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Adsorption of Organic Solutes on Membrane Filters during Aqueous Phase Filtration. I. Basic Rate and Equilibrium Studies Using Toluidine Blue

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Abstract

Membrane filters are made from a wide variety of polymeric materials, in a wide range of pore sizes, and are used in large numbers (several hundred million per year) to filter particulates from many types of solutions. However, during filtration, organic solutes are adsorbed by these membranes, often quite extensively. Thus, the composition of the filtrate can be very different from that of the original solution. A systematic study has been initiated to quantify and explain the adsorption of organic solutes during membrane filtration as affected by membrane type (material, pore size, presence/absence of wetting agents), solute type, pH, ionic strength, and filtration flow rate. Our first studies have employed a dye (toluidine blue) as the dissolved organic solute, and 11 membrane filters made of mixed cellulose esters, polyvinylidene difluoride, polytetrafluoroethylene, and polycarbonate. The results of these studies, which are both equilibrium and kinetic in nature, are presented. These results indicate how adsorption effects may be minimized.

INTRODUCTION

Membrane filters are used in great numbers for the removal of particulates from liquids. Examples include the analysis and purification of liquids for industrial, medical, electronics, pharmaceutical, food and beverage, and research applications. Such filters also are often used in gas-phase applications (e.g., the collection and analysis of air-borne particulates). However, we will focus only on liquid-phase applications in this paper, and, more particularly, only on aqueous systems. More specifically, membrane filters are used to remove particulate contaminants in the size range of 0.025 to 10 μm and higher by passage of fluids through microporous media having relatively well-defined "cut-off" pore sizes. Common "par-

ticulates" removed include microorganisms (fungi, bacteria), colloids, and solid particles.

Membrane filters, unlike "depth" filters, are thin and are made of a rigid, uniform, continuous mesh of polymeric materials such as cellulose esters (cellulose acetate, cellulose nitrate, or mixtures of these), polyvinylidene difluoride, polycarbonate, polytetrafluoroethylene, or such. The pore sizes in membrane filters can be controlled during manufacture to give a relatively narrow pore-size distribution and assure virtually total removal of particulates of diameters greater than the nominal "pore size" rating of the membrane.

Membrane filters often contain extractable materials such as pore-forming agents (e.g., glycerine), solvent residues from the casting process, and wetting agents (deliberately added to make the flow of aqueous solutions through the membrane much easier). Users of membrane filters need to be aware that such extractables exist, and that they may contaminate the initial portion of the filtrate. Prewashing the filters or discarding the initial portion of the filtrate can overcome the extractables problem to a large extent. Cooney (*4*) has quantified several aspects of the contamination of filtrates by extractables and has shown that prewashing can be effective.

However, the problem we wish to address in this paper is essentially one that is opposite to that of the extractables problem, namely, the adsorption of dissolved solutes from liquids during the filtration process. An example of this would be where one is using membrane filtration to clarify a water sample containing suspended matter as well as one or more dissolved organic solutes, the purpose being to produce a particle-free filtrate for subsequent analysis by spectrophotometry, chromatography, etc. in order to quantify the amounts (i.e., concentrations) of organics present. If the membrane filter were to adsorb a significant portion of such dissolved organics, then clearly one would obtain false values of the amounts of organics present as determined by the postfiltration analyses.

LITERATURE REVIEW

Previous researchers have made note of the adsorption of dissolved solutes from aqueous solutions. Chiou and Smith (*3*) studied the adsorption of 18 acidic or neutral organic compounds during filtration of aqueous solutions of these compounds through Millipore MF (cellulose ester) membranes of 0.025, 0.22, and 1.2 μm pore sizes, and through Whatman No. 4 filter paper. They showed clearly that 1) the repetitive filtration of an aliquot of solution through each type of filter gave successively greater total adsorption of the solute, 2) adsorption was greater as pore size decreased, 3) the Whatman filter gave much less adsorption than did the

Millipore filters, and 4) a Freundlich equation adequately represented the isotherms for two drugs (warfarin, griseofulvin) for which isotherms were determined. The degrees of adsorption obtained for a single filtration ranged from zero to nearly 100%, and in general the more water-soluble ionic forms of the compounds showed less tendency to adsorb than the less soluble neutral forms of the compounds. Shortcomings of this study were that 1) only one kind of synthetic membrane was studied, 2) flow control during filtration was very approximate (an aspirator was used to induce flow), 3) isotherms were obtained for only two compounds on a single type and pore-size membrane, and 4) only drug-type compounds were studied. Additionally, the effects of pH and ionic strength were not considered.

A few years later, Ghanem (*6*) did a study involving Millipore (0.22, 0.45, and 0.8 μm pore size) and Gelman (0.45 μm pore size) filters and four drug compounds. The exact type of each brand of filter was not specified, unfortunately (each manufacturer offers filters made of different materials, so simply stating "Millipore" or "Gelman" does not define the type of filter used). Ghanem's study again showed that total adsorption increases with repetitive filtration and that smaller pore-sized filters give greater adsorption. In addition, it was shown that the addition of small amounts of surfactants (0.005–0.10 wt%) strongly inhibited drug adsorption. Also, a brief study of the effect of varied pH on one compound (chlorpromazine) suggested that at higher pHs (at which the drug is nonionized), adsorption was enhanced. Shortcomings of this study were that 1) only two polymeric filters were studied, 2) only four chemical compounds (all drugs) were surveyed, 3) the flow rate control (by aspirator) was very rough, and 4) the pH study was very brief (5 data points). Additionally, the effect of ionic strength was not explored.

A year later, Chiou (*2*) published results of a study in which only two filters (0.025 and 0.22 μm Millipore) and four drugs were used. This study confirmed again that adsorption increases with repetitive filtration and for smaller pore sizes, but nothing else of significance was presented. Again, flow control (by aspirator) was very approximate.

