

# Sorption of Aromatic Compounds in Water Using Polymer Sorbents Containing Amino Groups

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## SYNOPSIS

Porous organic sorbents containing primary amino groups and crosslinked with divinylbenzene or ethyleneglycol dimethacrylate were used for the recovery of various organic pollutants from aqueous solutions. The kinetics of sorption of these solutes is dependent on the specific area and the average pore radius of the sorbent. Physical sorption and chemical interaction of the acid solutes with the amino functions are both involved in the sorption process. The variation of the sorption capacity with the specific area of the solute depends on the nature of the solute. Experiments with mixtures of organic solutes show that the sorption of a given solute may be increased or decreased by the presence of another one. The capacity is increased during cycles of using and regenerating the sorbent. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Solid phase extraction is now a widely used method for the treatment of effluent water contaminated with organic pollutants. This method is also used for the concentration of these pollutants with analytical purposes. The porous sorbents may be of mineral or organic origin. Mineral sorbents such as silica-based materials exhibit some problems such as pH instability or inconsistent results due to the presence of free silanol groups in amounts that cannot be controlled or reproduced.<sup>1</sup> For these reasons, the more stable organic polymer sorbents are now the most widely used and a variety of materials has been developed and tested, among which Amberlite XAD,<sup>2,3</sup> Tenax GC,<sup>3</sup> Separon,<sup>4</sup> Hitachi gels,<sup>5</sup> or Polysorb.<sup>6</sup>

Recently, polyurethane resins containing cyclodextrin units as specific sorption sites were prepared by cross-linking  $\beta$  cyclodextrin with diisocyanates.  $\beta$  Cyclodextrin forms stable inclusion complexes with specific organic compounds. It was found that the sorption capacities of these gel-type adsorbents are comparable or higher than those of Amberlite

XAD-2 and XAD-7, especially for the polar organic compounds.<sup>7,8</sup>

In a recent work,<sup>9</sup> we prepared porous polymers with high specific area and grafted with  $\beta$  cyclodextrin. It was found that these sorbents exhibit high sorption capacities toward benzene or phenol, despite the fact that introduction of  $\beta$  cyclodextrin decreases the surface area.

From the above results, it appeared that the sorption ability of the different sorbents is strongly dependent on the more or less hydrophobic nature of the polymer and of the solute to be collected. We describe in this article the use of sorbents of different polarity and specific area for the sorption of various aromatic compounds. These sorbents were prepared by suspension polymerization in water, in the presence of a porogenic agent. Different materials were prepared: all of them contain vinylamine as the polar part, but differ by the nature of the comonomer and of the cross-linking agent.

## EXPERIMENTAL

### Materials

Details of the materials and the synthetic procedure have already been described.<sup>10</sup> *N*-vinyl *t*-butylcar-

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**Table I** Composition of Different Monomer Mixtures

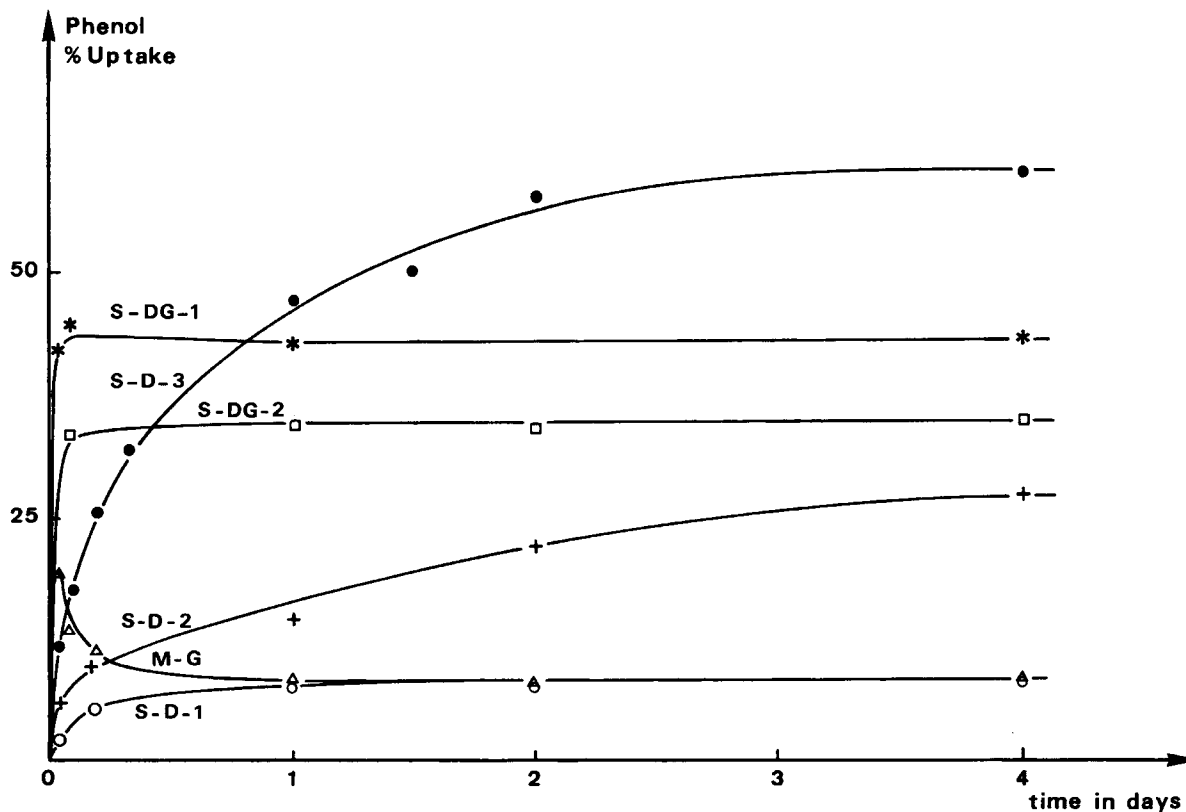
Sample	NVTBC (%)	Sty (%)	DVB (%)	DMG (%)	MMA or (MA %) <sup>a</sup>	Heptane (%)	VA (meq/g)	Porous Volume $V_p$ (cm <sup>3</sup> /g)	Average Pore Radius (Å)	Specific Area $S_{sp}$ (m <sup>2</sup> /g)
S-D-1	10	60	30	—	—	40	0.14	0.61	49	239
S-D-2	30	40	30	—	—	40	0.41	0.83	51	359
S-D-3	60	20	20	—	—	40	0.61	2.09	105	400
S-DG-1	70	10	10	10	—	40	2.35	1.67	205	163
S-DG-2	70	5	5	20	—	40	4.29	1.27	530	48
M-G	40	—	—	30	30	40	1.53	1.38	13800	2
A-G	40	—	—	30	30	40	0.12	1.92	6400	6

