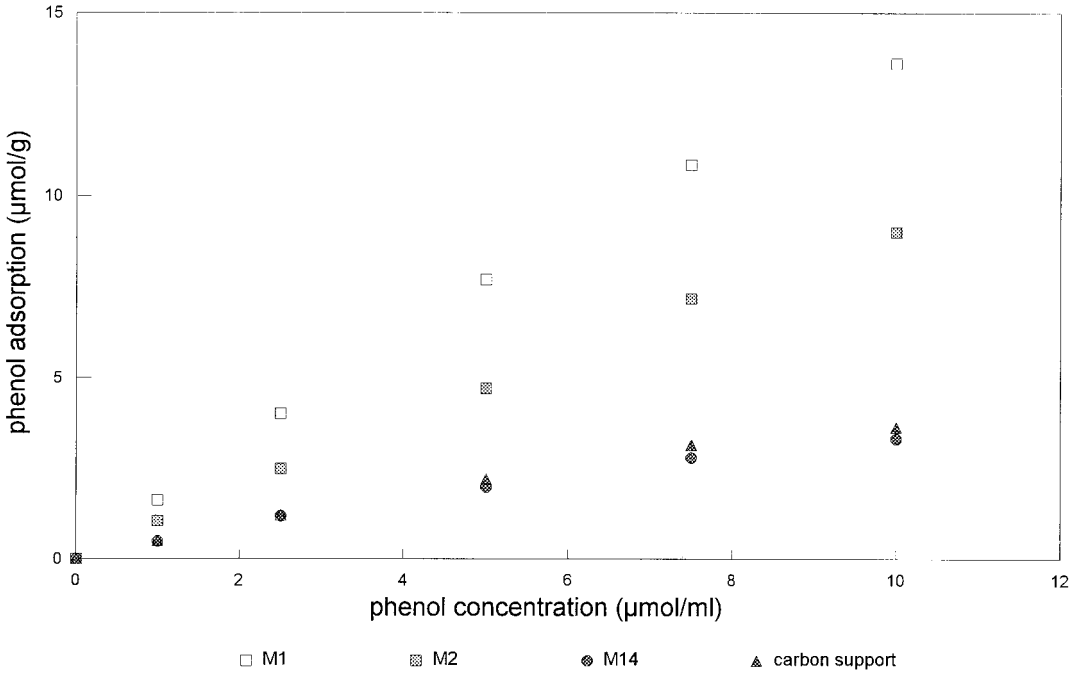

FIG. 1 Adsorption isotherms for phenol in static conditions on M1, M2, M14, and carbon support membranes.

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tion. Hansen et al. (11) showed that the BET model, although derived from gas adsorption, fits isotherms for adsorption well from solutions if p/p_0 is replaced by c/c_0. This is especially true if the solute is far more easily adsorbed than the solvent. We also intended to use this isotherm in order to compare it with the Langmuir one. The BET equation can be written in a linearized form (12) as follows:

$$\frac{c}{a(c_s - c)} = \frac{1}{Ka_m} + \frac{K-1}{Ka_m}\frac{c}{c_s} \tag{2}$$

As before, a is the adsorbed amount, c is the solution concentration, a_m is the BET monolayer capacity, c_s is the maximal solubility of a solute in a given solution, and K is a binding constant. Constants a_m and K can also be determined by a least-squares fitting of $c/a^*(c_s - c)$ vs c/c_s.

The BET isotherm has been successfully used by some authors (13) in solid/liquid systems of limited mutual solubility and for dye solutions (10, 11, 13, 14). The c_s value for phenol corresponds to its maximal solubility; a_m values have been calculated for a solubility limit of phenol equal to 1.1 mol/L at a temperature of around 20°C (15). This value was interpolated from a phase diagram. Yenkie and Natarajan (8) used a solubility limit for phenol of 0.97 mol/L while measuring the adsorption at 35°C. Because a_m was not found to be sensitive to c_s values higher than 100 mmol/L, we think that the difference in c_s can be neglected for final results.

Calculation of the Specific Surface Area. Using the isotherms mentioned above, one can obtain an a_m value and calculate the *SSA* (expressed in m^2/g) from the following equation:

$$SSA = k\mathcal{N}Aa_m \tag{3}$$

where A is the cross-sectional area of the phenol molecule ($A = 52.2$ Å^2), $\mathcal{N}$ is Avogadro's number, and k is a conversion factor that depends on the a_m unit.

