

Grafting of Cyclodextrins onto Polypropylene Nonwoven Fabrics for the Manufacture of Reactive Filters.

III. Study of the Sorption Properties

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ABSTRACT: Polypropylene nonwoven supports carrying α -, β -, and γ -cyclodextrins (CDs) were synthesized. The synthesis consisted of grafting glycidyl methacrylate (GMA) onto the fibers and reacting CDs with epoxide groups in the second step. This article concerns the sorption capacity of these supports toward organic pollutant models of 2-naphthol, 4-nitrophenol, pentachlorophenol, and (2,4-dichlorophenoxy) acetic acid in static (batch) or dynamic (filtration) conditions. The results confirmed that the grafting of CDs onto the supports gave them their specific sorption properties. Besides, it was observed that the best performances were attained when the GMA add-on was in the range of 76–113 % wt and the CD content was 87–118 $\mu\text{mol/g}$. We also evidenced that the interactions between the organic substrates and the filter occurred through specific interactions with CDs (host–guest inclusion compounds) and that to a lesser extent, nonspecific sorption phenomena also occurred. The data showed that the affinity between the pollutants with three different grafted CDs was not in agreement with the complex formation constants measured in homogeneous systems. Furthermore, the slow kinetics of exchange between the liquid and solid phases was a limiting factor that should prevent the use of the filters at elevated flow rates. At last, the great advantage of these filters is that they could undergo several cycles of use, thanks to intermediate regeneration steps with water–organic solvent mixtures. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1771–1778, 2002

Key words: cyclodextrin; poly(propylene) (PP); fibers; electron beam radiations; filtration; effluents

INTRODUCTION

Cyclodextrins (CDs) are cyclic polysaccharide oligomers whose host–guest inclusion-forming prop-

erties have been widely studied in the last three decades.¹ Inclusion complexes of long-chain aliphatic or aromatic molecules as fragrances, drugs, pesticides, or hormones have been synthesized and characterized.² They showed some real uses in many domains, such as in agrochemistry, pharmaceuticals, food, and cosmetics, so that CD production increased to over 1000 tons per year in

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the last decade.³ Besides, the production of CD-based materials has enlarged the field of their applications. Among them, incorporation of CDs onto textile fibers is of great interest.⁴ As a matter of fact, textile materials functionalized with CDs may, on the one hand, capture active or polluting substances and, on the other hand, they may release these substrates under controlled conditions. For example, fragrances may be released within a long period of time, thus offering a long-lasting perfumed fabric. On the contrary, a substrate can be effectively and rapidly desorbed from the support upon elution with a small volume of an apolar solvent. Covalent linking of CDs onto the support is suitable for the reuse of the former and the sorption-desorption phenomenon can be exploited infinitely. In this field of the research, we recently reported a method for grafting CDs onto polypropylene (PP) fibers.^{5,6} The originality of this work concerned the functionalization of a polyolefinic matter by CD that was never attempted before. The synthesis consisted, in the first step, to achieve graft polymerization of glycidyl methacrylate (GMA) after activation of the surface of the fabric under electron-beam irradiation; CDs were then reacted with the functionalized fibers by the intermediate of their epoxide groups. The present article aimed to discuss the complexing properties of these CD-grafted fabrics toward some aromatic compounds dissolved in aqueous media. Static (batch) and dynamic (filtration) decontamination experiments have helped us to evidence the role played by the grafted CDs in the sorption mechanism.

EXPERIMENTAL

Materials

Products

Beta-naphthol (BN), paranitrophenol (PNP), pentachlorophenol (PCP), and (2,4-dichlorophenoxy) acetic acid (24D) were Aldrich (Milwaukee, WI) chemicals and used without further purification.

CD-Grafted Textiles

The preparation of PP nonwoven supports was detailed elsewhere.⁵ They varied in their amounts of grafted poly(GMA) and CDs and also in the nature of the grafted CDs (α -, β -, or γ -CD). In this article, we use the following nomenclature: FA, FB, or FG represent filters carrying α -, β -, or

γ -CD, respectively. The first value in the parentheses represents the weight increase of the fabric upon graft polymerization of GMA (GMA % wt), and the second value reports the amount of grafted CD expressed in μmol per gram of the final support. For example, FA(113/121) has a GMA add-on of 113 wt % and contains 121 $\mu\text{mol/g}$ of α -CD.