<sup>a</sup> Methyl methacrylate (MMA) % for M-G or methacrylic acid (MA) % for A-G.

bamate (NVTBC; precursor of vinylamine, obtained by acid hydrolysis of the carbamate<sup>10</sup>) was the main component of all the polymers. Styrene, methyl methacrylate (MMA), or methacrylic acid (MA) was the comonomer. The cross-linking agents were divinyl benzene (DVB), ethylene glycol dimethacrylate (DMG), or mixtures of both. DMG was used with the purpose of obtaining more polar sorbents

with larger average pore radii, allowing a better access of the solute and higher sorption capacities. Heptane was used as the porogenic agent.

The following resins were prepared using styrene as the comonomer: in the first series (first three entries of Table I), DVB was used as the cross linker and the amount of NVTBC in the monomer mixture and thus from vinylamine (VA) in the sorbent was



**Figure 1** Kinetics of uptake of phenol by the different sorbents: (○) S-D-1; (+) S-D-2; (●) S-D-3; (\*) S-DG-1; (□) S-DG-2; (△) M-G.

increased. In this series (S-D samples), the hydrophilic character increases with increasing amount of VA and decreasing amount of styrene. In the second series (S-DG samples, entries 4 and 5), a mixture of DVB and DMG was used. DMG is more hydrophilic than DVB.

Some samples were also synthesized with MMA (bead samples M-G) or MA (bead samples A-G) as comonomer.

