ELSEVIER

Dyes and Pigments 53 (2002) 79–92

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

The sorption of several types of dye on crosslinked polysaccharides derivatives

F. Delval[a], G. Crini[b,*], N. Morin[c], J. Vebrel[a], S. Bertini[d], G. Torri[d]

[a]*Laboratoire de Chimie des Matériaux et Interfaces, Faculté Sciences et Techniques, 16 route de Gray, 25030 Besançon Cedex, France*
[b]*Centre de Spectrométrie, Université de Franche-Comté, 16 route de Gray, 25030 Besançon Cedex, France*
[c]*Laboratoire d'Ecophysiologie, Faculté Sciences et Techniques, Place Leclerc, 25000 Besançon, France*
[d]*Istituto Scientifico di Chimica e Biochimica, G. Ronzoni, 81 Via G. Colombo, 20133 Milan, Italy*

Received 23 November 2001; received in revised form 12 December 2001; accepted 7 January 2002

Abstract

Crosslinked polysaccharides containing tertiary amine groups have been used for the recovery of various textile dyes from aqueous solutions. These polymers were prepared by reticulation of starch-enriched flour using epichlorohydrin as a cross linking agent in the presence of NH_4OH. The reaction was optimized and the products analyzed by IR and NMR techniques. Several sorption studies are presented, focusing on the nature of the polymer, the structure of dyes, and the concentration. The results show that these polymers exhibit high sorption capacities: the kinetics of sorption are dependent on the presence of amino groups and the variation in the amount of the sorption also depends on the nature of the dye. Physical adsorption in the polymer network and chemical interaction of the solute dyes via ion exchange and hydrogen bonding are both involved in the sorption process. The sorption mechanism is also due to the presence of dye–dye interactions. Experiments with mixtures of textile dyes show that the sorption of a given solute may be increased by the presence of another one. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Dyes; Starch derivatives; Sorbents; Adsorption; Waste water treatment; Removal of dyes

1. Introduction

Environmental aspects of aromatic compounds have become increasingly important in recent years because the laws impose more and more drastic limits on the organic content of industrial effluents and waste water. Aromatic compounds are important pollutants of water and they may be found in trace quantities in these effluents. These substances which are often encountered in the environment as a result of their numerous industrial applications create serious water quality problems because many are known to be toxic or carcinogenic even at low concentration. These compounds are generated in the production of plastics, drugs, pesticides and in the petrochemical industry. So, a wide range of organic pollutants are found, including for example benzene derivatives, phenolic solutes (PCP, PCB), polycyclic aromatic hydrocarbons (PAH), polycyclic aromatic compounds (PAC), pesticides, herbicides and dyes [1–8]. A number of these toxic solutes are listed in the European Community Directive 76/464/EEC and

---

* Corresponding author. Tel.: +33-3-81-66-65-64; fax: +33-3-81-66-61-72.
E-mail address: gregorio.crini@univ-fcomte.fr (G. Crini).

PII: S0143-7208(02)00004-9

in the US Environmental Protection Agency list of priority pollutants [6,8].

The increasing number of recent publications on adsorption of toxic compounds shows that there is an increasing interest in the synthesis of adsorbent resins able to totally eliminate organic pollutants. Various chemical and physical processes are currently use. However, it is well known that solid phase extraction (SPE) using sorbents is one of the most efficient and popular methods for the removal of organic compounds from waste water [9,10]. The sorbents may be of mineral or organic origin. Silica beads, activated carbon, zeolites, polyamines beads, cyclodextrins gels, and polyurethanes resins are significant examples. In our group, a series of experiments is being conducted to evaluate the possibility of the use of chemically modified polysaccharides as sorbents in waste water treatment [11–15]. In particular, one of the potential applications is to valorize an industrial agroalimentary by-product. In two recent publications [11,12], we tried to chemically modify a starch-enriched flour by reticulation using epichlorohydrin as cross-linking agent. The results show that these polymers exhibit interesting sorption capacities toward substituted benzene derivatives.

In order to extend the sorption properties of these sorbents, we attempted the synthesis of a weakly basic ion exchanger by crosslinking a starch-enriched flour with epichlorohydrin in the presence of NH_4OH, according to the procedure introduced by Simkovic et al. [16,17]. Several polymers containing tertiary amine groups have been prepared and used for the recovery of various dyes from aqueous solutions. These polymers have been characterized using IR and NMR techniques. We also describe the adsorption properties using the batch method and the use of recycling columns. The results, in terms of sorption capacity, are presented and discussed.