In the same year, Batra (*1*) reported results on the adsorption of three steroids by a Millipore HAWP mixed cellulose ester filter and a Whatman GF/C glass fiber filter. It was shown that adsorption by such filters, after equilibration for 5 hours with steroid solutions, was much less for the glass fiber filter (1.3–10.9% adsorbed) than with the Millipore filter (38.6–96.2% adsorbed).

Liu, Carney, and Hurwitz (*7*) showed again that repetitive filtration and smaller pore sizes increase adsorption. Their study involved Millipore MF mixed cellulose ester filters (0.2 and 0.45 μm pore sizes), a Gelman GA-

8 mixed cellulose ester filter (0.22 μm pore size), a Nuclepore polycarbonate filter (pore size unstated), and 9 organic compounds (mostly drugs). The percentages of compounds adsorbed from the first 5 mL of dilute (11–25 micromolar) solutions passed through a 25-mm diameter 0.2 μm pore-size Millipore membrane were: benzocaine, 8%; griseofulvin, 25%; phenothiazine, 75%; dibenzofuran, 84%; and medrogestone, 96%. Again in this study, filtration flow rate was only roughly controlled. Additionally, pH and ionic strength effects were not investigated.

Several investigators, e.g., Van Ooteghem and Herbots (*10*), Udani (*9*) and Naido et al. (*8*), have reported on the adsorption of preservatives such as benzalkonium chloride from ophthalmic solutions undergoing membrane filtration sterilization. Significant adsorption occurred in all cases but varied with the type of preservative used, the polymeric nature of the filter, and the volume of solution filtered.

Additionally, there are several interesting studies dealing with the adsorption of various proteins on membrane filters. However, these studies will not be reviewed here since we are not concerned with macromolecule adsorption in the present work.

MATERIALS AND METHODS

The membrane filters used were all 25 mm in diameter and were of the white nongridded (i.e., "plain") type. All filters were Millipore brand since this manufacturer makes membrane filters out of a wide variety of polymers and with a wide variety of pore sizes. Membrane filters from other manufacturers will be evaluated in later tests.

We used six MF type mixed cellulose ester filters having the following pore sizes and manufacturer's code designations: 0.025 μm VSWP, 0.10 μm VCWP, 0.45 μm HAWP, 0.45 μm HATF, 1.2 μm RAWP, and 5.0 μm SMWP. All of these MF type filters contain some wetting agent ("Triton," a mixture of various polyoxyethylene ethers and other surface-active compounds), except for the HATF filter, which is stated to be "Triton-free."

We also used the following additional Millipore membrane filters: Durapore HVLP 0.45 μm (a "hydrophilic" membrane made of polyvinylidene difluoride), Durapore HVHP 0.45 μm (a "hydrophobic" membrane made of polyvinylidene difluoride), Isopore HTTP 0.40 μm (a track-etched polycarbonate membrane, 10 μm thick), Fluoropore FHLP 0.5 μm (made of polytetrafluoroethylene, bonded to high-density polyethylene to improve handling), and Mitex LSWP 5 μm (polytetrafluoroethylene with no backing material).

The "hydrophobic" Durapore membrane presumably has no wetting agent whereas the hydrophilic Durapore membrane presumably does con-

tain a wetting agent (type not stated) or incorporates some added hydrophilic copolymer (again, not described). The Fluoropore and Mitex membranes are hydrophobic, and hence presumably have no wetting agent. However, the Isopore membrane does have polyvinylpyrrolidone as a wetting agent.

The physical properties of the membranes are given in Table 1. The type of material and pore size for each membrane are as designated by the manufacturer. The weight values were determined by separately weighing 10 membranes of each type on an analytical electronic balance and computing arithmetic averages (standard deviations of the weight values averaged ±0.3 mg). The thickness values were determined with a precision micrometer and had an average standard deviation of approximately ±5 μm.

The density values are whole membrane densities computed from the measured weights and thicknesses, and using 25 mm (this was checked and found to be accurate) as the diameter. The polycarbonate (HTTP) and pure polytetrafluoroethylene (LSWP) membranes have densities in the range of 0.94 to 1 g/cm^3, the polyvinylidene difluoride membranes (HVLP, HVHP) have densities on the order of 0.64 to 0.69 g/cm^3, and the mixed cellulose ester (MCE) membranes have densities which vary with pore size. Figure 1 shows an interesting correlation between MCE membrane density and the log of the nominal pore size. One can see that smaller pore-sized membranes have greater densities than larger pore-sized membranes. One explanation for this may be that the porosities of smaller pore-sized mem-

TABLE 1
Membrane Physical Properties

Millipore code	Membrane material[a]	Pore size (μm)	Weight (mg)	Thickness (μm)	Density (g/cm^3)
VSWP	MCE	0.025	29.15	96	0.619
VCWP	MCE	0.10	28.21	124	0.463
HAWP	MCE	0.45	25.65	140	0.373
HATF	MCE	0.45	25.25	135	0.381
RAWP	MCE	1.2	20.58	136	0.311
SMWP	MCE	5.0	18.31	142	0.263
HVLP	PVDF	0.45	39.83	118	0.688
HVHP	PVDF	0.45	39.67	126	0.641
FHLP	PTFE/PE	0.50	32.78	194	0.344
LSWP	PTFE	5.0	60.26	122	1.006
HTTP	PC	0.40	4.62	10	0.941

[a]MCE = mixed cellulose esters (cellulose acetate, cellulose nitrate), PVDF = polyvinylidene difluoride, PTFE = polytetrafluoroethylene, PE = polyethylene (backing material), PC = polycarbonate.