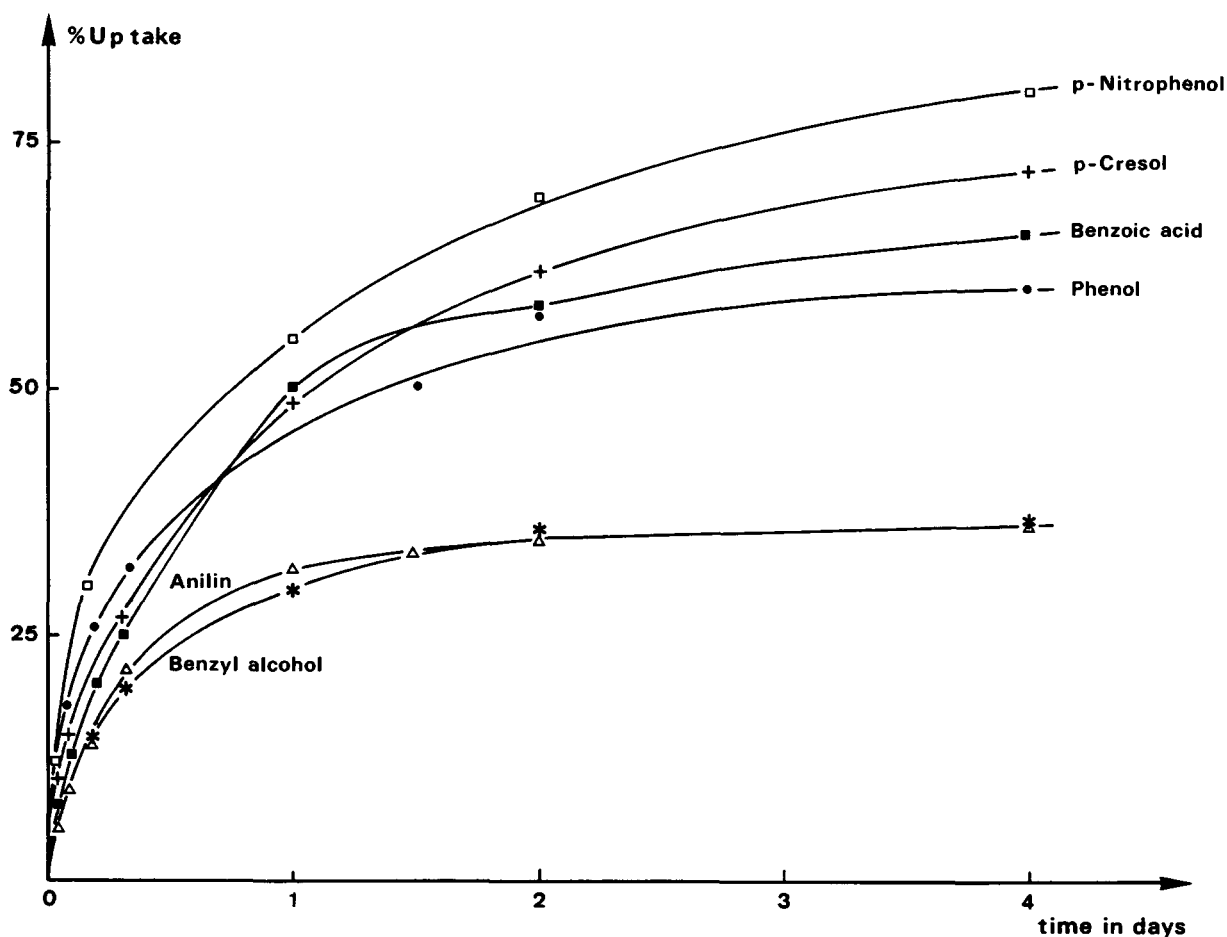
In Table I the composition of the different monomer mixtures used for the synthesis of the sorbents are indicated. The amount of heptane, the porogenous agent, is expressed with respect to the total amount of monomers. The content in VA groups was obtained from elemental analysis of nitrogen. The specific area was determined following the BET method.<sup>11</sup> Mercury porosimetry was used to determine the porous volume and the pore size distribution (Carlo Erba 800).

Beads with diameter ranging from 1 to 2 mm were used in this study.

The organic compounds to be sorbed were obtained from Aldrich and used without further purification.

### Methods

Sorption capacities of the polymers were determined by the following batch method: 20 mg of the polymer were mixed with 10 mL of an aqueous solution of the model organic compound (concentration range: 50–250 ppm) in a tightly closed flask that was shaken at ambient temperature. For the study of the kinetics of adsorption, the residual concentration of the organic compound in aqueous solution was determined from time to time by spectrophotometry and the sorption capacity calculated. For the determination of maximum capacities, the mixtures were allowed to stand for 7 days. All solutions were filtered before spectrophotometric measurements (0.47- $\mu\text{m}$  Millipore filters). The following wavelengths were used for the determination of the different compounds:



**Figure 2** Kinetics of uptake of different solutes by the S-D-3 sorbent: ( $\Delta$ ) anilin; ( $*$ ) benzyl alcohol; ( $\bullet$ ) phenol; (+) *p*-cresol; ( $\square$ ) *p*-nitrophenol; ( $\blacksquare$ ) benzoic acid.

Phenol, 269 nm; *p*-Cresol, 276 nm; benzoic acid, 270 nm; anilin, 300 nm; benzyl alcohol, 256 nm. The concentration of residual *o*-, *m*-, and *p*-nitrophenol was determined at 400 nm after adjusting the pH at 11 with NaOH.

The reusability of the sorbent was tested in the following way. After a sorption step, the sorbent was extracted with methanol in a Soxhlet, dried, and then submitted to a new sorption step. Up to 10 cycles were carried out on a given sorbent.

