



Synthesis and Characterization of Silica Gels Functionalized with Monochlorotriazinyl β -Cyclodextrin and their Sorption Capacities towards Organic Compounds

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Abstract. Different supports, containing a new derivative of β -cyclodextrin – monochlorotriazinyl β -cyclodextrin (β -CDMCT) – used for the reduction of pollutants in waste water, have been prepared. They are based on silica gel, initially either coated with polyethyleneimine (PEI) or grafted with 3-aminopropyltrimethoxysilane, functionalized in a second step with β -CDMCT. In order to obtain sorbents with high β -cyclodextrin content and maximum accessibility of the β -CD cavity, the functionalization was studied while varying experimental conditions. Thermogravimetry, Raman spectroscopy, specific surface area and pore size distribution were used for the characterization of supports. Sorption experiments show that these sorbents have sorption capacities towards some organic pollutants. The mechanism of sorption is both physical adsorption in the polymer network (for supports obtained by coating) and/or the formation of an inclusion complex between β -CDMCT and guest molecules.

Key words: monochlorotriazinyl β -cyclodextrin, silica gel, Raman spectroscopy, porosity analysis, sorption capacities

1. Introduction

Cyclodextrins are cyclic oligosaccharides converted from starch. They are well known for their ability to form inclusion complexes in solution or in the solid state with many different compounds, especially aromatic, through host–guest interactions. The inclusion process of cyclodextrins has received much attention in various fields [1, 2]. In our case, we have already been interested in applying the inclusion process to remove some polluting substances like pesticides or textile dyes from water [3, 4].

The immobilization of derivatives of cyclodextrin by chemical bonding [5–8] or coating [9, 10] onto inert support materials, such as silica gel, has been widely

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studied. To date, the main utilization of these composite supports are as chiral stationary phases for liquid chromatography.

In the present study, the immobilization of β -cyclodextrin, containing the s-triazine moiety, onto silica gel is studied. Two different ways of functionalization were chosen. In *the first*, called the coating method, silica was first modified by the adsorption of polyethyleneimine (PEI) using the known coating method [11], and the intermediate support was then coupled with the β -cyclodextrin derivative. In *the second one*, called the grafting method, the derivative of β -cyclodextrin was chemically bonded onto the silica gel initially functionalized with an amino silane coupling agent. The capacity of some of these compounds in adsorbing aromatic compounds and water-soluble dyes in water solution was tested using the batch method. The sorption capacity of these new adsorbents is evaluated and discussed in relation to their chemical and physical structures.

2. Experimental

2.1. MATERIALS

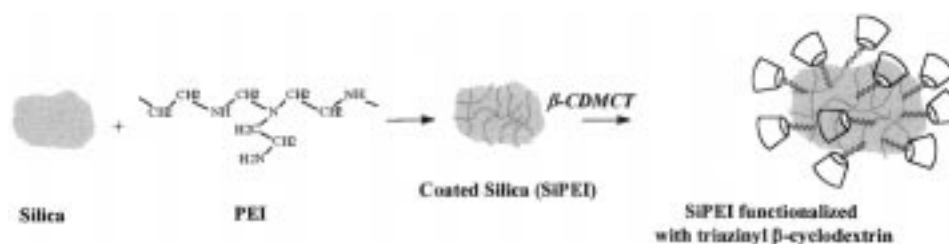
The β -cyclodextrin derivative was a gift from Wacker Chemie GMBH. Its chemical name is monochlorotriazinyl β -cyclodextrin (called β -CDMCT).

The silica gel, called Davisil, was obtained from Aldrich. Its characteristics are summarized below:

Characteristics	Supplier data	Our data		
Particle size / μm	30–75			
Specific surface area / m^2/g	300	269 m^2/g [BET] [12]		
Pore volume / cm^3/g	1.15	1.07 cm^3/g [BJH] [13]		
Average pore diameter / \AA	150	116		
Silanols /groups per nm^2			<i>Raw silica</i>	<i>Washed silica</i>
[14]		pH = 7	0.5	0.9
		pH = 9	2.9	3.3

Polyethylenimine (PEI) is a commercial branched polymer (Aldrich), in aqueous solution (50% in weight). Its average molecular weight (Mw) is 750,000 g/mol. This polymer contains primary, secondary, and tertiary amino groups in a ratio of approximately 25, 50 and 25% respectively.

3-Aminopropyltrimethoxysilane (γ APS) and pollutants were purchased from Aldrich and used without further purification.



Scheme 2. The reaction scheme for the preparation of coating supports.

purified by soxhlet extraction with water to remove any unreacted cyclodextrin and dried in vacuum at 60 °C for 24 hours.