2. Experimental procedures

2.1. Materials

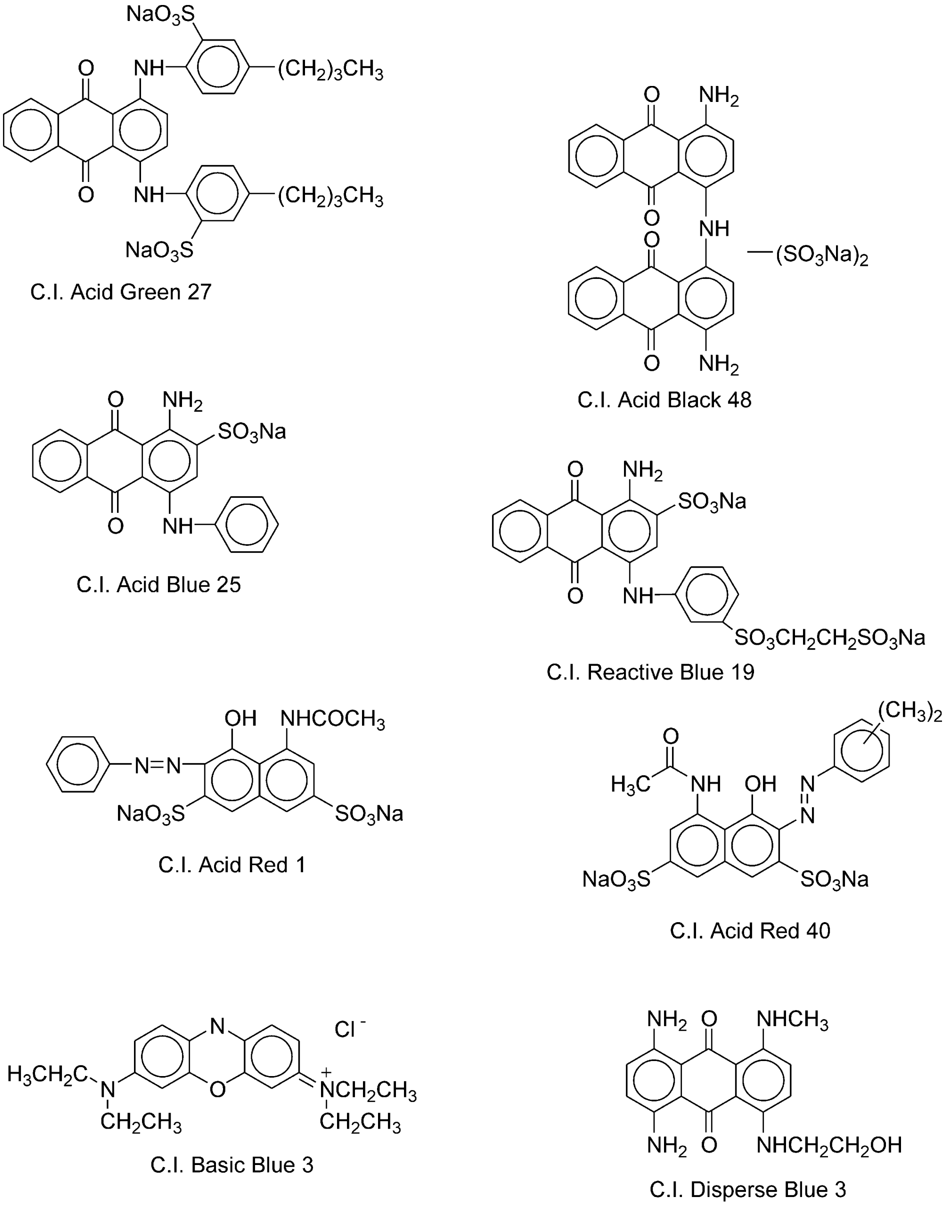
Starch-enriched flour was a gift from PONT S.A (Vincelles, France) and was used as received. Other compounds were the highest quality available and were purchased from various suppliers. The dyes solutes were commercial products and used without purification (see Fig. 1 for the structural formulae).