## RESULTS AND DISCUSSION

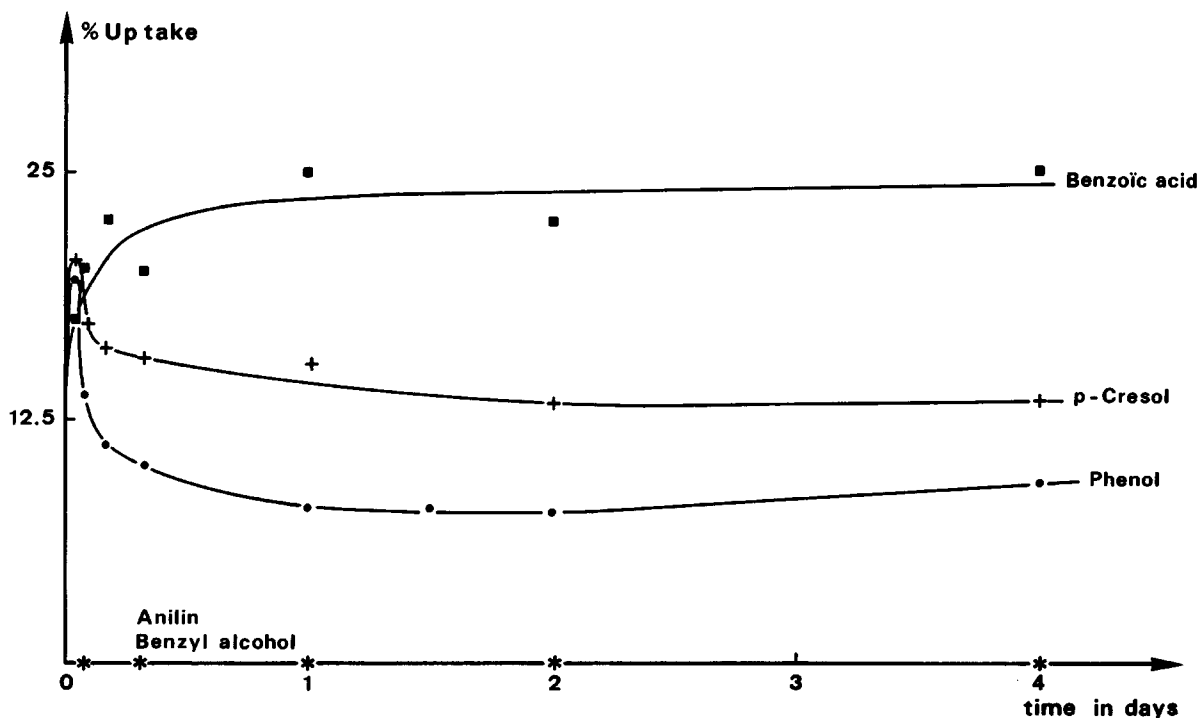
Table I gives the chemical and physical features of the different sorbents used in this work. Samples S-D-1 to -3 have increasing specific area and increasing VA contents (increasing polarity). Using increasing amounts of DMG instead of DVB decreases markedly the specific area but strongly increases the VA concentration, that is, the polarity.

The use of MMA instead of styrene leads to a very low value of  $S_{sp}$  but the VA content is rather high. For the last sample, A-G, in which MA is used as comonomer, both values are very low.

## Kinetics of Phenol Adsorption

Figure 1 gives the percent uptake for phenol as a function of time for the different sorbents. For the S-D series the kinetics of adsorption is very low. Maximum capacity is attained after 1 day for S-D-1 and only after 3 or 4 days for the two other samples. The maximum capacity increases both with increasing specific area and VA content in this series.

With samples S-DG-1 and -2, the kinetics is very different and the maximum capacity is attained after only 1 or 2 h. The maximum capacity is only slightly lower for S-DG-2 despite its much lower specific area. This is probably due to its higher VA and DMG content that both increase its hydrophilic character. For sample M-G the behavior is different. The percent of uptake strongly increases during the first hour of contact as for S-DG-1 and -2 then decreases rapidly down to less than half its maximum value. These three kinds of kinetic behavior seem to be related with the textural features of the sorbents. For S-D samples, the average pore radius  $R_a$  is in the range 0–100 Å and the diffusion of phenol inside the polymer is probably slow. For the S-DG samples,  $R_a$  is in the range 200–500 Å and the diffusion is much easier. For much higher  $R_a$  values (>5000 Å),



**Figure 3** Kinetics of uptake of different solutes by the M-G sorbent: (\*) anilin; (\*) benzyl alcohol; (●) phenol; (+) *p*-cresol; (■) benzoic acid.

the diffusion of phenol is also very easy but the difference is that the organic compound is not strongly adsorbed on the support. In order to get more insight into this process, the adsorption of various organic compounds was studied. As an example, Figure 2 shows the adsorption curves for S-D-3 (which has the higher specific area) with phenol, *p*-cresol, *p*-nitro phenol, benzoic acid, anilin, and benzyl alcohol. All these curves were obtained with 50 ppm solutions of the organic compound.

Two type of curves are obtained. With anilin and benzyl alcohol, the sorption capacity reaches a plateau after 2 days of contact. On the contrary, with the other compounds that all have an acidic nature, the sorption capacity has not yet reached its maximum value after 4 days. Thus, it seems that for this kind of sorbent with high specific area and containing basic functions, the sorption has two origins. The first origin is a physical sorption for compounds as anilin or benzyl alcohol with no specific interaction with the support. In this case, a plateau is reached. Second, chemical interactions between the amino groups of the support and the OH or COOH groups of the solute yield additional sorption capacity. Hydrogen bonds are probably involved in this second kind of interactions.