2.2.2. Coating procedure

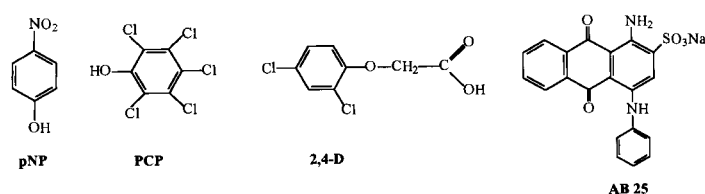
The two steps of this procedure are illustrated in Scheme 2.

PEI adsorption on silica. Branched polymer PEI was adsorbed onto silica by a procedure already described [15]. The concentration of the coating solution was 5% in weight of the polymer in methanol.

β -CDMCT coupling step. One gram of SiPEI at 50°C was added to a solution of 3 g of β -CDMCT in 50 mL of water. A saturated solution of NaHCO_3 was added dropwise under agitation to keep the pH of this suspension at about 8. After 24 hours, the modified silica was filtered, washed thoroughly with water and methanol, and then dried under vacuum at 60 °C for 24 hours.

2.2.3. Sorption tests.

The sorption capacity of the supports was investigated using *p*-nitrophenol (*p*-NP), pentachlorophenol (PCP), (2,4 dichlorophenoxy) acetic acid (2,4 D) and acid blue 25 (AB 25).



The β -CD/silica gel sorbent (20 mg) was suspended in 10 mL of an aqueous solution of selected pollutant and stirred with a vortex mixer for 4 hours at room temperature. After 30 min of decanting, the quantification of residual pollutant was measured by UV spectroscopy at 317 nm for *p*-nitrophenol, 319 nm for penta-

chlorophenol, 283 nm for (2,4 dichlorophenoxy) acetic acid and 602 nm for acid blue 25.

2.3. ANALYSIS

Porosity measurements for the characterization of modified silica gel were obtained with a Sorptomatic 1990 apparatus from Thermoquest (France). The specific surface area (S_p) was determined using the BET method [12]. The pore volume (V_p) and distribution of pores were obtained using BJH isotherms [13]. An UV-visible spectrophotometer (Varian Cary 50 Scan) was used to calculate the sorption capacities.

Local molecular analysis was carried out using a multichannel Raman spectrometer (Dilor XY) equipped with a C.C.D. (charge coupled device) detector. The spatial resolution was about 1 μm . Data was typically obtained with a laser excitation wavelength of 514.53 nm.

Elemental analyses were performed in CNRS Vernaison Service.

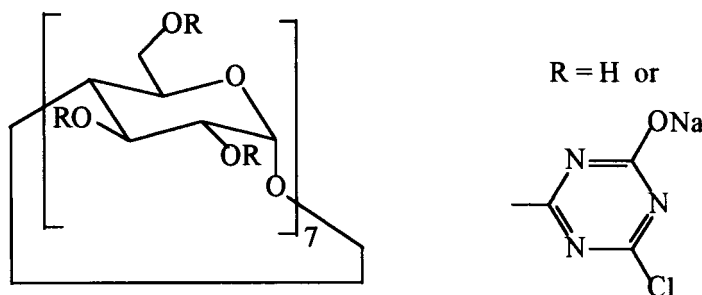
Thermogravimetric analysis, obtained on a Shimadzu TGA-51 analyzer, was used to quantify the yield of functionalization of silica gel. The samples were heated under an air atmosphere from ambient temperature up to 800 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. After water correction, the amounts were calculated from the difference between the weight loss of the modified silica and the initial one. This is a quick and reproducible method.

Acid base titration of 50mg γ -APS-silica sample was done with a Tacussel mini 80 pHmeter (from Bioblock Scientific) at ambient temperature. pH was measured every 24 hours after a known addition of HCl.

3. Results and Discussion

3.1. CHEMICAL ANALYSIS OF β -CDMCT

The structure of β -CDMCT is drawn below:



The nitrogen and the chlorine percentages, revealed by elemental analyses of β -CDMCT, are respectively 7.5 and 6.3. Thus, the estimated value of the average