2.2. Synthesis

The crosslinked polymers have been prepared in one step by reticulation of starch-enriched flour using only epichlorohydrin. The synthetic procedure has already been described in detail [12]. For the synthesis of crosslinked polysaccharides containing tertiary amine groups, the procedure introduced by Simkovic et al. was used with some minor modifications consisting of an increase in the amount of epichlorohydrin in order to obtain mechanically stable polymers. A typical reticulation reaction was carried as follows (polymer 6 in Table 1): in a thermostated reactor vessel, NaOH (20 ml, 50% w/w) was heated to 50 °C and after 5 g of starch-enriched flour was suspended. The solution was vigorously stirred with a mechanical stirrer for two hours. The desired amount of epichlorohydrin and NH_4OH were added slowly dropwise. The viscosity of the solution increased so strongly and rapidly that it could not be stirred, and after few minutes a solid polymer was obtained. Acetone was then added and heating was continued for 30 min. After cooling, the polymer was purified as described previously [12] and finally granulated to particle sizes of 1–2 mm in diameter. A series of polymers were prepared with different molar ratios of epichlorohydrin and NH_4OH as described in Table 1.

2.3. Characterization

NMR and FT–IR spectra were recorded on a Bruker AC-300 spectrometer and a Nexus-470 Nicolet spectrophotometer respectively. The procedures have been described in a previous work [12]. Elemental analysis of nitrogen was recorded on a Thermo Finnigan EA 1108 W apparatus using the Dumas and Pregl classical method, in order to quantify the number of tertiary amine groups contained in the polymer (Table 1).



C.I. Acid Green 27

C.I. Acid Black 48

C.I. Acid Blue 25

C.I. Reactive Blue 19

C.I. Acid Red 1

C.I. Acid Red 40

C.I. Basic Blue 3

C.I. Disperse Blue 3

Fig. 1. Structure of dyes.

2.4. Adsorption procedure

Adsorption isotherms, sorption capacities and kinetics of the polysaccharides were determined by the following two techniques. The first is the batch method. The polymer (20 mg) was mixed with 4 ml of a NaCl 0.1 mol l^{-1} aqueous solution of the dye at a known concentration in a tightly closed flask that was shaken at room temperature. Preliminary kinetic experiments [11,12] had shown that one hour contact time was sufficient for an equilibrium to be reached. The residual concentration of the dye solute was determined by spectrophotometry. The sorption capacity was then calculated and

Table 1
Experimental conditions

Polymer	EPI (cm^3)	NH_4OH (cm^3)	T (°C)	Yield[a]	% N[b]	% N[c]
Polymer 1	10	0	50	73	0	0
Polymer 2	20	0	50	123	0	0
Polymer 3	35	0	50	240	0	0
Polymer 4	50	0	50	257	0	0
Polymer 5	70	0	50	308	0	0
Polymer 6	10	13.5	50	170	8.3	8.3
Polymer 7	20	27	50	380	8.7	8.8
Polymer 8	35	47	50	564	9.1	9.2
Polymer 9	50	67.5	50	710	9.3	9.3
Polymer 10	70	94.5	50	740	9.5	9.4

[a] Calculated on basis of flour, in %.
[b] Nitrogen content from elemental analysis.
[c] Nitrogen content after soxhlet extraction treatment.

expressed in percentage uptake (R in %) which represents the ratio between the amount adsorbed dye and the starting amount dye. The second technique involved the use of open columns. We used the following equipment: a tank containing the dye solution, a peristaltic pump, a column and a fraction collector. The column was filled with 100 mg of polymer. The dye was dissolved in a NaCl 0.1 mol l^{-1} solution at a known concentration and then passed through the column for various times. The sorption capacity was calculated and expressed in percent uptake (R in %) or in 10^{-5} mol adsorbed dye per g of polymer according to the carried out study.

3. Results and discussion

3.1. Characterization

Polysaccharides form insoluble gels on reaction with epichlorohydrin (EPI) under alkaline conditions. In particular, the crosslinking of starch with EPI has been studied in detail [18–21]. There is no doubt that EPI is today the most popular crosslinking agent for the chemical modification of starch. Moreover, reacting EPI with NH_4OH is a convenient and inexpensive way of introducing weakly basic anion-exchange groups into polymer matrices [16]. In order to valorize an industrial agroalimentary by-product, we used the reaction described in the literature. We tried to modify by reticulation a starch-enriched flour using EPI in presence of NH_4OH. Fig. 2 represents a possible structure of the crosslinked starch-polymer. The polymer is a mixture containing glucose units joined by repeating glyceryl linkers and poly (hydroxylamine) groups.