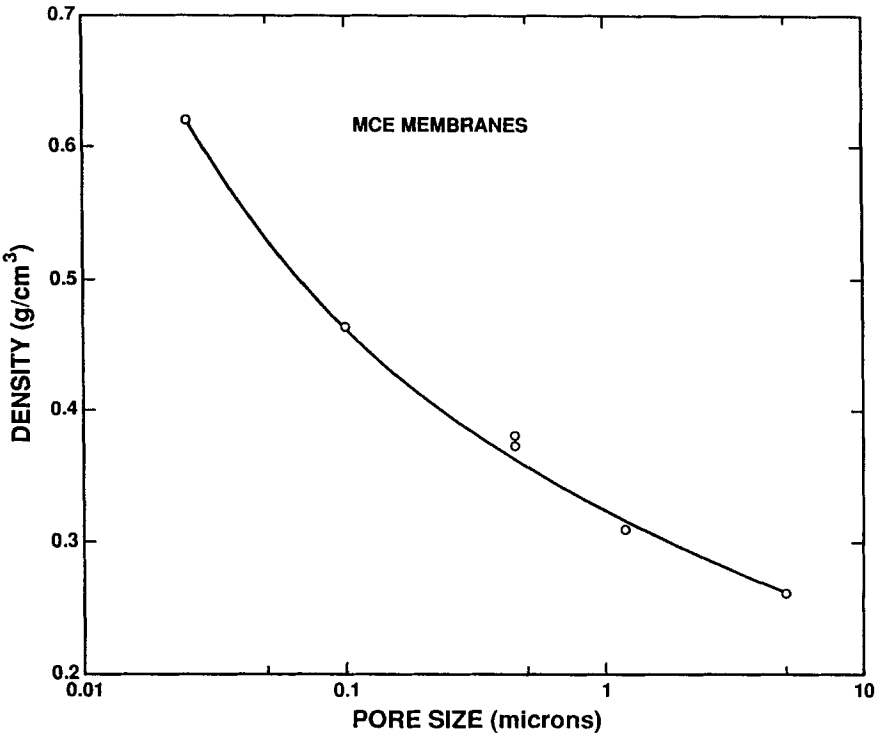

FIG. 1. Density variation with pore size for Millipore mixed cellulose ester membranes.

branes are lower than those of larger pore-sized membranes; however, porosities were not measured in this study, so this hypothesis has not been proved. Indeed, membrane densities are probably more a product of the phase-inversion phenomena and solvent evaporation processes which are integral to the casting of the membranes rather than just a simple matter of porosity alone. Note from Table 1 that the two smallest pore-sized MCE membranes are not only more dense but are slightly thinner than the other membranes of the MCE series. In appearance, they have one side that is shiny and one side that is not shiny. The remaining MCE membranes have no shiny surface.

The solute selected for our first studies was toluidine blue O dye (hereafter called "TB"), MW 305.83, from Sigma Chemical Company. The TB was prepared in distilled water at 10 mg/L. The solution was buffered to the extent of 4.30 g/L Na_2HPO_4 and 1.18 g/L KH_2PO_4 (this is a "standard" kind of phosphate buffer), to give a pH of 7.41 at 25°C and an ionic strength of 0.10 *M*. The reason for buffering was twofold: (a) pH is an important

parameter affecting adsorption and needs to be controlled, and (b) the intensity of colored aqueous solutions, particularly dye solutions, usually varies somewhat with pH. Since our assay method for TB was visible spectroscopy (550 nm), pH had to be controlled to eliminate color intensity variations due to pH changes.

The TB was chosen primarily because (a) it is easily assayed colorimetrically, (b) extractables and other stray contaminants which would interfere in ultraviolet spectrophotometric analysis present no problem when visible spectroscopy is used, and (c) it was found to adsorb reasonably well on many of the membranes used. Many other solutes could have been selected, some of which would perhaps be of greater interest, and indeed other such solutes will be reported upon in future work. However, as we will see, TB gave us some interesting and valuable information in this initial work.

Batch adsorption experiments were carried out at room temperature by contacting 20 mL of the 10 mg/L solution of TB with four 25 mm diameter membranes in 25 mL capacity high-density polyethylene vials having metal foil lined urea caps (borosilicate glass vials could not be used, as TB was found to adsorb significantly to glass). The TB solution was prepared in a 1-L polypropylene volumetric flask (again, because TB was found to adsorb to glass flasks). Equilibrium studies were done with all 11 membranes. In these equilibrium studies, 4 weeks time was allowed to ensure that adsorption equilibrium was closely attained (preliminary rate studies validated this assumption). The stack of four membranes used in each vial in each batch test was cut so that the membranes were essentially quartered, and these pieces were dropped into vials containing 20 mL of the TB solution. The solutions from the vials were assayed colorimetrically after 4 weeks time to determine the TB concentrations in the solutions. At the same time, the solutions from three "control" vials (20 mL solution but no membrane) were assayed to permit a correction to be made for TB adsorption to the vials and caps themselves. These corrections turned out to be fairly small.

The vials were not shaken for two reasons: (a) it was assumed that the primary mass transfer resistance would be due to diffusion in the membranes themselves, rather than in the external fluid, and hence agitation of the external fluid would have no effect, and (b) preliminary experiments with shaking disclosed that agitation caused debris of some sort or membrane material itself to be released into the fluid, thereby interfering with the spectrophotometric analysis (blockage of incident radiation caused the apparent absorbance to increase with time, which is opposite to that which should occur). As will be shown later, analysis of adsorption rate data confirmed that the external mass transfer resistance is indeed negligible compared to the mass transfer resistances in the membranes.

Following these simple equilibrium experiments, which showed that the MCE membranes adsorb TB well, careful rate-of-adsorption studies were done with four selected MCE membranes: the 0.025 μm VSWP, 0.45 μm HAWP, 1.2 μm RAWP, and 5.0 μm SMWP membranes. Again, four quartered membranes were used per vial. Each vial contained 20 mL of the 10 mg/L TB pH 7.41 stock solution. As before, the vials were not shaken. At selected times during a total period of 4 days, the absorbance of the solution in each vial was determined by pouring about 2–3 mL of the supernatant solution into a spectrophotometer cell and measuring the absorbance value. After each measurement the solution was poured back into the polyethylene vial. Very little solution was lost in this process. Again, control vials were used so that the contribution due to TB adsorption to the vials themselves could be corrected for.