Methods

Sorption Capacity Determination

The batch (static system) method used for the screening and the kinetic experiments consisted of dipping a weighted amount of a filter in 5 mL of an aqueous solution of pollutant compounds (BN or PNP; concentration 5×10^{-4} M) contained in a stoppered flask that was shaken at ambient temperature ($20 \pm 2^\circ\text{C}$) for 4 h. The ratio *mol of solute in the solution/mol of CD present on the filter* was adjusted to 2. Sorption isotherms were obtained from solutions (50 mL) with an initial concentration in the substrate of 20 to 720 ppm, put in the presence of 110–140 mg of the filter during 4 h.

Filtration Experiments

Filtration experiments (dynamic system) consisted of introducing 150–500 mg of filters into an HPLC column (50-mm length and 5-mm diameter). All the precautions to avoid a preferential path of the flux were taken. A peristaltic pump ensured a constant flow (of 0.2–1 mL per minute) through the column. A fraction collector apparatus was used to separate the filtrate into 10-mL aliquots.

In all cases, the residual concentration of the organic solute in the supernatant solution was determined by UV-visible spectrophotometry (CARY UV 50). Then, by the difference in the initial concentration, it could be possible to calculate the amount of substrate trapped per gram of filter: Q_e ($\mu\text{mol/g}$).

RESULTS AND DISCUSSION

Kinetic Study

The kinetics of sorption of several supports toward PNP and BN showed that a time of 4–6 h was sufficient to observe equilibrium, as shown in Figure 1.

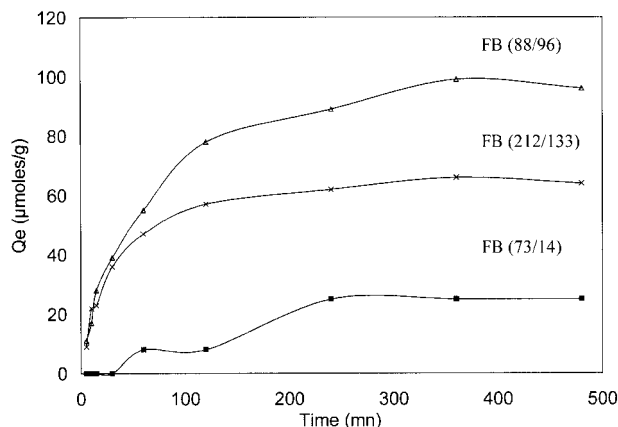


Figure 1 Kinetics of sorption of BN onto β -CD carrying supports.

Influence of the Chemical Characteristics of the Filters

As previously reported,⁶ the maximum amount of incorporated CD onto the PP filter varied with the

quantity of epoxide groups grafted in the first step of the synthesis. The screening of the sorption capacity of the various supports thus obtained was carried out using BN and PNP as substrates in the batch system. This experiment was conducted with the aim to observe how the sorption capacity of our panel of filters varied with their composition characteristics. Besides, the ratio of the amount of the trapped substrate versus that of CD present on the filter could be calculated. This value, reported as $Q_e/CD \times 100$ in Table I, was interpreted in terms of the percentage of occupied CD sites.

The results presented in Table I show, on the one hand, that sorption properties only appear when CD is present on the filter. On the other hand, it is observed that both poly(GMA) and CD contents influence the performances, as graphically represented in Figures 2 and 3, respectively.

From the graphs presented in Figures 2 and 3, it is observed that, in correlation with their com-

Table I Sorption Rates in Batch System of Filters of Different Compositions in Poly(GMA) and Different Nature of CDs Toward PNP and BN