The polymers have been characterised using IR and NMR techniques. In the IR spectra presented in Fig. 3, we observe that:

- The characteristic ring vibrations and the especially anomeric CH deformations are still present in the polymers in the 900–550 cm^{-1} region [22].
- At 1060–1150 cm^{-1} the spectra of the polymers show broad peaks suggesting additionnal CO and CC bonds as present in the glyceryl bridge introduced during the reticulation step.
- The intensity of the coupled COH group vibration and COC stretching mode at 1150 cm^{-1} is lowered with increasing of reticulation. This is not in disagreement with the introduction of one bridge that introduces two CO for one OH bond.
- An increase with reticulation of the peaks at 1025 cm^{-1} due to the tertiary amine groups, and at 1450 cm^{-1} due to the CH_2 groups is observed, according with the bridges introduction.
- At 1720 and 2820 cm^{-1} two bands appear corresponding respectively to CN and CH_2N vibrations. The intensity of these peaks increase with the amount of epichlorohydrin/NH_4OH added to the reaction mixture.

In order to confirm the structure, a characterisation was also carried out using ^{13}C nuclear magnetic resonance (NMR) and cross polarisation magic angle spinning NMR (CPMAS NMR). The NMR spectra of the starch-enriched flour has been described in detail in previous work [11,12]. The solid and liquid ^{13}C NMR spectra of three polymers having different amount of EPI and NH_4OH are represented in Fig. 4a and b, respectively. Firstly, in the ^{13}C NMR spectra (Fig. 4b),