Following these detailed rate studies, equilibrium adsorption isotherm studies were done for the VSWP, HAWP, RAWP, and SMWP membranes. As before, a contact time of 4 weeks was allowed for equilibrium to occur. Five vials were used for each membrane type. They contained 0, 1, 2, 3, and 4 membranes each (quartered as before). The "zero membrane" vial was the control. The weights of membrane added to each vial were recorded. After 4 weeks time the absorbances of the TB solutions were measured, and the equilibrium solution concentrations were computed. Since a mass balance gives $Wq = V(C_0 - C_\infty)$, where C_0 and C_∞ are the initial and final liquid phase concentrations (g/L), respectively, V is the solution volume (0.02 L), W is the weight of the membranes (g), and q is the membrane phase adsorbate concentration (g TB/g membrane), we could calculate q values for each vial. A plot of q versus C_∞ constitutes the equilibrium adsorption isotherm.

Next, using only one MCE membrane (the SMWP type), the equilibrium adsorption tests (four weeks contact) were repeated using 20 mL of pH 7.41 TB solution and four SMWP membranes per vial, using the same protocol as described earlier. However, in this part of the study the ionic strength (I) of the phosphate buffer was varied. Values of $I = 0.20$, 0.10, 0.05, 0.02, and 0.01 were used in a series of five otherwise identical vials.

The effect of pH on TB adsorption was studied next. Again, four SMWP membranes were contacted for 4 weeks with 20 mL of a 10 mg/L TB solution. However, in these tests the pH of each solution was different. The buffers were made of HCl, KH_2PO_4, $NaHCO_3$, Na_2HPO_4, $NaB_4O_7 \cdot 10H_20$, and NaOH. The pH values ranged from 1.76 to 9.38. Ionic strength was kept constant at 0.1 M.

Finally, flow studies were carried out using various filters in a Swinny type of filter holder which was connected to a 50-mL plastic syringe. The syringe was mounted on a Sage syringe pump which could be set to deliver

various flow rates. Flow rates of 2.5, 3.4, 5.1, 8.4, and 13.3 mL/min were used along with a HATF-type membrane filter in the first series of flow tests. Here, a pH 7.41 solution of TB (10 mg/L) was pumped through the filter holder assembly, and samples of the outlet stream were collected in a cuvette over prescribed time intervals (e.g., at 2.5 mL/min, samples were collected for a period of 1 minute each, whereas at 13.3 mL/min, samples were collected for a period of 15 seconds each). The samples were analyzed at 550 nm to determine their TB concentrations. Since the glass cuvette tended to adsorb TB, we had to invoke the following procedure: 1) collect a given sample over the prescribed time interval, say, 1 minute, 2) shut off the pump at the end of this time, 3) quickly measure the sample absorbance with the spectrophotometer, 4) discard the sample, 5) rinse the cuvette several times with acetone to get rid of any TB adsorbed to the cuvette walls, 6) dry the cuvette with a stream of clean air, 7) place the cuvette under the filter holder outlet, and 8) turn on the syringe pump for the next sample collection interval. Steps 2 through 8 generally required only about a minute.

RESULTS

Table 2 shows the percent TB adsorbed from solution by each of the 11 membranes selected for study after 4 weeks time. One can see that the hydrophobic HVHP, FHLP, LSWP, and HTTP membranes adsorbed little TB (less than 10%). Indeed, visual inspection of these membranes as they rested in the TB solutions clearly indicated that no significant wetting of the membranes was occurring. It seems likely that no significant penetra-

TABLE 2
Equilibrium Adsorption Results

Membrane type	Percent TB adsorbed
VSWP (0.025 MCE)	96.9
VCWP (0.10 MCE)	95.1
HAWP (0.45 MCE)	93.8
HATF (0.45 MCE)	95.4
RAWP (1.2 MCE)	88.3
SMWP (5.0 MCE)	66.4
HVLP (0.45 PVDF)	68.2
HVHP (0.45 PVDF)	8.6
FHLP (0.50 PTFE/PE)	5.2
LSWP (5.0 PTFE)	3.7
HTTP (0.40 PC)	3.4

tion of solution into the membrane pores took place. Hence, adsorption of TB probably occurred primarily on the outer surfaces of the membranes and not in the membrane interiors (some slow diffusion of TB from the outer surfaces into the membrane interior would be expected, however). The hydrophilic HVLP and MCE membranes, in contrast, were well wetted by the TB solution and consequently adsorbed significant amounts of TB. In the MCE series, the percentage TB adsorbed increased with decreasing pore size. Since the weight of these membranes increases as the pore size decreases (Fig. 1), there is simply more solid phase available for adsorption, and also presumably more internal "surface area" for adsorption. Interestingly, the lack of wetting agent in the HATF membrane did not prevent the HATF membrane from adsorbing TB well. The reason is that the MCE membrane is sufficiently hydrophilic by itself so that the lack of wetting agent does not hinder significant fluid penetration into the membrane structure.

Figure 2 shows the rate of TB adsorption as a function of time for the 0.025, 0.45, 1.2, and 5.0 μm pore-sized cellulose ester membranes. No rate