Figure 3 shows the adsorption curves for the sorbent M-G with the same organic compounds. In this case, no adsorption is observed for the solutes with no acidic nature (aniline and benzyl alcohol) even after 1 week. This supports the assumption that, for such solutes, the adsorption is related with the specific area of the sorbent. Phenol and *p*-cresol undergo a very rapid adsorption within the first 2 hours but are then partially desorbed with a plateau after 1 day. Only the more acidic of this set of compounds,

namely benzoic acid ( $pK = 4.2$ ), is strongly retained on the sorbent.

The maximum capacity of the different sorbents toward the organic solutes was determined after 1 week of contact. The values are reported in Table II as  $\mu\text{mol}$  of solute per gram of sorbent. The higher value is for benzoic acid with sorbent S-GD-1 and corresponds to about 104 mg/g, that is, the sorbent is able to retain about 10% of its own weight. The sorption ability of this solute depends not only on the amount of amine groups in the sorbent (in this case, S-DG-2 should have the higher capacity) but also on the specific area. The relation between the specific area of the sorbent and the sorption capacity is shown in Figure 4 (a,b).

With aniline for which only physical adsorption is likely to occur, the sorption capacity increases linearly with the specific area independently of the nature of the comonomer or the cross-linking agent. With all the other solutes, the variation of the sorption capacity [Fig. 4(b)] is different. The left part of the Figure is for the sorbents crosslinked with DMG or DMG/DVB mixtures that have rather low specific area but rather high VA content. The capacity increases more or less rapidly with increasing area. When going to the right part of the figure that corresponds to sorbents crosslinked with DVB only, having low VA content and high areas, the capacity decreases sharply, then increases again with increasing  $S_{sp}$ .

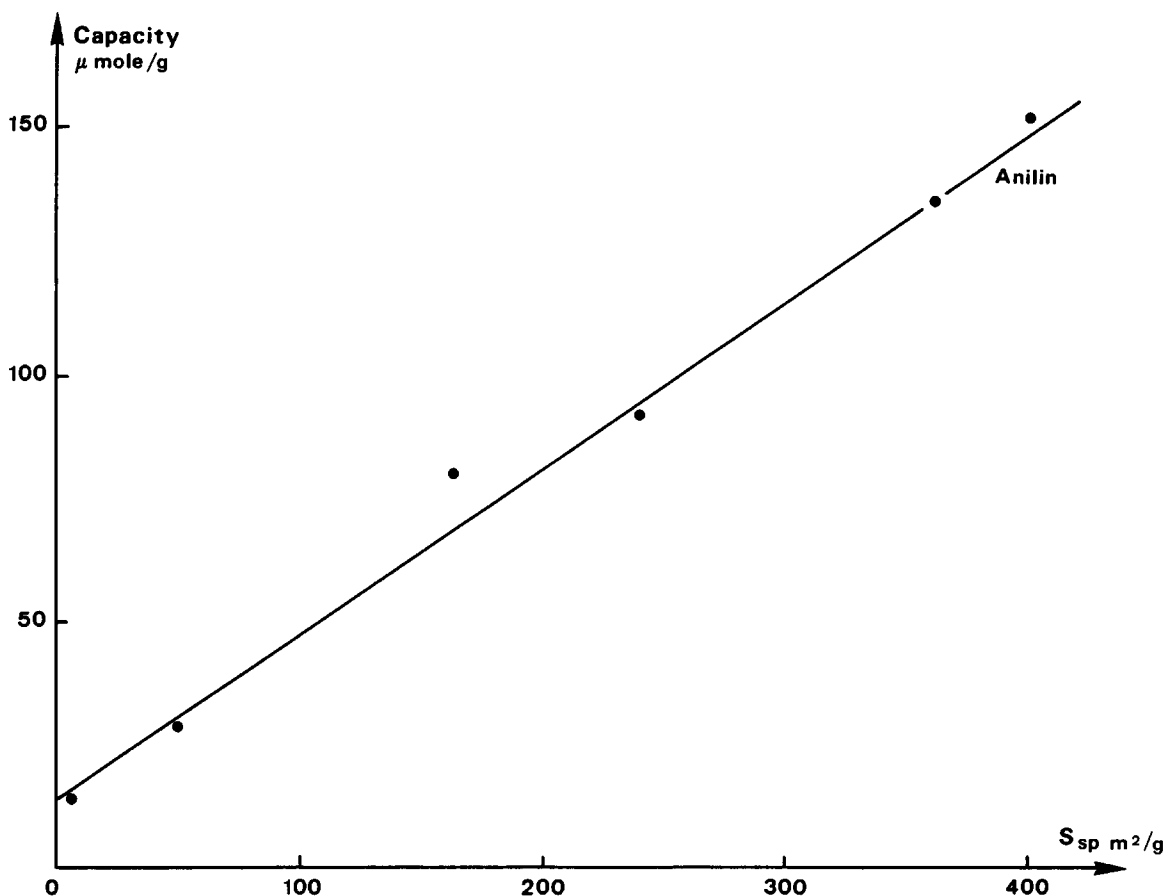
The only solute retained by sorbent A-G is aniline. This is a confirmation that this sorbent has an acidic nature due to its low VA content and the use of MA as comonomer. Among the isomers of nitro phenol, the *meta* and *para* derivatives behave as phenol or *p*-cresol, but the *ortho* isomer is much