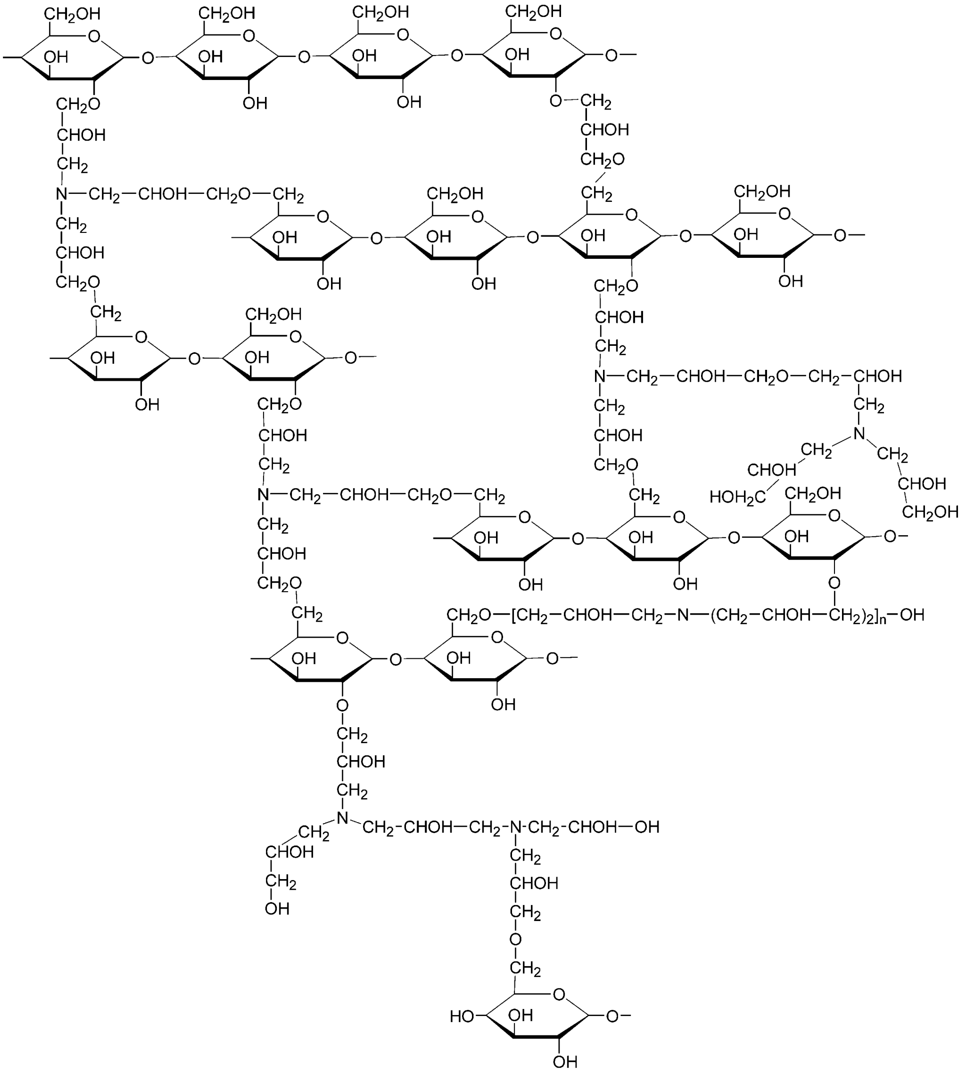


Fig. 2. A possible structure of a crosslinked starch-polymer containing tertiary amine groups.

we observe an important broad band in the range 35–85 ppm attributable to the glucose unit and also to the groups introduced by the two crosslinking agents (EPI and NH_4OH). Moreover, an increase in the amount of crosslinking agent added during the synthesis induces a broadening of this band and also a decrease of the resolution due to the higher rigidity of the polymers. The peak at 104 ppm is attributed to the anomeric carbon C1: this confirms the presence of glucose units in the polymer. Secondly, we observe an intensive signal at 76.6 ppm that was previously ascribed to CH_2 groups linked to nitrogen [16]. Finally, a characterisation was carried out using solid state NMR spectra (Fig. 4a) in order to confirm these hypothesis. The two principal results are the following: we note a decrease of the intensity of anomeric signal with the reticulation due to the increase of the rigidity of the polymer. We observe also an increase of the intensity band at 50–75 ppm probably as a result of more crosslinking in the polymer. This fact was confirmed by the 740%