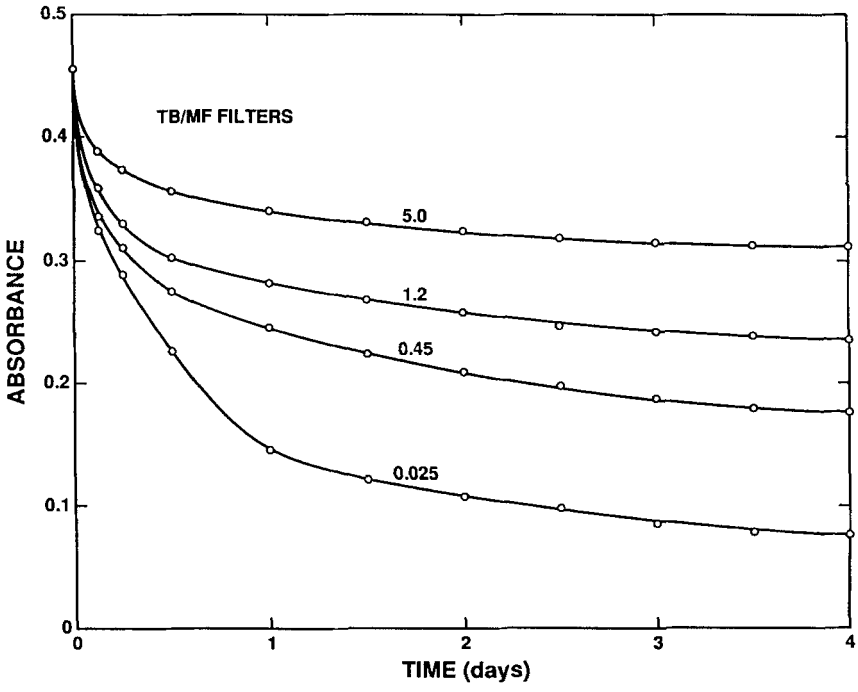

FIG. 2. Rate of adsorption results for four MCE membranes.

studies were done for the HVHP, FHLP, LSWP, and HTTP membranes because, as Table 2 indicates, the extent of TB adsorption on most of these membranes is so slight that rate studies would be pointless. Within the MCE series of six membranes, the four selected were chosen on the basis of obtaining a broad "spread" of pore sizes. None of the membranes used in these rate studies were outgassed prior to the start of the experiments because existing literature suggests that the combination of the hydrophilic nature of the membrane material (cellulose polymers, which, due to their large numbers of hydroxyl groups, are extremely hydrophilic), the large capillary forces generated in the small pores, and the presence of wetting agent in these membranes all combine to make displacement of air initially in the pores by the penetrating liquid very rapid.

The data of Fig. 2 show several interesting features: 1) the rate of adsorption is reasonably rapid near the start, as one might expect, but slows down considerably after roughly one-half to one day, and 2) the vertical spread between the curves is different from what the equilibrium data imply. For example, the amounts of TB adsorbed after 2 days are (from top to bottom) 26.0, 40.8, 51.9, and 73.7%. Table 2 indicates that after 4 weeks, the values become 66.4, 88.3, 93.8, and 96.9%. Dividing the percentages of TB adsorbed after 2 days by the "ultimate" amounts (4 week values) gives 0.39, 0.46, 0.55, and 0.76. In other words, the smaller the pore-size of the membrane, the larger is the extent of TB adsorption after 2 days expressed as a fraction of its ultimate adsorption. Expressed in a different way, the smaller the pore size, the faster the membrane approaches its ultimate adsorption. The most logical explanation for this is that TB penetration into the membranes (once the pores become filled with liquid, which occurs rapidly—perhaps in the first few minutes) occurs by surface diffusion along the polymer chains of the membrane material. Since a smaller pore-sized membrane has a greater internal density of polymer networking, surface diffusion is greatly enhanced by having smaller pore sizes. Diffusion in the liquid filling the pores (so-called pore diffusion) would be, if anything, slower for small pore-sized membranes because of porosity and tortuosity effects. Hence pore diffusion does not appear to be the dominant mechanism for TB transport.

The result of comparing the equilibrium data to the kinetic data in this way is that, in terms of solute adsorption during actual filtration operations, which are carried out quickly (over a time span on the order of a few seconds), it is the kinetic data which are of much more importance in determining what will occur. That is, while our equilibrium data indicate that 1.2-μm RAWP membranes are capable of a fairly large ultimate TB adsorption (88.3% TB adsorption in the 4-week test), our kinetic data show that the rate of adsorption is low due to the relatively large pore size.

Of course, even the kinetic data of Fig. 2 are in a sense "irrelevant" to actual filtration operations since the time frame in Fig. 2 is hours or days versus seconds in actual filtration operations. Yet, in terms of achieving an understanding of the *fundamental* physical and chemical processes involved in solute adsorption during filtration, the equilibrium and kinetic results of Table 2 and Fig. 2 are of value. Comparison of these data has indicated, for example, that 1) substantial adsorption during filtration is a distinct possibility for certain membrane materials, and 2) greater adsorption can logically be expected with smaller pore-sized membranes of a given material, for two reasons: smaller pore-sized membranes possess larger equilibrium capacities for adsorption, and smaller pore-sized membranes exhibit faster adsorption kinetics (most likely because of surface diffusion effects).

Crank (5) has shown that adsorption rate data may be plotted in a fashion which allows one to estimate the diffusivity (D_m) of a solute in a membrane. He presents a plot of M_t/M_∞ versus $(D_m/tL^2)^{1/2}$ for the uptake of solute from a solution of limited volume into a planar sheet of half-thickness L.