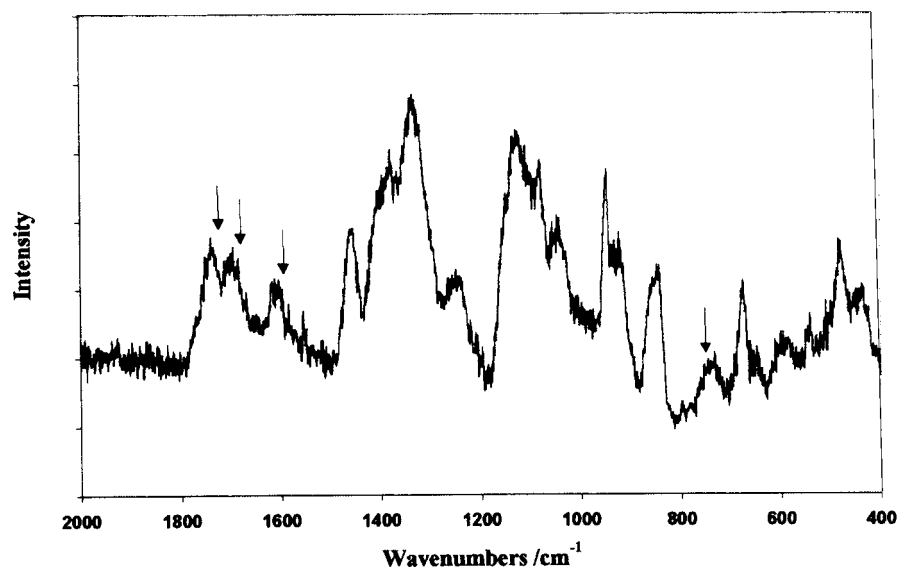


Figure 1. The Raman spectrum of β -CDMCT.

Table I. Assignments of bands for the Raman spectrum of β -CDMCT

$\Delta\nu / \text{cm}^{-1}$	Intensity	Assignment
1740, 1700	medium	$\nu_{\text{C}=\text{N}}$ (triazine ring)
1614	weak	Triazine ring stretching
1460	medium	δ_{OH}
1400–1350	strong	$\delta_{\text{C}-\text{H}}$ (in CH_2OH , CHOH , CHOR)
1150–1050	strong	$\nu_{\text{C}-\text{OH}}$, $\nu_{\text{C}-\text{O}-\text{C}}$
950	strong	Skeleton vibration [16]
853	medium	$\delta_{\text{C}1-\text{H}}$ (anomeric carbon) [16]
740	weak	$\nu_{\text{C}-\text{Cl}}$
679	weak	Not assigned
< 600	weak	Skeleton vibration

number of s-triazine rings attached to each molecule of β -cyclodextrin is 2.74. The average molecular weight of this derivative is 1560 g/mol.

The Raman spectrum of the β -CDMCT is reported in Figure 1 and the band assignments in Table I confirm the presence of the triazine group on the β -CD.

Table II. Series of supports "SiPEI coupled with β -CDMCT" (SiPEI: 1 g, time: 24 hours (a) 110 mg PEI/g, 2 mmol primary and secondary amino groups/g

Sample	Molar ratio (N)	β -CDMCT $\mu\text{mol/g}$	Sp m^2/g	Vp cm^3/g
	β -CDMCT to amino groups of PEI			
E2C	0.25	100	187	0.6
E2G	0.5	152	172	0.42
E2H	1	178	204	0.49
E2I	2	169	169	0.42
E2J	4	183	/	/
SiPEI ^a	/	0	207	0.84

^a110 mg PEI/g, 2 mmol primary and secondary amino groups/g.

Table III. γ APS grafted silica supports

Sample	Reaction time (hours)	γ APS content ($\mu\text{mol/g}$)			Sp m^2/g	Vp cm^3/g
		T.G.A.	Elemental analysis	Acid base titration		
G2A1	20	1147	1178	960	221	0.85
G2B1	8	1081	946	876	222	0.81
G2D1	2	1025	903	805	245	0.86

3.2. COATING PROCEDURE

The chemical and physical characteristics of the initial PEI coated silica gel are listed in Table II.

More details about the adsorption of PEI onto silica gel are given in a previous study, using a Raman microprobe [15].

For the β -CDMCT coupling step, two synthesis parameters have been studied: reaction time and cyclodextrin monomer quantities. The reaction time varied from 6 hours to 60 hours, does not improve the coupling of β -CDMCT onto coated silica.

By varying the relative amount of β -CDMCT/amino groups, we obtained supports with different β -CDMCT content. Results are reported in Table III.