RESULTS AND DISCUSSION

Adsorption Isotherms

Phenol adsorption isotherms determined for M1, M2, M14, and carbon support membranes are shown in Fig. 1. It can be seen from the figure that M14 membranes and carbon support membranes behave similarly. The greatest difference is only observed for the highest concentrations. Adsorption on carbon support membranes was always slightly higher. Adsorptions on M1 and M2 membranes were also appreciably higher.

Generally it can be stated that the shape of adsorption isotherms is quite regular, without a well-established plateau in the range of the concentrations in-

vestigated. This is especially evident for M1 and M2 membranes. Therefore we believe that we are below a full monolayer region of phenol adsorption. The plateau value would be reached at higher concentrations, but for our study the most important thing is to have a monomolecular adsorption that does not exceed a full monolayer coverage. Therefore, as far as our results are concerned, some effects (such as aggregation of phenol in solution and aggregate adsorption) which may disturb monomolecular adsorption are negligible in the range of phenol solution concentrations investigated so that adsorption data can be fitted to Langmuir and BET equations. If a good correlation is obtained with these two equations, one can reasonably assume that adsorption is of the monomolecular type and that isotherms immediately provide the monolayer capacity a_m.

Using the data of phenol static adsorption, we have determined the monolayer capacity for M1, M2, M14, and carbon support membranes from Langmuir (via Eq. 1) and BET (via Eq. 2) isotherms and calculated the SSA of the membranes from Eq. (3). In calculations, the cross-sectional area of the phenol molecule was set at 52.2 $Å^2$. This value was used by Puri (5, 6) as well as by Yenkie and Natarajan (8). This value seems to be quite reasonable taking into account the data presented by McClellan et al. (9); these authors give a cross-sectional area of 43.6 $Å^2$ for benzene and 55.2 $Å^2$ for toluene. Giles (10), assuming close packing and a flatwise orientation of *p*-nitrophenol, gave it as 52.5 $Å^2$.

Determination of the Specific Surface Area of the Membranes

Results

In Table 2 the specific surface areas based on phenol static adsorption and derived from Langmuir (column 2) and BET (column 3) equations are listed. If we analyze these two columns, we can see differences in the *SSA* values cal-

TABLE 2
Specific Surface Areas (SSAs) of the M1, M2, M14, and Carbon Support Membranes Determined from Phenol Static Adsorption (Eq. 3) Isotherms Fitted to Langmuir and BET Equations (m^2/g)

Membrane type	Langmuir (Eq. 1)	BET (Eq. 2)	Average
M1	30.3	22.6	26.4
M2	15.4	19.2	17.3
M14	3.3	2.8	3.1
Carbon support	4.7	3.8	4.2

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culated from the two equations; however, these differences are not very large (ca. 20–25%). Yenkie and Natarajan (8) obtained differences in *SSA* values in the 10–15% range but their *SSA* values were hundreds of square meters per gram. In general, *SSA* values determined from Langmuir are higher than those determined from BET. Only in the case of the M2 membrane were the BET data higher. It therefore seems reasonable to use an average value as listed in column 4 of Table 2. UF membranes of smaller average pore size have the highest *SSA*; M1 membrane has the highest *SSA* (26.4 m^2/g), and M2 also has a higher *SSA* than M14 and carbon support (17.3 m^2/g). As expected, M14 membrane and carbon support have a much lower *SSA* (3.1 and 4.2 m^2/g, respectively).

An analysis of the precision of the fitting of experimental results to Langmuir and BET equations has been carried out. The corresponding correlation coefficients are listed in Table 3. These coefficients are very high, especially in the case of the Langmuir isotherm for which they are higher than 0.999 (the highest value is 0.9999 for M1 membrane). The fitting of data to the BET equation is less good, although quite close (the lowest value is 0.9334 for M2 membrane and the highest is 0.9870 for M14 membrane). Therefore the fitting of data to Langmuir and BET equations is good, and the hypothesis of a phenol monolayer adsorption was confirmed.