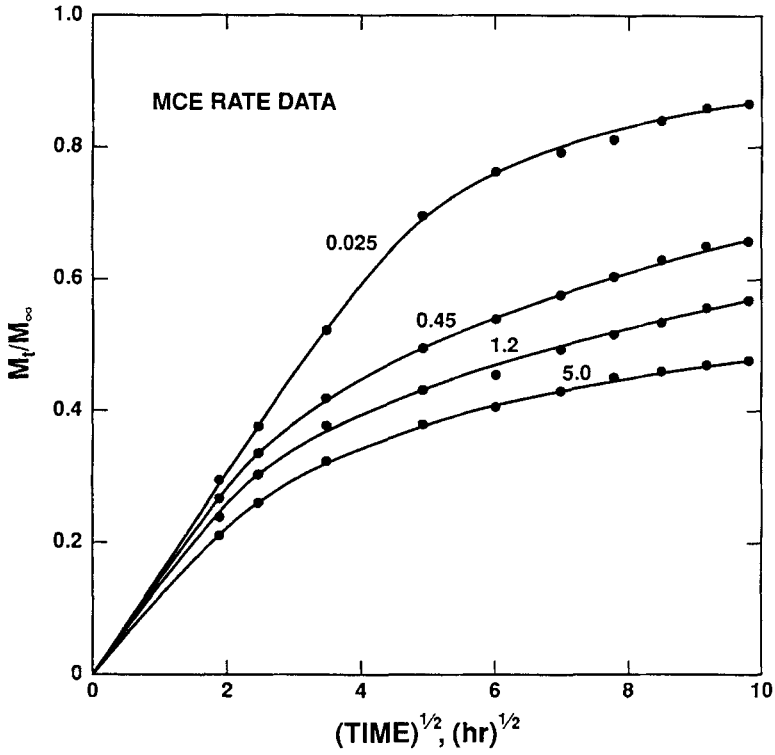

FIG. 3. Rate data presented as Crank-type plot.

Here, M_t is the total amount of solute taken up into the membrane at any time t, and M_∞ is the amount corresponding to infinite time. Since $M_t = V(C_0 - C)$ and $M_\infty = V(C_0 - C_\infty)$, where C_0, C, and C_∞ are the solute concentrations in the solution at time zero, at any time t, and at infinite time, then $M_t/M_\infty = (C_0 - C)/(C_0 - C_\infty)$. Thus, using the data of Fig. 2 (concentration is linear in absorbance, so absorbances may be used in place of the C's in the last equation), the rate data were plotted as shown in Fig. 3. C_∞ values were obtained from the results in Table 2. Comparison of Fig. 3 to the plot of Crank gave estimated D_m values on the order of 2×10^{-10} cm^2/s. Compared to a diffusivity value of 0.5×10^{-5} cm^2/s for the free solution, obtained from the Wilke–Chang (*11*) equation, one can see that the ratio of D_m to the free-solution diffusivity is on the order of 4×10^{-5}. Thus, the external mass transfer resistance is negligible compared to the mass transfer resistances in the membranes.

Figure 4 shows the adsorption isotherm results for the VSWP, HAWP, RAWP, and SMWP membranes. These results again show that the degree of TB adsorption increases with decreasing pore size. The isotherms gen-

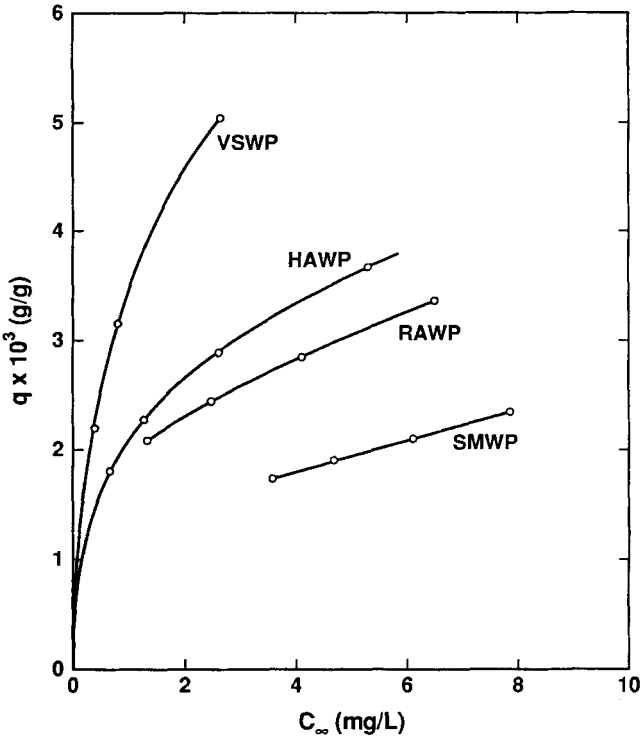

FIG. 4. Adsorption isotherms for TB and four MCE membranes.

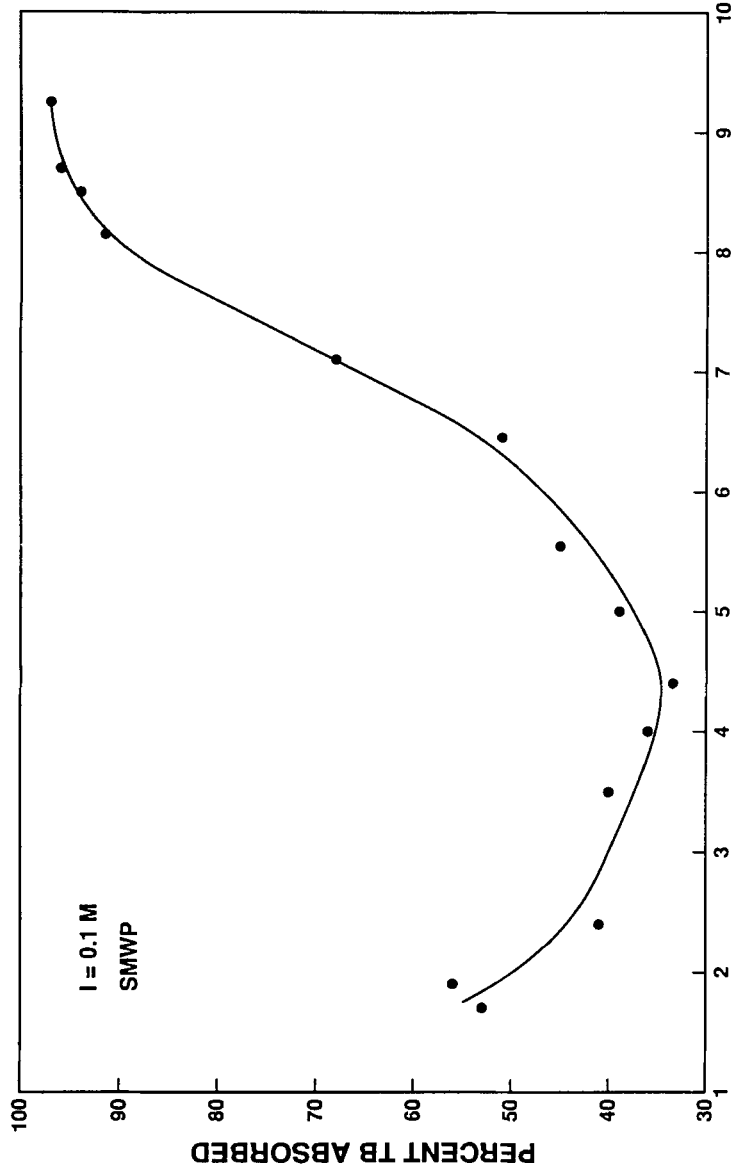

FIG. 5. Effect of pH on TB adsorption to SMWP membranes.