The β -CDMCT content increases with the molar ratio N and reaches a limiting value at about 180 $\mu\text{mol/g}$ for N=3. If we assume that one mole of β -CDMCT condenses with three moles of amino groups (because there are on average three monochlorotriazin rings for each β -cyclodextrin molecule), only 25% of amino groups reacted with β -CDMCT monomer. Several reasons can be considered: the steric hindrance of β -CDMCT, the lower accessibility and reactivity of the second-

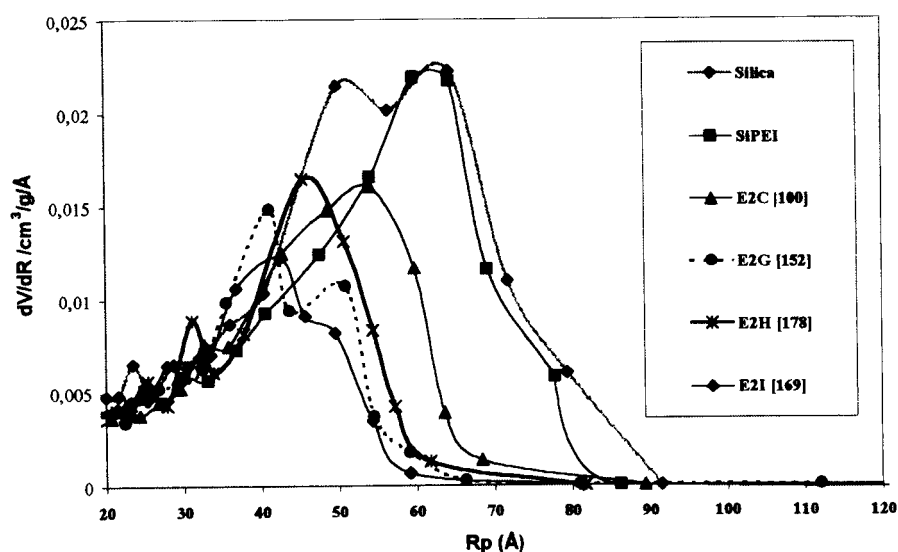


Figure 2. Pore size distribution of supports "SiPEI coupled with β -CDMCT."

ary amino groups of PEI, and some of the amino groups are engaged in the coating process onto silica.

Figure 2 shows that the coating process (sample SiPEI) fills up the smallest pores (50 Å), while in the second step, coupling β -CDMCT with coated silica, the pores with pore radius around 62 Å have completely disappeared. For that reason, the pore volume has markedly decreased compared to native silica, as reported in Table III. Globally, V_p decreases as the amount of fixed β -CDMCT increases. The disappearance of the large pores could lead to new populations of very small pores (radius < 40 Å), which contribute in an extensive manner to S_p . This is why S_p varies differently according to the support.

The presence of β -CDMCT on the silica surface was also characterized by Raman spectrometry (Figure 3). The characteristic bands in the range 1400–1200 cm^{-1} ($\nu_{\text{C-C}}$, $\delta_{\text{O-H}}$, $\delta_{\text{C-OH}}$) and 950–800 cm^{-1} ($\nu_{\text{C-O-C}}$, $\delta_{\text{C1-H}}$) for the β -CDMCT are observed in the spectrum of support E2G. The disappearance of the $\nu_{\text{C-Cl}}$ band at 740 cm^{-1} indicates the condensation between chlorine groups of the β -CDMCT derivative and the amino groups of coated silica. Also, the band at 3296 cm^{-1} , characteristic of the NH_2 stretching vibration, decreases and is replaced by a broad OH stretching band of β -CDMCT.

3.3. GRAFTING PROCEDURE

There has been considerable study of the modification of silica gel with aminosilane in the literature [17–21]. The process occurring during the modification is a really complex phenomenon, since various kinds of bonds like hydrogen bonds,