TABLE 3
Statistical Analysis of the Correlation between Adsorption Calculated from Langmuir and BET Isotherms and Adsorption Measured for the Various Membranes[a]

Membranes	Correlation coefficient	t_{cal}	0.05[b] 2.776[c]	0.01[b] 4.604[c]	0.001[b] 8.61[c]
		Langmuir Isotherm			
M1	0.9999	199.96			*
M2	0.9999	124.23			*
M14	0.9995	64.90			*
Carbon support	0.9999	124.86			*
		BET Isotherm			
M1	0.9862	11.90			*
M2	0.9334	5.20		*	
M14	0.9870	12.28			*
Carbon support	0.9762	9.01			*

[a] Degrees of freedom $i = 4$; number of correlated points $k = 6$.
[b] Significance level.
[c] Student's *t*-test for $i = 4$.
* Significant correlation.

Student's t-Test Analysis

We used Student's *t*-test (16) to ensure that the correlation coefficients were truly significant for each of the eight systems. A tested null hypothesis was that the correlations presented were not significant and were only caused by random errors. Results of this analysis are presented in Table 3 which includes the following columns: membrane type, correlation coefficient, and t_{cal} value. If t_{cal} is greater than the t value, then we cannot accept the null hypothesis that the correlation is not significant. In the next three columns, corresponding to three different significance levels, significant correlations are marked by asterisks. As shown in Table 3, correlation coefficients are very significant for the Langmuir isotherm (significance level higher than 0.001). They are also fairly significant for the BET isotherm, and the correlation coefficient is only essential at the 0.01 significance level for the M2 membrane, whereas for the rest of the membranes it is significant at the 0.001 level. This test demonstrates that our data fit both equations very well, which leads us to claim that the adsorption of phenol on the membranes studied is of a monomolecular type and that the *SSA* calculated from these data is essential.

Characterization of the Membrane Carbon Support Using Specific Surface Area Data

Calculation of the Apparent Average Pore Diameter from the Specific Surface Area

We used the *SSA* values determined in Table 2 to characterize the porous structure of the various membranes. It would seem that the adsorption technique can deliver some interesting information with regards to the porous body structure. This technique is especially suitable to investigate the microporous structure of a membrane layer, its sublayers and a given support as a whole. However, since in the case of inorganic tubular membranes the mass of the support is much greater than that of the membrane selective layer, adsorption effectively provides some new information about the structure of the microporous support. If the adsorption is taken to be monomolecular, the amount of solute adsorbed in the thin selective layer is negligible (there is about 0.8 g of zirconium oxide in a 1.2-m long Carbosep membrane weighing about 104 g) in comparison with the amount adsorbed inside the support porous volume. Therefore we think that adsorption of low molecular weight solutes may give some information on the internal microstructure of the membrane support. For this purpose, simple calculations have been made in order to show that *SSA* determined from adsorption data can confirm this deduction.

The calculations are based on a very simple porous structure model that assumes the porous matrix is made up of a packed bed of spherical particles. Most porous membranes have a more tortuous structure, however, with blind

passages and a range of channel dimensions. A reasonably realistic approximation of this structure is a packed bed of particles. In the case of the MF and UF membranes studied here, this representation has to be quite close to the actual porous structure since Carbosep mineral membranes are composed of an assembly of particle layers whose mean particle diameter varies from one layer to another (asymmetric structure). Due to the complexity of the porous matrix structure, only such simplified calculations have been considered here. An exact modelization of porous bodies is still a very difficult task from a mathematical point of view. For instance, the widely used mercury porosimetry method is based on the simple model of a bundle of cylindrical pores, which is far from reality. In the microscopic analysis of dusts and other particles (17), the following formula is used to calculate *SSA*:

$$SSA = \frac{\Psi_1}{\Psi_2 d_g \gamma_p} \tag{4}$$

where Ψ_1 and Ψ_2 are shape coefficients (surface and volumetric, respectively), d_g is the particle size, and γ_p is the particle density. For particles of spherical shape, $\Psi_1/\Psi_2 = 6$, Eq. (4) simplifies to

$$SSA = \frac{6}{d_g \gamma_p} \tag{5}$$

After rearranging, we can calculate d_g from the *SSA* value:

$$d_g = \frac{6}{\mathrm{SSA}\gamma_p} \tag{6}$$

In turn, Kozeny and Carman (18) have introduced a model of a porous layer from which we can calculate an average pore diameter on the basis of particle diameter (d_g) and porosity (ε). This model assimilates the packed bed of particles into a bundle of noninterconnected cylindrical pores of a given length L and the same diameter d_p (19). In order to specify the whole geometry of the porous medium, the model medium has to have the same porosity and specific surface area as the actual porous medium. The Carman–Kozeny model gives satisfactory results in the case of laminar flow through a porous medium whose texture is granular, whose porosity is less than 0.7, and which has spherical particles. According to the Carman–Kozeny model, the mean pore diameter for a spherical particle layer is given by (19)

$$d_p = \frac{2 d_g \varepsilon}{3(1 - \varepsilon)} \tag{7}$$

Introducing Eq. (6) into Eq. (7), we obtain

$$d_p = \frac{4\varepsilon}{SSA\gamma_p\,(1 - \varepsilon)} \tag{8}$$

TABLE 4
Apparent Average Pore Diameter d_p Calculated from Eq. (8) Using *SSA* Data

	Apparent average pore diameter d_p (μm) (Eq. 8)		
Membrane type	Langmuir	BET	Average
M1	0.020	0.027	0.023
M2	0.028	0.022	0.025
M14	0.129	0.150	0.139
Carbon support	0.090	0.113	0.100

Results

The average membrane pore diameter d_p has been calculated from the values of *SSA* given in Table 2 by using Eq. (8). Results are presented in Table 4. The following values of γ_p and ε were used: $\gamma_p = 2000$ kg/m^3 and $\varepsilon = 0.175$ (average value for the carbon support, see Table 1). For the M1 membrane, ε was set as equal to 0.23 because this membrane had an apparent density which is about 25% lower than that of the other membranes. The values of d_p were calculated for *SSA* as determined from Langmuir (column 2) and BET (column 3) as well as the average value of both equations (column 4). It is clearly seen from Table 4 that the results can be divided into two groups. The first corresponds to M1 and M2 ultrafiltration membranes, and the second to M14 microfiltration membranes. It is obvious that the carbon support studied has a texture similar to that of the support of the M14 membrane.

Discussion

These results do not mean that the pore size distribution of the membrane is centered on the average pore diameter listed in Table 4. According to TechSep data (20), the median pore diameter in volume is equal to 2.5 μm for the carbon support. It is thus suggested that the carbon support void volume is composed of two populations of pores: the small ones and large ones (this was confirmed by mercury porosimetry measurements for which the log differential intrusion volume curves exhibit two peaks: a large one centered on 3 μm plus a small one centered on 0.16 μm). It is well known that membrane permeability is very sensitive to the population of large pores whereas small pores do not have a significant influence on membrane permeability. The participation of small pores in total porosity determination may not be very high, but they can change the *SSA* appreciably. We can show this by making use of Eq. (8). For example, if we assume that pores of 3 μm contribute 90% of the total porosity, and pores of 0.005 and 0.001 μm contribute 5% each, then the total

SSA is equal to 26.2 m^2/g. A similar calculation for the same percentages and pores of 5, 0.01, and 0.005 μm, respectively, gives a *SSA* equal to 6.49 m^2/g. These calculations were made to demonstrate the influence of small pores on the total value of *SSA*. In fact, the model presented idealizes the situation because *SSA* is not only influenced by existing pores but also by the fact that channels of the pores are very tortuous (there are cracks, cavities, pits, sharp edges, and so on). Therefore we can consider d_p to be an apparently average pore diameter corresponding to a given value of *SSA*. Pores of larger sizes probably exist, but this d_p value remains a good measure of structural nonhomogeneity and texture of the support volume. If we assume that the carbon support is composed of uniform pores of 3 μm diameter, we calculate a *SSA* value from Eq. (8) which is only equal to 0.14 m^2/g. Therefore a large discrepancy between the *SSA* calculated from porosity data and from adsorption indicates that the porous structure of the support is highly asymmetric and structurally nonhomogeneous. Any structural heterogeneity may be easily found by determining a monolayer capacity or *SSA*. Large differences between various samples confirm the variability of the microscopic porous structure of the samples.