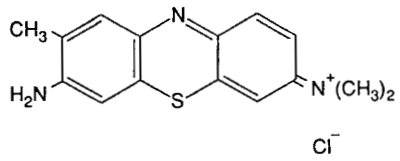

FIG. 6. Structure of toluidine blue.

erally exhibit the convex shapes typical of adsorption isotherms. Had data been gathered at higher equilibrium C_∞ values, we would undoubtedly have found that the isotherms would each approach a unique plateau value representative of one complete monomolecular layer of coverage on the membrane material "surface."

The effect of pH on TB adsorption to SMWP membranes is presented in Fig. 5. To interpret the behavior shown, one must refer to the TB structure given in Fig. 6. At high pH the $N^+(CH_3)_2$ group becomes hydroxylated and the TB molecule is uncharged. In this state the TB adsorbs strongly onto the cellulose polymer surfaces. However, as the pH decreases, the $N^+(CH_3)_2$ group becomes unhydroxylated and tends toward a

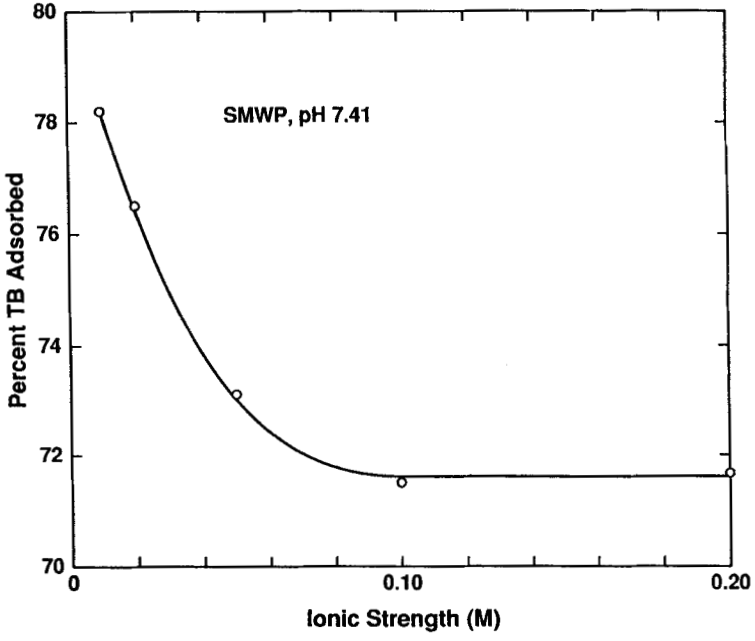

FIG. 7. Effect of ionic strength on TB adsorption to SMWP membranes.

+1 charge; moreover, the NH_2 group tends toward an NH_3^+ state and the N atom in the middle ring tends toward an NH^+ state. Thus, the TB carries an increasingly positive charge. Adsorbed TB molecules can no longer pack closely together on the membrane surface due to severe electrostatic repulsion, and the percentage of TB adsorbed drops precipitously. At even lower pH values, fewer hydroxyl and acetate groups on the polymer itself are in an ionized state and, although the TB molecule is still highly charged, the polymer itself is less charged. Hence, the percentage of TB adsorbed rises somewhat. (The exact pH values at which the membranes reach their isoelectric points are unknown since isoelectric points were not measured; thus, arguments concerning the charged states of the membranes are quite speculative at this point.)

Figure 7 gives the results for TB adsorption on SMWP membranes at different ionic strengths. Low ionic strengths appear to enhance TB adsorption, and the effect of ionic strength seems to level out above roughly

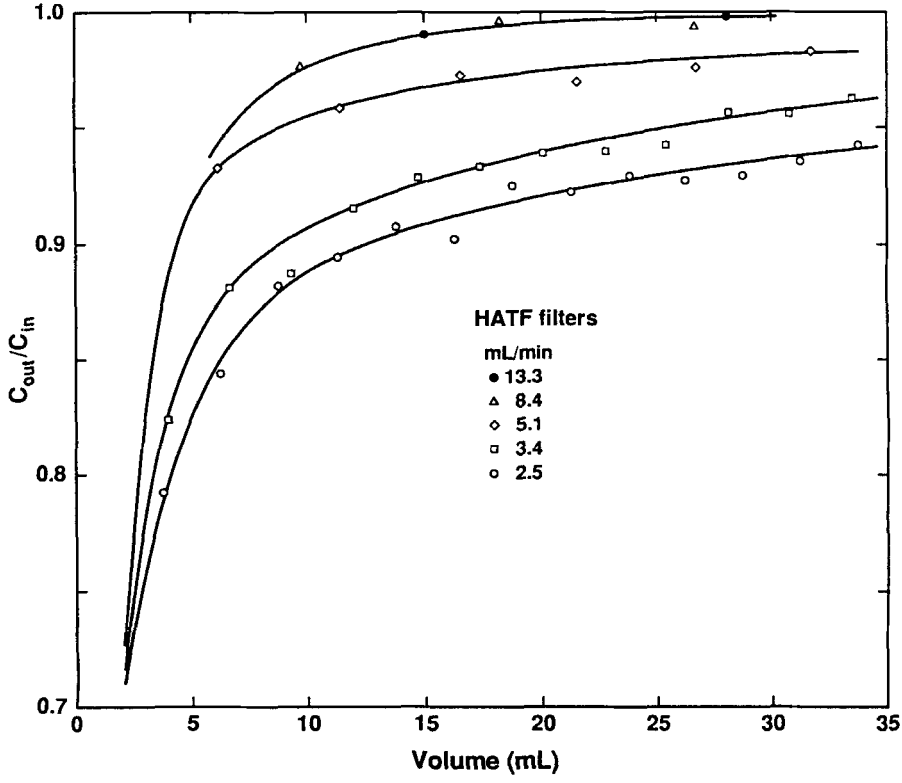

FIG. 8. Adsorption of TB to HATF membranes during filtration at various flow rates.