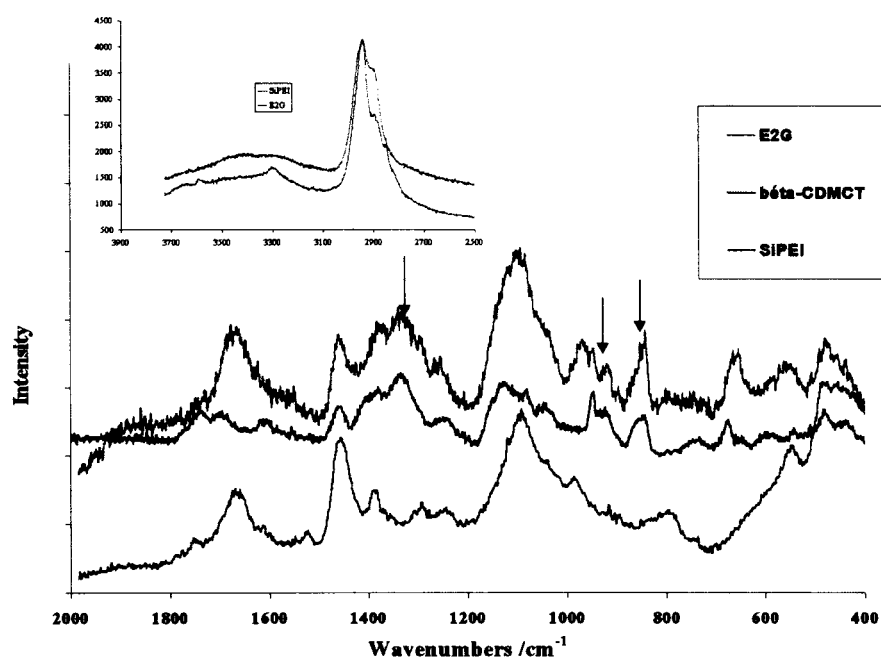


Figure 3. Superposition of Raman spectra of E2G ($152 \mu\text{mol } \beta\text{-CDMCT/g}$), $\beta\text{-CDMCT}$ and SiPEI \rightarrow Characteristic bands of $\beta\text{-CDMCT}$.

acid base bonds and siloxane bonds can be formed between aminosilane molecules and the silica surface [18, 22].

The γ APS content in our aminized silica gel supports was determined from the nitrogen percentage obtained by elemental analyses, the weight loss by thermogravimetry, and the acid base titration of amino groups. These results are summarized in Table III.

Reaction time has little influence on the concentration of γ APS at the silica surface. The longer the time, the greater the γ APS content; but the variation is not important. Among three chosen methods to determine the γ APS content, the acid base titration gives a lower content than the two other methods. Indeed, by acid base titration, we measured only the accessible NH_2 groups and then the real quantity of NH_2 that could react with $\beta\text{-CDMCT}$ during the second step.

As expected, after modification, the porous volume and specific area of supports decrease (Table IV) 20% compared to native silica. Analyzing the pore size distribution graph (Figure 5), indicates the same bimodal distribution in modified silica as in the initial silica except for G2D1.

There have been many studies on the infrared spectra of aminosilane [19, 21] onto silica gel but no Raman study. The Raman spectra of γ APS and γ APS-silica are given in Figure 5. Table IV gathers tentative assignments of bands found in the Raman spectrum of γ APS and the grafted silica support. The γ APS-silica spectrum shows some modification due mainly to hydrolysis of methoxy groups.

Table IV. Assignments of bands in the Raman spectrum of γ APS and grafted silica support

$\Delta\nu / \text{cm}^{-1}$	Assignment of γ APS		Modified bands of γ APS in grafted silica support
3376	$\nu_{\text{N-H}}^{\text{a}}$ [NH ₂]	w	Slightly shifted
3316	$\nu_{\text{N-H}}^{\text{s}}$	w	
2987	$\nu_{\text{C-H}}^{\text{a}}$ [CH ₂]	s	Modification of the relative intensity of the bands: Sharp bands disappeared
2837	$\nu_{\text{C-H}}^{\text{s}}$	s	
2882	$\nu_{\text{C-H}}^{\text{a}}$ [CH ₃]	m	Specific band of δ_{NH_2} (weak)
2837	$\nu_{\text{C-H}}^{\text{s}}$	s	
1650	absent		
1455		s	Not shifted
		w	
1345	δ_{CH} in CH ₂ and CH ₃	w	Disappeared
		w	
1225		w	
1302	$\nu_{\text{C-N}}$	m	Slightly shifted
1074	$\nu_{\text{Si-O-C}}$	s	Disappeared and replaced by a broad band characteristic of $\nu_{\text{Si-O-Si}}^{\text{a}}$
1025	$\nu_{\text{C-O-Si}}$	m	Disappeared
871	$\nu_{\text{Si-O-C}}, \nu_{\text{Si-CH}_2}$	m	Not shifted
643	Coupling between O-CH ₃ vibration and those of Si(OCH ₃) ₃ [23]		Disappeared

w: weak, m: medium, s: strong.

In the second step, the cyclodextrin derivative is chemically bonded onto aminized silica as drawn in Scheme 1. For a given aminized silica (G2D1 with 1025 $\mu\text{mol } \gamma\text{APS/g}$), the initial amount of β -CDMCT was varied. The results reported in Table V are expressed in relation to the molar ratio, N, between the initial β -CDMCT and the γ APS grafted onto the silica surface.

Increasing the quantity of β -CDMCT in the same volume increases the β -CDMCT grafted onto the silica surface. An optimum is reached with the β -CDMCT content at 109 $\mu\text{mol/g}$ for N=7. For N=10, the β -CDMCT content decreases. When N is too high the solution becomes more viscous and then diffusion parameters limit the β -CDMCT grafting.