Filter	CD ($\mu\text{mol/g}$)	GMA (% wt)	PNP		BN	
			Q_e ($\mu\text{mol/g}$)	$Q_e/CD \times 100$ (%)	Q_e ($\mu\text{mol/g}$)	$Q_e/CD \times 100$ (%)
PP	0	0	0		0	
PG	0	78	0		0	
FB(10/10)	10	10	23	230	12	120
FB(73/13)	13	73	17	131	14	108
FB(80/31)	31	80	36	116	31	100
FB(76/87)	87	76	67	77	70	80
FB(88/96)	96	88	97	101	81	84
FB(88/103)	103	88	77	75	73	71
FB(212/133)	133	212	47	35	49	37
FB(353/139)	139	353	31	22	50	36
FB(328/143)	143	328	47	33	44	31
FB(398/143)	143	398	30	21	21	15
FB(465/143)	143	465	36	25	33	23
FA(50/34)	34	50	10.5	31	36.2	106
FA(90/108)	108	90	69	64	59.7	55
FA(90/118)	118	90	60.6	51	60	51
FA(157/145)	145	157	64.4	44	58.9	41
FA(207/149)	149	207	58.5	39	59.2	40
FA(210/154)	154	210	65.2	42	73.2	48
FG(50/95)	95	50	55.3	58	58.7	62
FG(90/89)	89	90	71.3	80	72.4	81
FG(113/98)	98	113	69.8	71	67.3	69
FG(207/116)	116	207	52.8	46	63.7	55
FG(210/117)	117	210	63.5	54	59	50

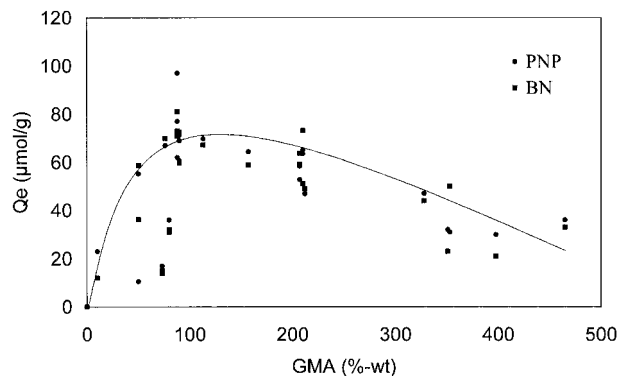


Figure 2 Rates of adsorption of BN and PNP versus GMA % wt. All types of grafted CDs are included.

position, three different classes of filters appeared:

- (i) The first class has low amounts of fixed poly(GMA) (10–80 % wt) and CD (10–34 $\mu\text{mol/g}$), which is the limiting factor of the sorption capacity. Besides, it is observed that the rate of occupation of the CD sites is superior to 100%. This indicates that physical adsorption, hydrogen bonding between the solute and CDs, and hydrophobic guest–guest interactions may occur besides inclusion complex formation with CDs.
- (ii) The second class (the most efficient) consists of supports with medium quantities of poly(GMA) (76–113% wt) and CD (87–118 $\mu\text{mol/g}$). The rate of occupancy of the CD sites reached 70–100%. These filters present the best compromise between the

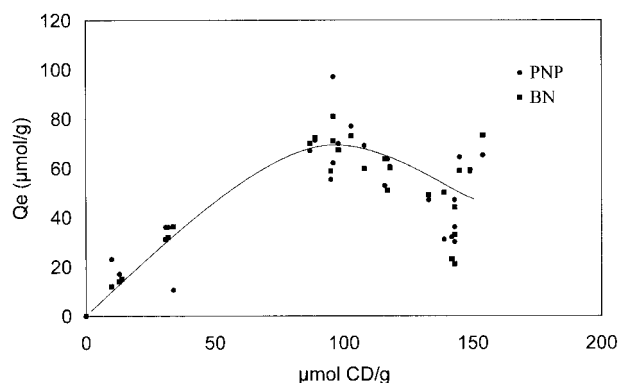


Figure 3 Rates of adsorption of BN and PNP versus CD content of the filters. All types of grafted CDs are included.

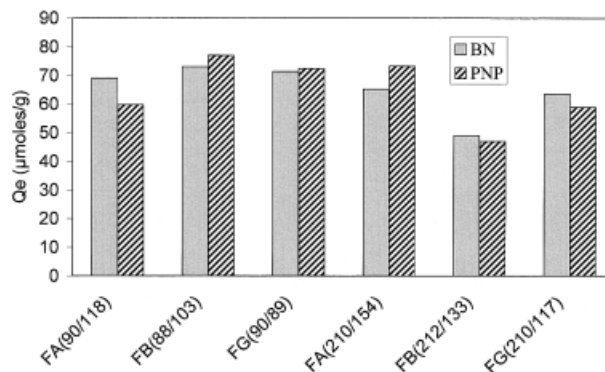


Figure 4 Comparison of the sorption rates of supports carrying α -, β -, or γ -CD toward BN and PNP.

amount of CD molecules grafted and their accessibility toward the substrates.