**Table II** Maximum Capacity of Different Sorbents

Solute <sup>a</sup>	S-D-1	S-D-2	S-D-3	S-DG-1	S-DG-2	M-G	A-G	XAD-2 <sup>b</sup>	XAD-7 <sup>b</sup>
Aniline	90	135	151	81	28	0	14		
Benzyl alcohol	120	344	198	350	195	0	0	29	32
Phenol	41	80	114	111.5	91	38	0	28	75
<i>p</i> -Cresol	85	103	152	147	65	16	0	41	97
2-Nitro-phenol	182	190	192	200	13	0	0		
3-Nitro-phenol	6	18	26	164	15	6.5	0		
4-Nitro-phenol	3	16	25	174	20	2	0		
Benzoic acid	52.5	322	660	960	79	52.5	0	28	69

<sup>a</sup> The adsorption is expressed in  $\mu\text{mole}$  of solute per gram of sorbent.

<sup>b</sup> From Kawaguchi et al.<sup>8</sup>



**Figure 4** Capacity versus specific area of the sorbents: (a) (●) anilin; (b) (▲) benzyl alcohol; (●) phenol; (○) *p*-cresol; (Δ) *p*-nitrophenol; (\*) benzoic acid.

more adsorbed than the others. Among all the sorbents used in this study, sample S-DG-1 exhibits the higher capacity for most of the solutes. This is the best compromise between the specific area and the VA content.

The comparison with the sorption capacity of commercial sorbents as Amberlite XAD-2 or XAD-7 is of interest (Table II). XAD-2 is based on styrene and DVB whereas XAD-7 also contains acrylic esters and has a more polar nature. Our sorbents S-D-1-3, also crosslinked with DVB, but containing amino groups, have higher capacities especially for benzoic acid.

Figure 5 shows the influence of the concentration of the solute on the uptake percent. As expected and reported in previous works,<sup>8</sup> the sorbents are more efficient in dilute solution especially when the contact time is low.

One of the sorbents (S-D-3) was also tested for the competitive sorption of two solutes [Fig. 6(a,b)].

The curves uptake percent versus time are similar to those of Figure 2 but differences appear in the sorption capacities at the plateau after 4 days. Whereas the sorption of *p*-cresol alone and benzyl alcohol alone are, respectively, 18 and 9 μg/g, the corresponding values are 16 and 42 μg/g when these two solutes are brought simultaneously in contact with the sorbent. The change in the sorption capacity for the alcohol is drastic. In the same way, the sorption capacities for phenol and benzyl alcohol change from 15 and 9 μg/g to 9 and 33 μg/g, respectively, when they are mixed. In this case the increase of sorption of the alcohol occurs to the prejudice of the other solute. At the present time, we have no clear explanation for this effect but com-