The amount of β -CDMCT grafted appears small (the amount of β -CDMCT expected may be at least 342 $\mu\text{mol } \beta\text{-CDMCD/g}$). This result can be explained by the three following factors: the steric hindrance of the cyclodextrin monomer which prevents free access to the reaction sites, the partial hydrolysis of siloxane bonds

Table V. Characteristics of grafted supports (G2D2X series)

Sample	Molar ratio (N) of β -CDMCT to amino groups of APS	β -CDMCT content $\mu\text{mol/g}$	S_p m^2/g	V_p cm^3/g
G2D2A	0.53	48.8	255.3	0.78
G2D2B	1.32	54.4	272.0	0.79
G2D2C	2.12	65.8	270.9	0.76
G2D2D	3.17	75.5	254.5	0.71
G2D2E	5.00	97.2	251.4	0.66
G2D2F	7.00	109.2	259.2	0.67
G2D2G	10.00	94.0	300.0	0.74

existing between silica and silane groups [24] and the desorption of the physisorbed silane species at the silica surface [25].

The texture of porous materials is defined by their specific surface area, porous volume and pore size distribution. The pore characteristics for grafted silica gel supports were carried out and gathered in Figure 4.

The step of β -CDMCT grafting leads to important modifications in the pore distribution. New populations of pores appear especially for 40 Å and 65 Å. The presence of smaller pores leads to an increase of specific area. For example, G2D2C presents a great proportion of 40 Å pores and therefore the highest S_p (Table V). It is impossible to find a correlation between the β -CDMCT content and the pore evolution.

3.4. SORPTION

Some preliminary tests were undertaken to compare the different sorbent capacities. Depending on the support, the molar ratio between cyclodextrin and pollutants was in the range 3.26–0.5.

Figure 6 reports the comparative capacities of two sorbents with the same cyclodextrin content but obtained by the two different synthesis steps, and also the intermediate samples without cyclodextrin. Note that the increase of the pollutant affinities is in the order: AB25 (10^{-4}M) > *p*NP ($1.4 \times 10^{-3}\text{M}$) > 2,4 D ($1.4 \times 10^{-4}\text{M}$) > *p*NP (10^{-4}M) > PCP ($0.56 \times 10^{-4}\text{M}$). PCP shows the lowest affinity, although there was a lack of it compared to cyclodextrin. It could be attributed to the hindrance of the five chlorines on the phenyl ring. In the literature, *p*NP was proved to form easily inclusion complexes with cyclodextrin [26]. For our support, it is the same but given that we are in solid/liquid interaction it is necessary to increase the pollutant concentration (comparison of *p*NP $1 \times 10^{-4}\text{M}$ and $1.4 \times 10^{-3}\text{M}$). 2,4-D is moderately extracted. AB 25 has the best affinity, as already shown in the literature [3].