- (iii) The third class is featured by the highest grafted amounts of both poly(GMA) (157–465 % wt) and CD (133–154 $\mu\text{mol/g}$). However, the maximum sorption capacity has not been observed with these supports. It was observed that the high poly(GMA) content was responsible for a bad wettability of the material, thus preventing exchange between the solid and liquid phases. On the other hand, it was also observed, by a microscopy study, that the thickness of the poly(GMA) sheath surrounding the core PP fiber varied with the GMA % wt.⁶ We suppose that the major ratio of the grafted CD is incorporated into the bulk of this poly(GMA) thick layer. This explains why the occupation rate of the CD sites of this class of filters is rather low (23 to 55%). In other words, grafted CD can be distinguished into two categories: those present on the surface that present the maximum activity and those imprisoned inside the matter whose specific properties are somewhat deteriorated.

Nature of the Grafted CD and Specific Affinity of the Filters

Figure 4 represents the sorption capacity of filters with similar chemical compositions toward PNP and BN. Despite literature reports⁷ that PNP is preferably complexed by α -CD and that BN has a better affinity to β -CD, no obvious differentiation occurred in the sorption of both substrates by sorbents carrying the three kinds of CDs tested.

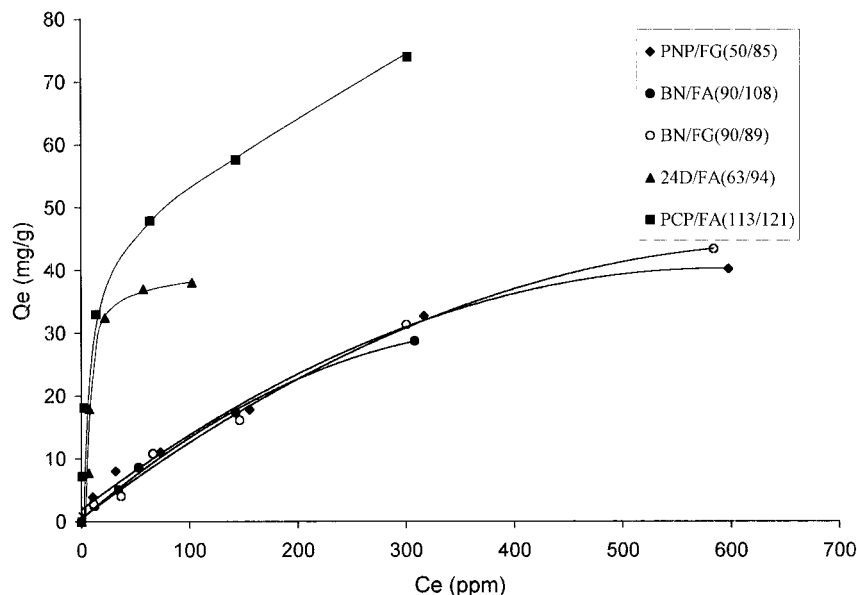


Figure 5 Equilibrium isotherm for sorption of PNP, BN, 24D, and PCP onto various filters.

These results show that the grafting reaction of the three CDs has led to a leveling of their complex formation constant toward both substrates. The reaction of more than one hydroxyl group of a CD unit with several epoxide functions of poly(GMA) may have caused a crosslinked network that created some steric hindrance in the surroundings of the entries of the CD cavities.

Sorption Isotherms

Sorption isotherm experiments consisted of dipping a fixed amount of the filter in the presence of substrates in variable concentrations and in batch conditions. After the equilibrium was reached, we could plot Q_e against C_e (ppm), the equilibrium concentration of the batch solution, as presented in Figure 5.