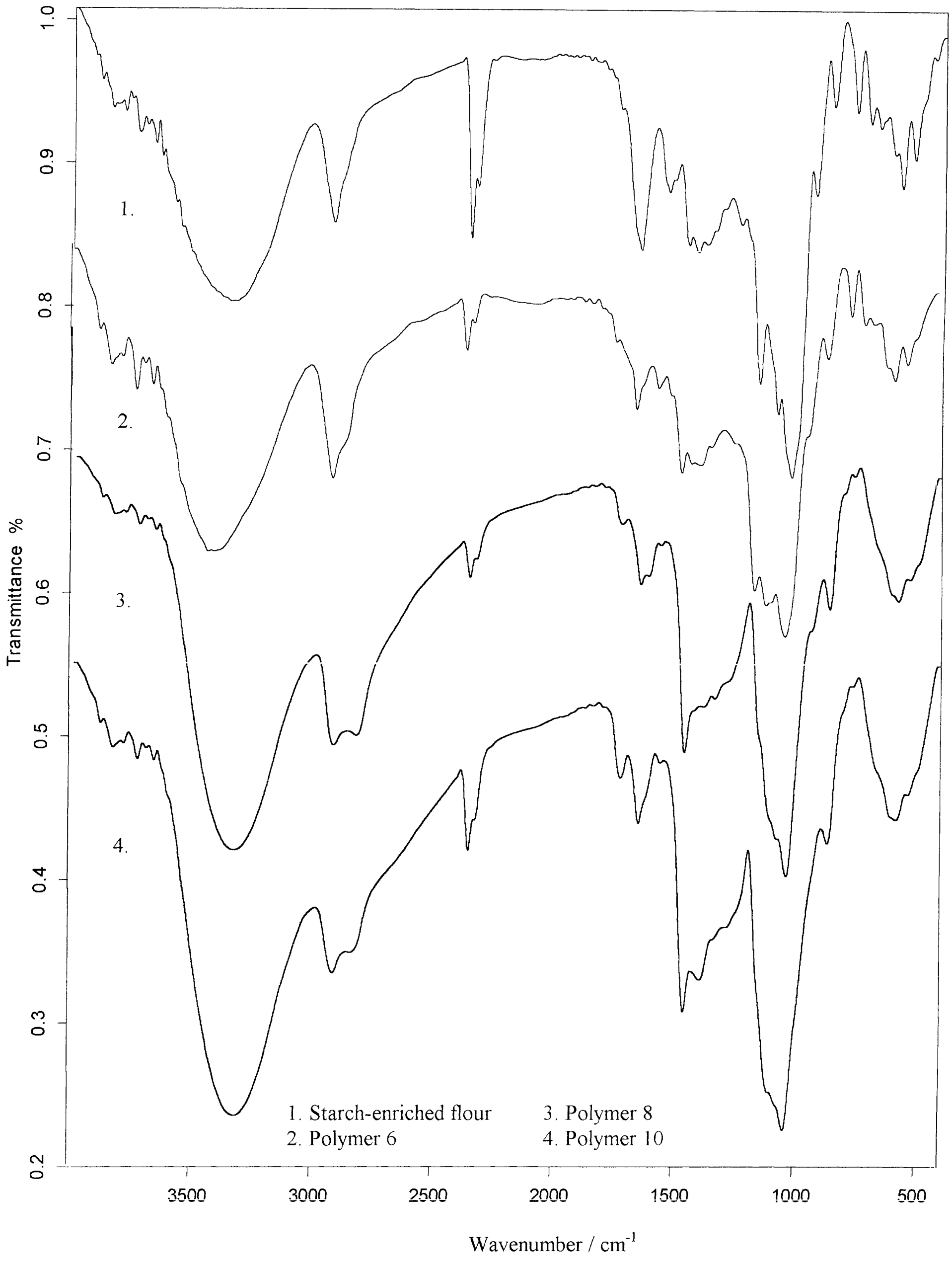


Fig. 3. FT–IR spectra of the starch-enriched flour used and three polymers.

yield (Table 1) and by the nitrogen content of the polymer which is close to that of polyhydroxypropylamine ($N = 10.72\%$) indicating that the polymer contains only a small amount of starch [16]. By comparison with the CPMAS spectra of crosslinking polymer using only EPI as crosslinking agent performed previously [11,12], we observed the presence of additional peaks, probably due to the tertiary amine groups in the range of 50–60 ppm. In particular, the band at 50–75 ppm is more intense than for the polymer without NH_4OH, and totally hides the CH_2OH