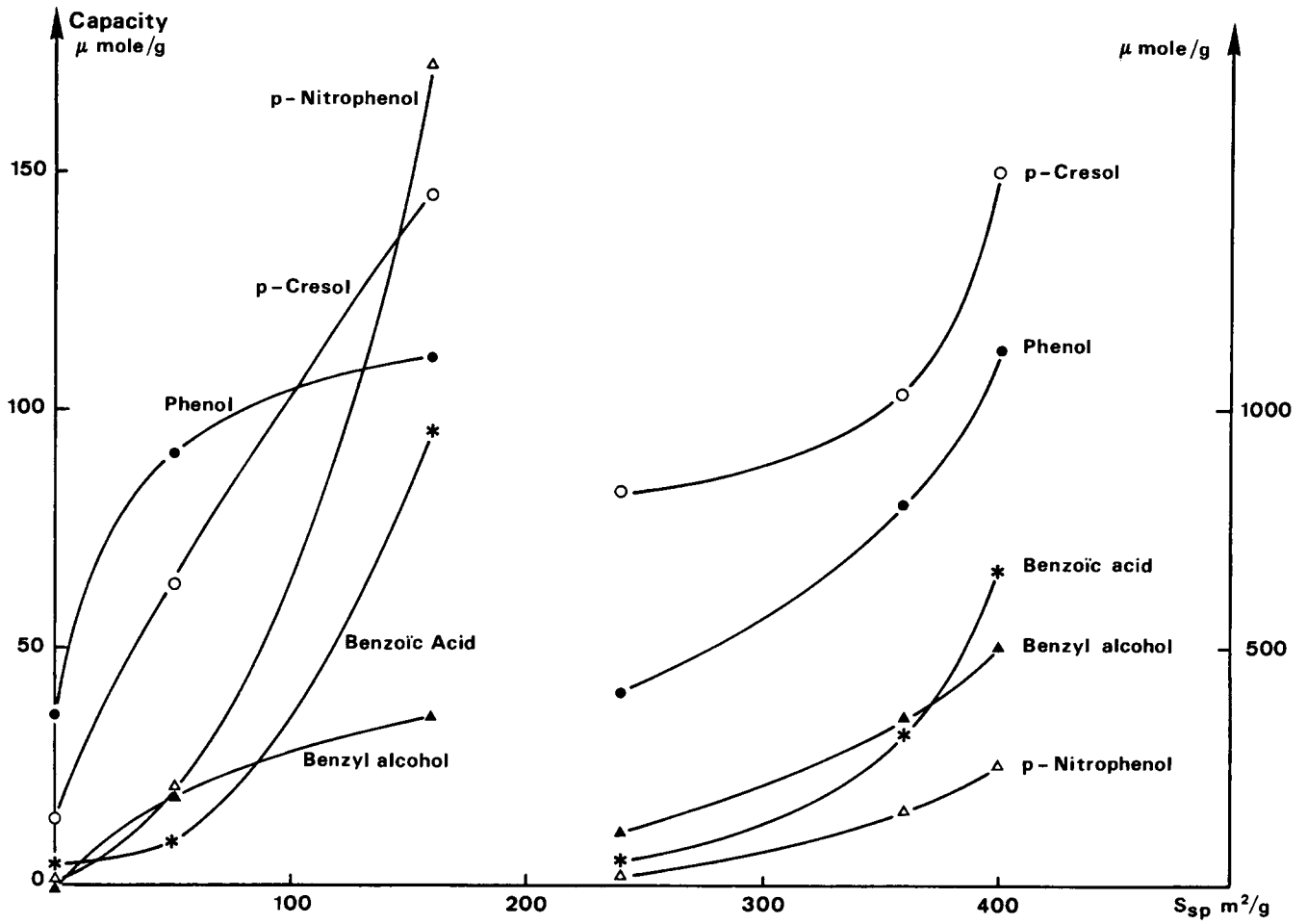


Figure 4 (Continued from the previous page)

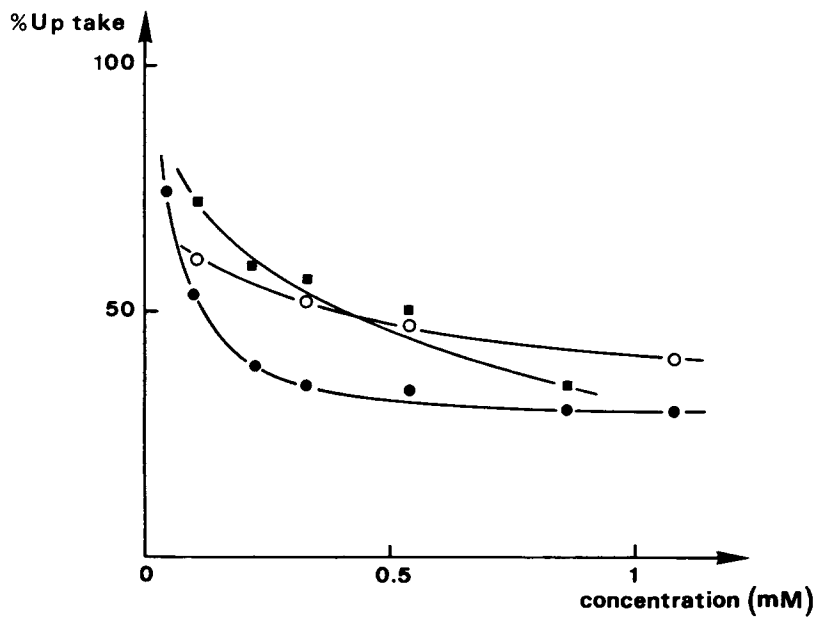
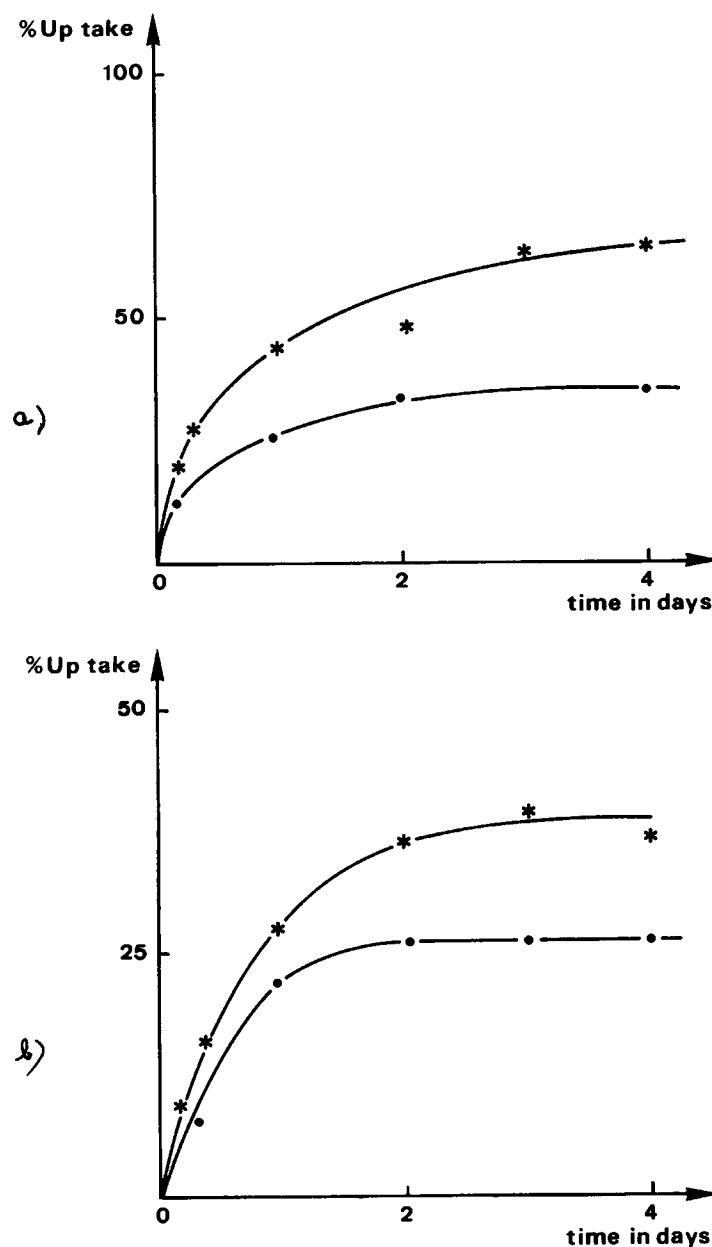