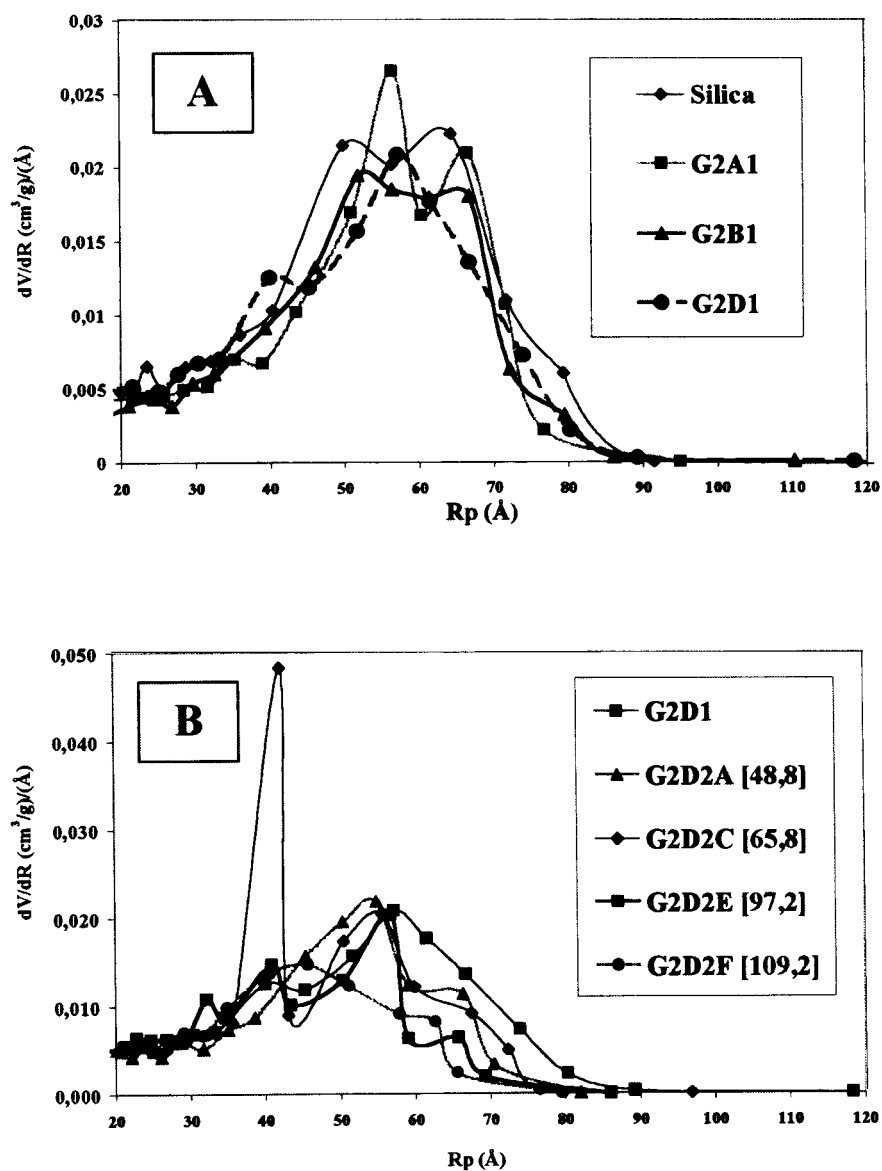


Figure 4. Pore size distributions of γ -APS-silica (a) and β -CDMCT grafted supports (b).

Globally the coated sorbent (E2C) has a better sorption capacity than the grafted one (G2D2E). In fact, in the **coated sorbents**, the macromolecular structure of PEI gives a part of loops and tails which show a good swelling in solution. In addition, the intermediate product SiPEI shows, especially for AB25 and also for *p*NP, a good affinity. This can be explained by chemical interaction between the amino group of PEI and the polar groups of AB 25 or *p*NP. For *p*NP, the

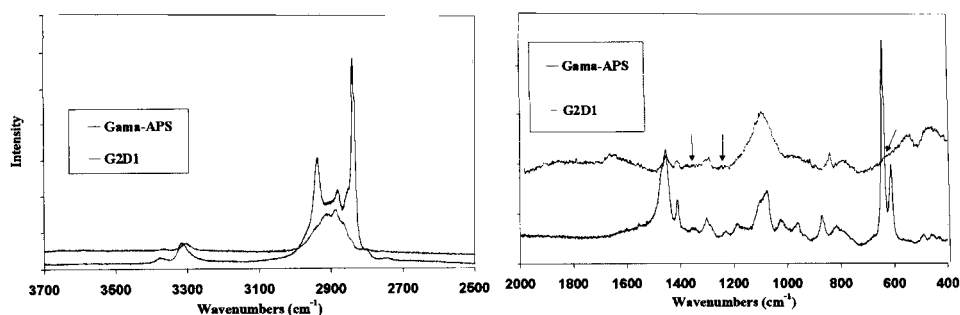


Figure 5. Superposition of γ APS and γ APS-silica (ex:G2D1) spectra.

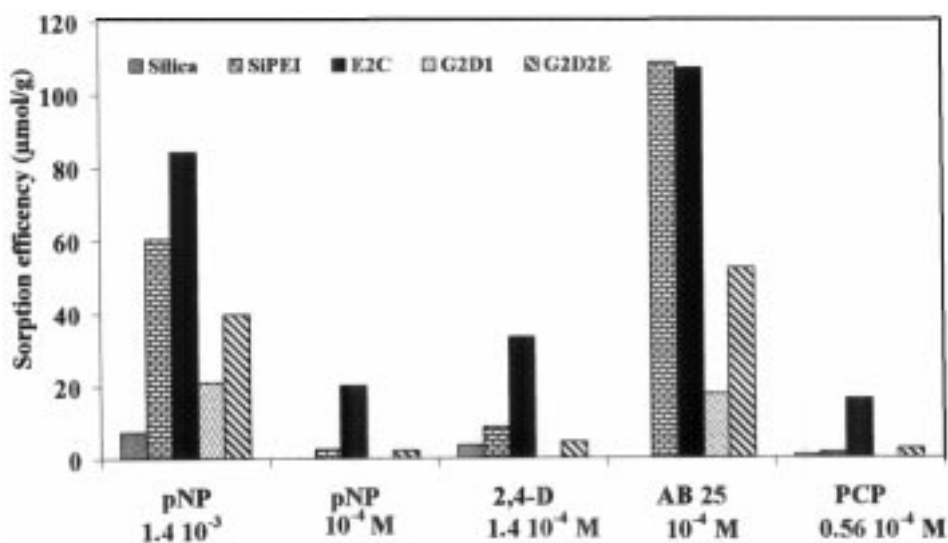


Figure 6. Sorption efficacy of several pollutants by the coated and grafted sorbents having both 100 $\mu\text{mol CD/g}$.