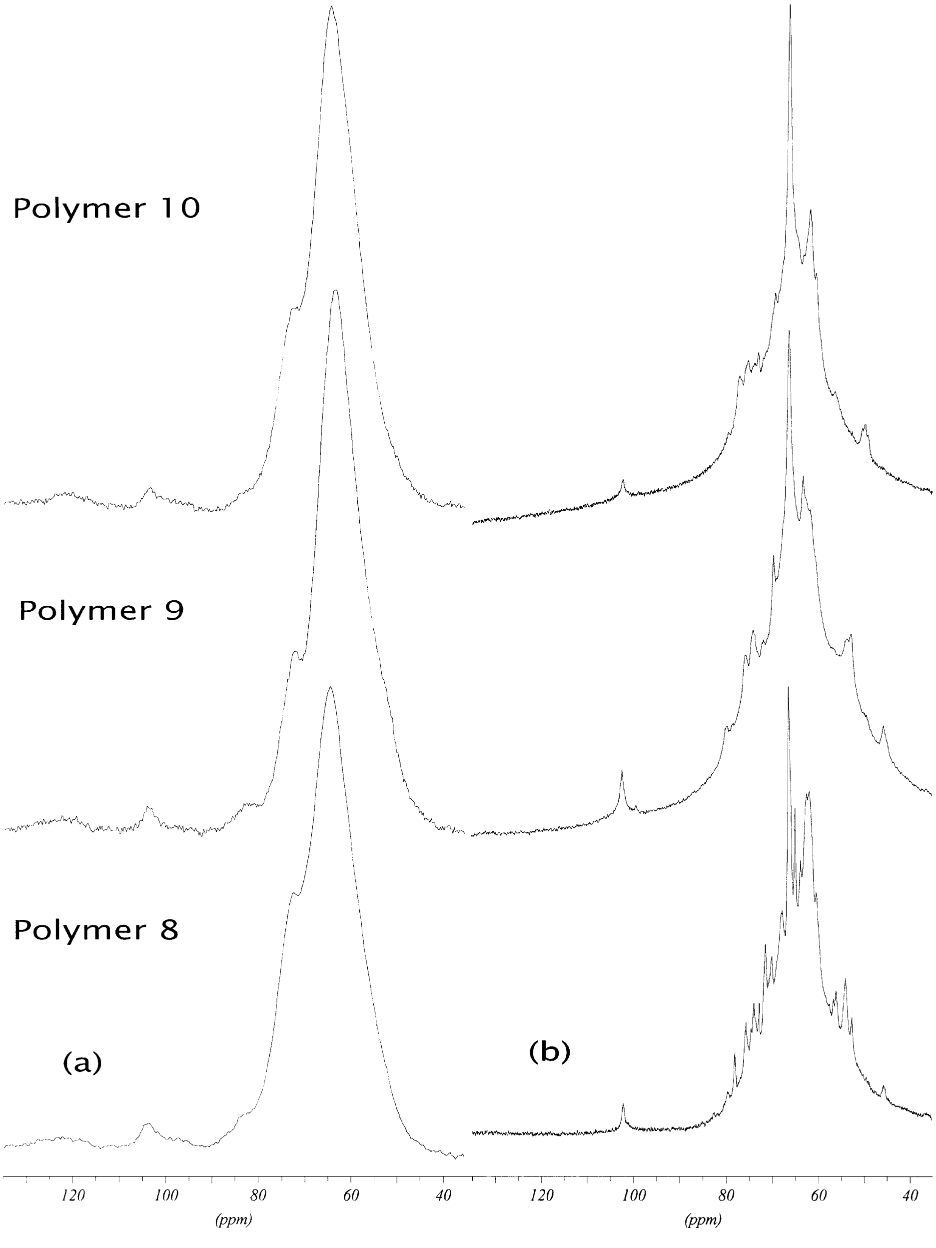


Fig. 4. (a) CPMAS and (b) ^{13}C NMR spectra of three polymers.

signals (65 and 61 ppm) due to the substitution of the glyceryl bridge by the tertiary amine groups.

3.2. Batch experiments

The sorption capacity is investigated using C.I. Acid Black 48 (AB 48), C.I. Acid Green 27 (AG 27), C.I. Acid Blue 25 (AB 25), C.I. Acid Red 1 (AR 1), C.I. Acid Red 40 (AR 40), C.I. Reactive Blue 19 (RB 19), C.I. Disperse Blue 3 (DB 3) and C.I. Basic Blue 3 (BB 3) as model guest solutes (Fig. 1). The following conditions were optimised in a previous work [12]: concentration 3×10^{-5} mol l^{-1}, stirring time 1 h and 20 mg of polymer used for each measure.

Fig. 5 shows the sorption capacity of several dyes on polymers 3 and 8, respectively without and with tertiary amine groups. The two polymers display interesting sorption properties. Polymer 3 without tertiary amine groups exhibit lower sorption capacities: in this case, the sorption is based only on the presence of physical adsorption in the polymer network and hydrogen bonding between the hydroxyalkyl groups of the polymer and the dye. If we compare the values obtained for AR 1, AR 40, AB 25 and AG 27 using polymer 3, we observed an important decrease in the sorption for AR 1 and AR 40 ($R = 10\%$ instead of $R = 70\%$ for AB 25 and AG 27). Thus, AR 1 and AR 40 dyes do not interact with polymer 3: the capacity is very low due to poor physical adsorption interaction and poor hydrogen bonding. We suppose also that the difference in the chemical structure between these four dyes can explain the obtained values. It seems that the presence of N=N groups in AR 40 and AR 1 (Fig. 1) disfavours sorption. More experiments will be carried out using other types of dyes.

For polymer 8 which contains amine groups, the sorption is much greater, due to the presence of other interactions: this point will be discussed in detail later. The order of sorption for the dyes examined is the following: AB 25 > RB 19 > AR 40 > AG 27 > AR 1 > AB 48 > DB3 ($R = 0$ for BB 3). In particular, for AB 25 and RB 19 dyes, we note that polymer 8 displays very high sorption capacity. Practically, all the dye present in the solution is adsorbed (R near to 100%). This result confirms that the presence of tertiary amine groups in the polymer strongly increases the sorption values. This conclusion is particularly demonstrated in the case of AR 1 and AR 40 dyes where we found $R = 10\%$ using polymer 3 and $R = 95\%$ using polymer 8. This clearly indicates that, apart from the interactions of the dye with the polymer network (physical adsorption), the tertiary amine groups play the major role. It seems that functional groups such as sulfonic acid moieties in the dye molecule interact with the amine groups.