The Langmuir equation is valid for a monolayer sorption on a surface containing a definite number of sites. This model assumes uniform energies of sorption on the surface and no transmigration of the sorbate in the plane of the surface. The linearized form of the Langmuir isotherm corresponds to eq. (1):

$$\frac{C_e}{Q_e} = \frac{1}{Q_M} + \frac{bC_e}{Q_m} \quad (1)$$

where C_e and Q_e are as mentioned above, b (dimensionless) is related to the energy or net en-

thalpy of sorption, and Q_m (mg/g) corresponds to the maximum capacity of the sorbent.

On the other hand, data were also treated by the Freundlich isotherm whose linear form is presented in eq. (2):

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

in which K_f is a value that depends on the sorption capacity and $1/n$ is relative to the sorption intensity. $1/n > 1$ means weak adsorption properties, while $1/n < 0.5$ reflects the most favorable sorbent. Experimental data were treated according to eq. (1) and (2), and the constants relative to each model are reported in Table II.

It is observed in Figure 5 that CD supports have a strong affinity for the chlorophenyl compounds, especially in the low concentration domain, compared to BN and PNP. After treatment of the data according to both equilibrium isotherm models, the value of r^2 , the linear correlation coefficient, revealed that sorption of the chlorophenyl compounds, 24D and PCP, were in agreement with the Langmuir model (Fig. 6), while phenol derivatives (BN and PNP) preferably followed the Freundlich one (Fig. 7).

As observed above, we could not detect any preferential sorption of BN onto an α - or β -CD-functionalized support. On the other hand, Q_m

Table II Constants Obtained from the Freundlich or Langmuir Models Applied to Sorption Isotherms Reported in Figure 5

Filter	Freundlich Model			Langmuir Model		
	K_f	$1/n$	r^2	b	Q_m (mg/g)	r^2
PNP/FG(50/85)	1.008	0.5819	0.9903	0.004	53.2	0.9194
BN/FA(90/108)	0.359	0.7737	0.9938	0.002	78.74	0.9427
BN/FG(90/89)	0.398	0.7448	0.9655	0.003	56.18	0.7435
24D/FA(63/94)	4.96	0.49	0.7271	0.132	41.1	0.9984
PCP/FA(113/121)	10.38	0.36	0.9357	0.052	75.2	0.9807

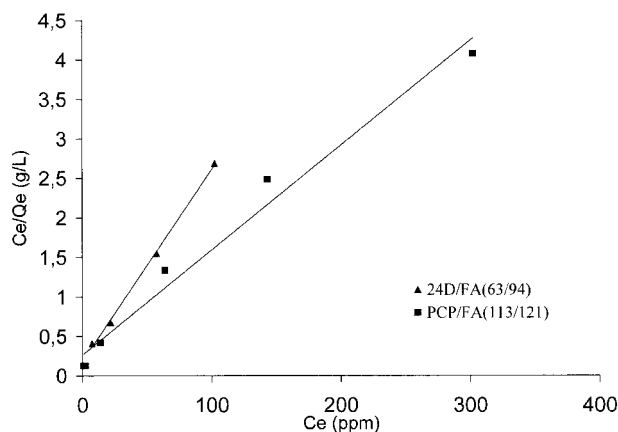
values (Table II) showed that PCP is fairly better adsorbed than is 24D onto the α -CD-grafted support.

Sorption in Dynamic Systems

Our supports were applied in dynamic open column systems, that is, the filtrate was collected into fractions, rather than reinjected in the feeding tank. These series of experiments were carried out to investigate if filters kept a sufficient porosity in both steps of the grafting reactions and also to observe if the kinetics of exchange between the textile and the solution under dynamic flux was favorable to allow the filtration application.

Q_x , the amount in μmol of sorbed substrate per gram of sorbent after elution of x mL of a contaminated solution was calculated from eq. (3):