I = 0.10 M. However, the effect of ionic strength variation is not large (78.2% TB adsorbed at I = 0.01 M versus 71.6% adsorbed for $I \geq 0.10$ M). The reason why low ionic strength has a favorable effect is probably because the lower total density of charged entities (these include the buffer salts, the charged TB molecules, and the charged polymer chains) which occurs at low ionic strengths leads to smaller electrostatic interactions—a situation more favorable for TB adsorption.

The syringe pump data for a HATF membrane are shown in Fig. 8. Clearly, as the volume of solution filtered increases, the membrane adsorbs less and less TB because its adsorption sites are becoming progressively more saturated. Also, as expected, at higher flow rates (lower residence times in the membrane), the outlet stream is nearer in concentration to the inlet stream.

Figure 9 gives dynamic filtration data for three membranes, all at a filtration rate of 2.5 mL/min. Results for an HATF membrane (also shown in Fig. 8) are compared to those for SMWP and HVHP membranes. The

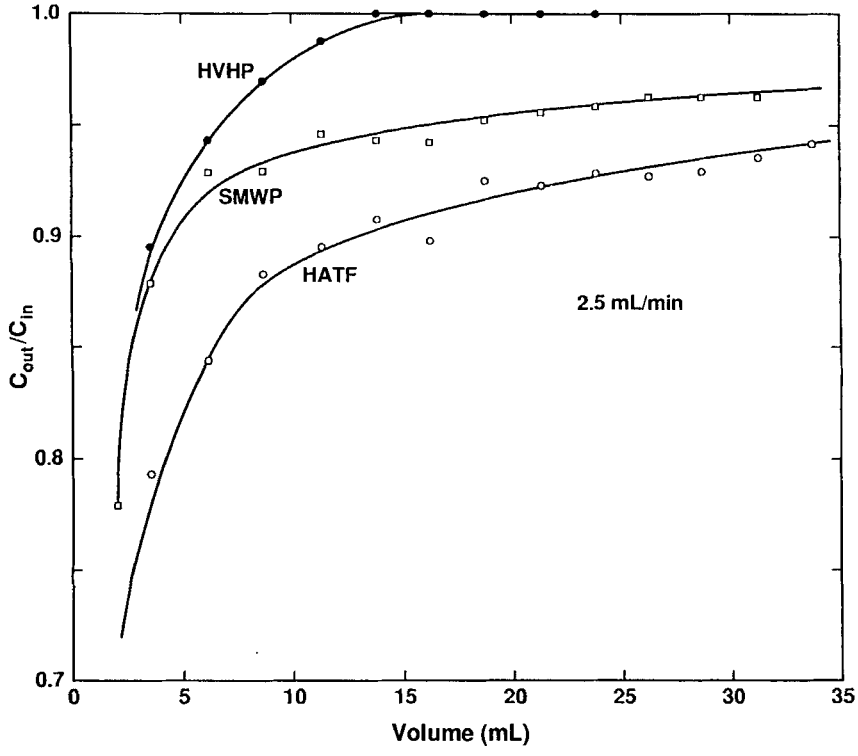

FIG. 9. Adsorption of TB to three membranes during filtration at 2.5 mL/min.

HVHP membrane is quite hydrophobic and was wetted with methanol prior to use, so that filtration could be initiated more easily. The relative behaviors are as one would expect based on the equilibrium adsorption data of Table 2. That is, the HVHP membranes would be expected to adsorb very little TB and the SMWP membrane would be expected to adsorb a significant amount of TB, but not as much as the HATF membrane. Figure 9 shows this behavior. For the HVHP membrane, C_{out}/C_{in} approaches a value of 1.0 at a volume of about 15 mL. For the HATF and SMWP membranes, some adsorption (>3%) still occurs at the 35-mL mark. For these, a filtration rate greater than 2.5 mL/min should be used to achieve $C_{out}/C_{in} \simeq 1.0$, as Fig. 9 suggests.

CONCLUSIONS

We have shown many basic features concerning the adsorption of one organic solute, toluidine blue, on membrane filters. It has been shown that TB adsorption depends strongly on the type of polymer comprising the membrane. Hydrophilic membranes adsorb TB strongly; hydrophobic ones do not. TB adsorption varies with pH in a complex manner, but increases dramatically at high pH values as the TB takes on an uncharged form. TB adsorption also increases as the solution ionic strength decreases below 0.1 *M*.

The rate of TB adsorption in batch experiments is fairly slow—even after several days the TB concentration in the solution is still changing at an easily measurable rate. However, in fairly "short time" dynamic filtration tests, the rate of TB adsorption is high enough to cause the outlet concentration to be significantly less than the inlet concentration. Minimizing the effects of TB adsorption during membrane filtration can be achieved by: (a) using a hydrophobic membrane (although this may make the filtration mechanically difficult to carry out), (b) reducing the solution pH with a simple acid such as HCl (it can be readjusted to its original level after filtration, using NaOH, assuming the NaCl introduced by doing this presents no problems), (c) filtering a large volume of solution before collecting the sample to be analyzed, and (d) performing the filtration at a high flow rate.

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