We must realize, however, that instances of such high structural heterogeneity are mainly responsible for precipitation, deposition, and coagulation of some components of filtered mixtures. Even if those places do not contribute significantly to liquid permeation across the membrane, they may be responsible for changes in some properties of the mixtures (such as color, taste, flavor, etc.), which can be very important in the processing of food products (e.g., fruit juices, wine, beer). It is almost impossible to remove all those absorbed species during the membrane cleaning process because they are accessible only by diffusion and not by convection of the cleaning solution. If cavities and cracks located in the main support pores are responsible for flux, these places are capable of adsorbing filtered mixture components, and these deposits can grow during filtration to the point where they start to occupy even those pores responsible for flux.

Comparison of Adsorption and Mercury Porosimetry Data

For porous solids, one of the most widely used techniques in the characterization of the membrane structure is mercury porosimetry (also called the mercury intrusion method). It seemed to us to be of interest to compare this technique with the adsorption method. For this purpose additional measurements using a mercury porosimeter (Micromeritics 9320, USA) were carried out for M14 and the carbon support membranes. Unfortunately, it was impossible to determine porosity for exactly the same pieces of membrane which were used

for adsorption determination. However, we wanted at least to discover the approximate relationship between adsorption and mercury porosimetry results.

Mercury porosimetry data are presented in Table 5 in which the following data are listed: total intrusion volume (column 2), total pore area (column 3), median pore diameter in volume (column 4), median pore diameter in area (column 5), average pore diameter (derived from $4V/A$, column 6), and porosity (column 7). In the four porosimetry measurements of Table 5, two were performed with a membrane piece coming from the same manufacturer batch (Techsep, France).

From a comparison of Tables 2 and 5, it can be seen that the average *SSA* determined from adsorption data (i.e., 3.1 m^2/g for M14 membrane and 4.2 m^2/g for carbon support) is consistent with mercury porosimetry data (i.e., 4.33 and 2.75 m^2/g for M14 membrane, and 2.27 and 4.02 m^2/g for carbon support). The scatter of data might have been less if the *SSA* had been measured for the same pieces of membrane for the two techniques. It can be seen from Tables 4 and 5 that the values of the average pore diameter d_p calculated from the two methods are closer for the membrane pieces coming from the same manufacturer batch (0.139 μm against 0.146 μm for M14 membrane and 0.1 μm against 0.112 μm for carbon support). Structural properties of the membranes are likely to vary from one piece to another. Indeed, it is believed that about 20 measurements are required in order to obtain a reliable characterization of the porous structure of a mineral membrane (20). However, of most interest is the comparison of column 6 (Table 5) with the data of Table 4. It can be seen that the average pore diameter d_p is similar to that calculated from adsorption for both M14 and carbon support membranes and is close to 0.1 μm.

Therefore, a comparison of the two methods was performed in an alternative way: We calculated d_p from Eq. (8) using the values of *SSA* determined from phenol adsorption and mercury porosimetry, but this time slightly different values of membrane porosity and density were used. Porosity ε was taken from Table 5 (column 7) and density γ_p was calculated experimentally from the volume and weight of a piece of membrane and corrected by porosity. Densities calculated in this way were found to be 2.04 (for M14) and 2.05 (for carbon support) in comparison with the value of 2.00 used for previous calculations; *SSA* data were the same as used previously. The corresponding apparent pore diameter d_p is listed in Table 5 (column 8, adsorption). The last column of Table 5 lists d_p values calculated from *SSA* determined by the porosimetric method. If we compare these data with the values in column 5 of Table 5, it can be seen that the results are very close. This means that there is a common basis between the Carman–Kozeny equation and the porosimetric determination of the ratio $4V/A$. Indeed, it is well known that the average pore diameter calculated from $4V/A$ has a high physical significance. The similari-

TABLE 5
Mercury Porosimetry Data for Carbon Support and M14 Membrane

Membrane	Total intrusion volume V (mL/g)	Total pore area A (m^2/g)	Median pore diameter (in vol) d (V, 0.5) (μm)	Median pore diameter (in area) d (A, 0.5) (μm)	Average pore diameter d_p ($4V/A$) (μm)	Porosity ε	Average pore diameter d_p (μm) calculated from SSA (Eq. 8) determined from	
							Adsorption	Porosimetry
M14	0.114	4.33	1.6	0.01	0.105	0.196	0.153	0.109
M14[a]	0.1	2.75	2.3	0.0093	0.146	0.167	0.127	0.143
Carbon support	0.11	2.27	2.5	0.01	0.194	0.189	0.109	0.202
Carbon support[a]	0.113	4.02	1.83	0.0093	0.112	0.184	0.105	0.109

[a] Membranes coming from the same manufacturer batch (Techsep, France).