presence of cyclodextrin improves the capacity, and we have probably inclusion in the cyclodextrin cavity. In the case of AB 25, the presence of cyclodextrin does not increase the capacity. Polar interactions are probably preponderant. For **grafted sorbents**, the spacer (aminosilane) is short, the cyclodextrin is fixed closer to the silica surface and thus less accessible. In this case, the grafting of β -CDMCT increases the sorption capacity compared to the intermediate aminosilane silica.

The study of the influence of the β -CDMCT content on the sorption capacity towards pNP at a concentration of 10^{-4} M and PCP at a concentration of 0.56×10^{-4} M for the two series of sorbents is reported in Figure 7. These results show that the sorption capacity of the coated sorbents is about five times better than those of the grafted sorbents. But the main conclusion is that it is unnecessary to have a high cyclodextrin content to improve the sorption. On the contrary it is a drawback. A part of the cyclodextrin molecules are buried in the network or hamper

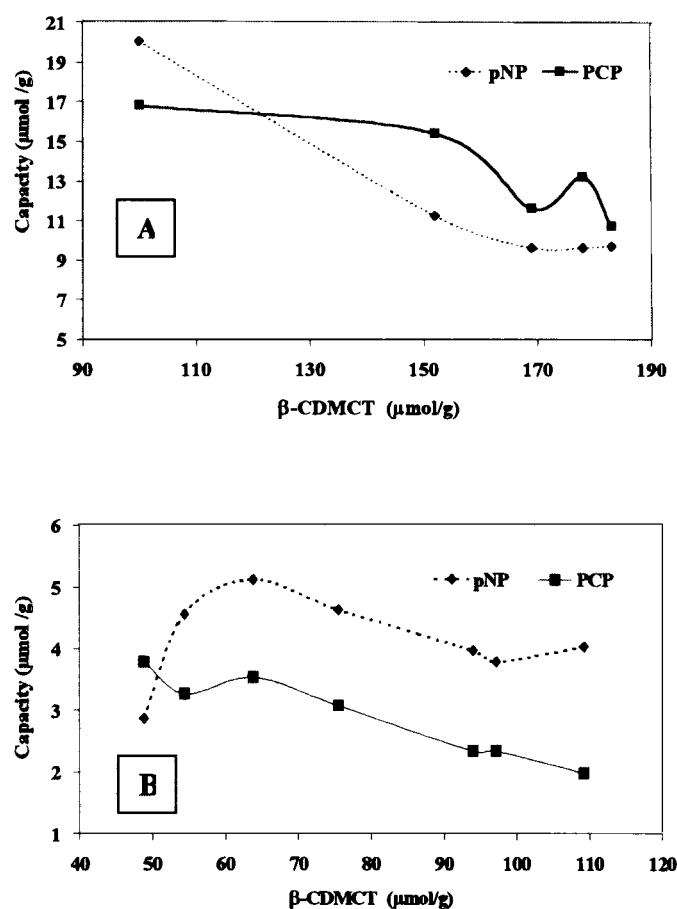


Figure 7. Influence of the β -CDMCT content on the sorption capacity of *p*NP (10^{-4} M at pH5) and PCP (0.56×10^{-4} M at pH 7). (A) Coated sorbents, (B) Grafted sorbents.

each other when they are in high quantity. The optimum contents of β -CDMCT are respectively 66 and 100 $\mu\text{mol/g}$ for grafted and coated sorbents.

4. Conclusion

Several sorbents containing different amounts of β -CDMCT were prepared using the coating and the grafting methods. These two methods led to supports having similar physical parameters (surface area, pore size distribution). However, the coating method produced sorbents with greater amounts of immobilized β -CD. These sorbents were used for the recovery of organic pollutants (phenolic derivatives, herbicide and dye). The results of the present investigation showed that the sorption mechanism combines both the inclusion complex formation resulting from the presence of β -CDMCT, and physico-chemical interactions. It depends

on the chemical structure of the pollutant, the type of sorbent (presence or not of a polymer network), but the inclusion complex plays a more dominant role in this mechanism. For the two types of sorbents, the optimal concentration of cyclodextrin in relation to sorption capacities were found. For equal β -CD content, the “coated” supports are better than “grafted supports”. Nevertheless the latter could be more suitable for successive sorption-desorption tests because of the stable chemical bond between silica and the β -CD derivative.

Acknowledgements

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