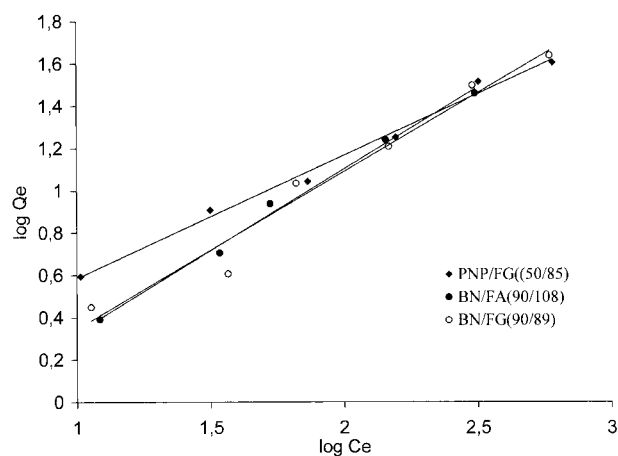
$$Q_x = \frac{V_f \times 10^{-6}}{m} \sum_{i=1}^n (C_n - C_0) \quad (3)$$

**Figure 6** Langmuir plot of 24D and PCP sorption onto α -CD functionalized filters.

where V_f is the fraction volume; m , the filter weight introduced into the column; C_n and C_0 , the concentrations in the substrate in the fraction volume and in the stock tank, respectively. In addition, the *breakthrough volume* was defined as the volume of the eluate within the concentration in the pollutant substrate that remains inferior to 10% (value arbitrarily chosen) of that of the stock solution (*breakthrough concentration*).

Influence of the Flow Rate

Filtration experiments under different flow rates were carried out with FB(88/96) (Fig. 8). One can observe that the performance of the filter diminishes with increasing values of the flow rates. This was also confirmed by the evolution of the values of the breakthrough volumes and Q measured at the total volume of elution that was arbitrary fixed to 66 mL, as reported in Table III. This experiment highlighted that the sorption phenomenon is driven by a slow kinetics of trans-

**Figure 7** Freundlich plot of PNP and BN sorption onto α - and γ -CD functionalized filters.

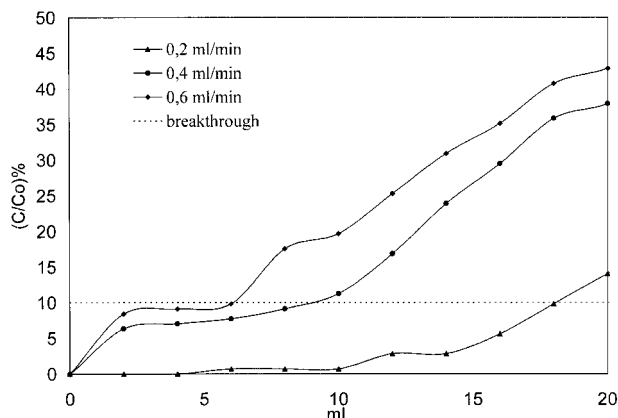


Figure 8 Filtration of a BN solution using FB(88/96) as a filter at various flow rates: concentration of BN in the filtrate against the elution volume.

fer of the substrate from the aqueous phase to the fibers. We conclude that this phenomenon is limited by the kinetics of diffusion of the substrate in the poly(GMA) layer, before attaining the CD sites. Consequently, 0.2 mL per minute was the applied flow rate for the following series of experiments.

Figure 9 shows the evolution of BN in the eluent as a function of the volume of stock contaminated solution passed through the column. Figure 9 displays that FB(10/10) is the most rapidly saturated filter and has a breakthrough volume of only 3.2 mL. As already observed in the static system, the filter of the second class FB(88/96), modified by medium amounts of CD and GMA, offered the best performances with a breakthrough volume that increased at 18.5 mL. This filter fixed 1.5 more BN than FB(212/133) in the overall experiment, as displayed in Table IV. Furthermore, it is observed that the concentration of the eight first collected 0.2-mL fractions remained close to 0. This means that the sorption capacity of FB(88/96) is not dependant on the rate of occu-

Table III Breakthrough Volumes and Quantity of BN Sorbed onto FB(88/96) After Elution of 66 mL at Different Flow Rates

Flow Rate (mL/min)	Breakthrough Volume (mL)	Q_{66} ($\mu\text{mol/g}$)
0.2	18.0	84.3
0.4	9.0	65.8
0.6	6.0	63.0