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ties of these ratios as determined by both methods are due to the fact that both methods assume the constancy of the volume/surface ratio $4V/A$ for a given porous body, which is the expression of the average pore diameter for a cylinder of volume V and lateral surface A. Indeed, both methods involve the same geometric model of the porous medium, i.e., a cylindrical shape with a circular cross-sectional area, for which the average pore diameter d_p is calculated from the formula $4V/A$, where V is the total porous volume and A is the total pore area.

We therefore conclude that data calculated from Eq. (8) depend chiefly on *SSA* value and that the mean pore diameter values calculated from porosimetry (via $4V/A$) and from adsorption (via Eq. 8) are completely consistent. If we obtain similar *SSA* data from both methods, similar values of the mean pore diameter will be obtained.

The above results can be summarized as follows. A scatter of *SSA* data may be due to the fact that different pieces of membrane were used for the two kinds of measurements. Different pieces of membranes exhibit differences in adsorption in the 20–25% range. It is also well known that *SSA* values determined from porosimetry and nitrogen adsorption can differ by a factor greater than 10. Therefore the consistency of our results is quite satisfactory. However, more detailed studies on the determination of *SSA* and the average pore diameter of inorganic membranes using both methods are still necessary.

CONCLUSIONS

Based on the data presented in this paper, the following set of conclusions may be drawn:

1. The statistical Student's *t*-test showed that phenol adsorption data are well fitted to the Langmuir and BET isotherm equations; it was concluded that phenol adsorption was monomolecular and that the specific surface area calculated from these data was essentially reliable.
2. M1 and M2 ultrafiltration membranes were found to have a larger specific surface area than microfiltration M14 and carbon support membranes.
3. By assuming a simple model of the porous structure consisting of a packed bed of spherical particles, it was possible to determine an average membrane pore diameter from *SSA* data using the Carman–Kozeny equation. This average membrane pore diameter was defined as the apparent average pore diameter of the membrane.
4. Specific surface area determined from phenol adsorption was found to be consistent with that measured from mercury porosimetry. Indeed, there is a common basis for the Carman–Kozeny equation and the determination of the ratio $4V/A$ by mercury porosimetry since both methods involve a constant volume/surface ratio along the membrane thickness.

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5. It was found that data calculated from Eq. (8) depend chiefly on the value of *SSA* and also that the average pore diameters calculated from mercury porosimetry (via $4V/A$) and from phenol adsorption were completely consistent.

Finally, it was shown that aqueous adsorption of a given adsorbate allows the porous structure (i.e., specific surface area and average pore diameter) of the support of an inorganic ultra- and microfiltration membrane to be characterized with the same accuracy as from mercury porosimetry measurements. The determination of the specific surface area of a microporous membrane based on adsorption of specific adsorbates (e.g., phenol for carbon-supported membranes) requires a simple experimental procedure and, unlike mercury porosimetry, is a nondestructive method. Moreover, this method provides an accurate *SSA* value for microfiltration membranes (which typically have *SSA*s in the range of a few square meters per gram) unlike the N_2–BET method which is convenient only for porous solids having a *SSA* of a few hundred square meters per gram. Aqueous phase adsorption also has the advantage of being carried out under wet conditions (conditions similar to those in which the membrane is likely to be used in crossflow filtration).

SYMBOLS

a	amount adsorbed (mg/g)
a_m	Langmuir or BET monolayer capacity (mg/g)
A	total pore area (m^2)
c	solution concentration (mg/mL)
c_s	maximal solubility of solute, Eq. (2) (mol/L)
d_g	particle size (μm)
d_p	average membrane pore diameter (μm)
K	binding constant (Eqs. 1 and 2)
SSA	specific surface area (m^2/g)
V	total porous volume (m^3)

Greek Symbols

ε	porosity (vol/vol)
γ_p	particle density (g/cm^3)

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