Figure 5 Percent uptake versus the initial concentration of the solute after: (●) 24 h; (○) 4 days; (■) 7 days (sorbent S-D-3).



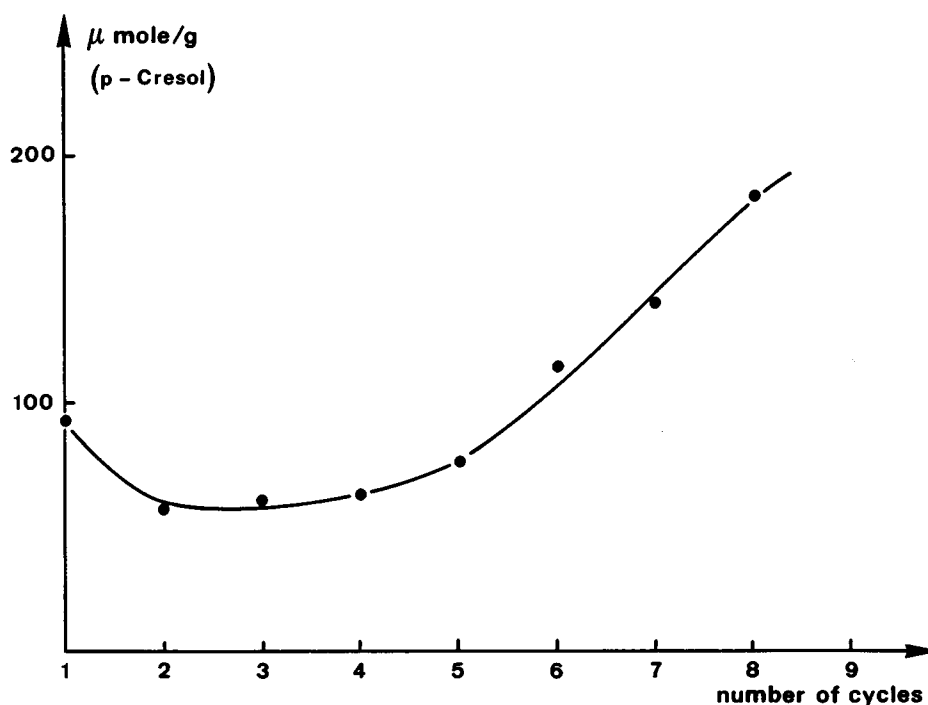
**Figure 6** Competitive sorption of: (a) (\*) *p*-cresol; (●) benzyl alcohol; (b) (\*) phenol; (●) benzyl alcohol (sorbent S-D-3).

petition between physical sorption and chemical interaction is likely.

Figure 7 gives the reusability of the S-D-3 sorbent. This test was carried out with *p*-cresol as described in the experimental part. The capacity of the sorbent decreases after two cycles, then increases strongly to attain almost twice the initial value after eight cycles.

It can be said in conclusion that such sorbents containing primary amino groups are suitable for the extraction of organic pollutants, especially acidic ones, from aqueous solutions. As the kinetics of adsorption is a critical factor, especially in view of column use, sorbents such as S-DG-1 with rapid kinetics of sorption and high capacities toward all the solutes are very suitable.





**Figure 7** Variation of the sorption capacity of S-D-3 with the number of using-regenerating cycles.

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