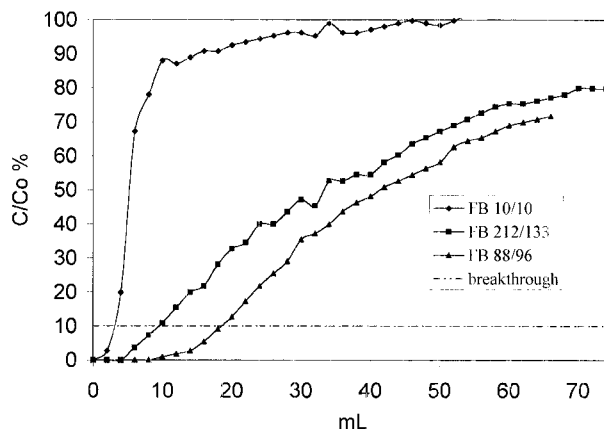


Figure 9 Breakthrough curves from filtration of BN solutions using different filters carrying β -CD.

pancy of its binding sites within this elution volume.

Regenerability of the Filters

FA(90/109) was saturated with BN before being treated by a water-ethanol mixture (1-1 vol) in dynamic conditions. BN was desorbed from the filter and was detected in this binary eluate. Eighty percent of BN was recovered in the first 10-mL fraction and that 80 mL of the eluent was necessary to recover 98% of the preliminarily fixed BN. These results show that this operation permits one to obtain a concentrated solution of the pollutant, after treatment of 150 mL of the diluted polluted effluent. They also display that the filter can be easily reusable.

Therefore, three successive cycles of sorption-desorption were applied to filters FA(90/109) and FG(210/118). As reported in Table V, only 66 and 57% of BN were recovered after a second and a third cycle of use of FA(90/109), respectively. On the contrary, the same experiment carried out with FG(210/118) showed that the regeneration rate was superior to that observed with FA(90/

Table IV Breakthrough Volumes and Quantity of Fixed BN Sorbed onto β -CD Grafted Supports After Elution of 150 mL

Filter	Breakthrough Volume (mL)	Q_{150} ($\mu\text{mol/g}$)
FB(10/10)	3.2	—
FB(88/96)	18.5	166
FB(212/133)	9.8	110

Table V Sorption–Desorption Cycles of BN onto FA(90/109) and FG(210/118).

Cycle	FA(90/109)			FG(210/118)		
	Q_v	Q_r	% BN Recovered	Q_v	Q_r	% BN Recovered
1st cycle	91	89	99	84	63	75
2nd cycle	99	65	66	83	88	120
3rd cycle	128	72	57	103	96	93

Q_v : BN sorbed in the sorption step; Q_r : BN recovered in the desorption step ($\mu\text{mol/g}$).

109). Amazingly, some BN that was recovered in the first desorption step was probably released in the second one (120% of recovered BN). Despite this accumulation of the substrate onto the filters, the quantity of BN sorbed onto the filter tends to increase at every cycle of use for both filters (Table V). We suppose that the desorption step that involves the use of ethanol contributes to the swelling of the poly(GMA) network and thus facilitates the migration of the substrates to the CD sites.

These experiments confirmed that different mechanisms of sorption occurred: A first fraction of the substrate was trapped by the CD cavities and formed inclusion complexes that were reversible upon elution with a nonpolar solvent. Besides, hydrogen bonding between the solute and CDs and hydrophobic guest–guest interactions may occur.

CONCLUSIONS

The results have confirmed that the grafting of CDs onto the supports gave them their specific sorption properties. Besides, it was observed that the best performances were attained when the GMA add-on was in the range of 76–113 % wt and the CD content was 87–118 $\mu\text{mol/g}$. This range of functionalization was the best compromise for which the major ratio of the CD sites were easily accessible to the substrates.

The expected specificity of α -, β - and γ -CD toward the different substrates was not observed. This was due to the chemical modification undertaken by the CD units upon the graft reaction, on the one hand, and to its incorporation into a dense

poly(GMA) polymeric network, on the other hand. This latter problem should be prevented by an optimization of the grafting reaction that could adjust the swelling conditions. Besides the specific interactions of the trapped substrates with CDST nonspecific sorption phenomena were also evidenced.

Furthermore, the slow kinetics of exchange between the liquid and solid phases was a limiting factor that should prevent the use of the filters at elevated flow rates. At last, the great advantage of these filters is that they could undergo several cycles of use, thanks to intermediate regeneration steps with small volumes of a water–organic solvent mixture.

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