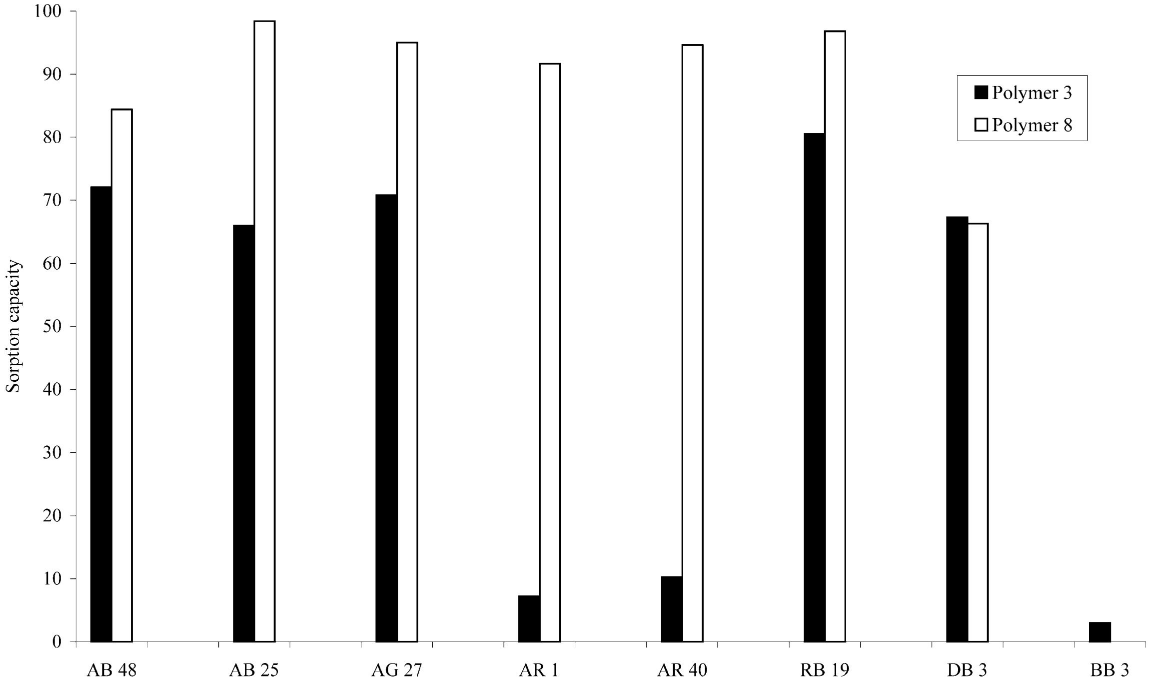


Fig. 5. Comparison between sorption capacity (expressed in percentage uptake) of several dyes on polymers 3 and 8. Polymer 8 contains tertiary amine groups while polymer 3 does not (dye concentration 3×10^{-5} mol l^{-1}).

The results obtained for DB 3 confirm this hypothesis. In fact, a substantial decrease in the sorption using polymer 8 ($R=66\%$) is obtained for this dye by comparison with others ($R=95\%$). However, if we compare the sorption for polymers 8 and 3, the values are similar. In this case, the presence of amine groups is not an important factor. The chemical structure of this dye is totally different from the others (Fig. 1). This demonstrates that the six dyes which have sulfonic acid groups in their structure are able to interact with the amine groups of polymer 8. The chemical structure of the dye influence the results. Using these preliminary results, we can assume that the mechanism of sorption is a combination of physical adsorption in the polymer network, ion exchange and hydrogen bonding due to the tertiary amino groups.

In order to confirm these first conclusions, we also studied the sorption abilities of others polymers. They can be divided in two groups: those having tertiary amine groups (polymers 6, 8 and 10) and those without amine groups (polymers 1, 3 and 5). Table 2 shows the influence of the tertiary amine group content on the sorption capacity using several dyes in water. The concentration is fixed at 3×10^{-5} mol l^{-1} in each case. The results show that all the polymers have high sorption capacity: $R=65$–75% for polymers 1, 3 and 5 and $R=90$–100% for polymers 6, 8 and 10 (except for AR 1, AR 40 and BB 3). When the polymer contains amine groups an important increase of the sorption capacity is thus observed. This confirms that the values are correlated with the amount of amine groups. The increase of the sorption is due to the presence of additional interactions such as ion exchange and hydrogen bonding between the tertiary amine groups of the polymer network and the functional groups present in the dye. Moreover, it is interesting to note that no sorption was observed for BB3 which is basic dye containing cationic functions that are not efficient for the dye–polymer interaction. This is a confirmation of above results.

To evaluate the influence of the tertiary amine groups on the sorption and to clarify the role of the different interactions that take place in the mechanism, different tests were carried out using five polymers containing varying amounts of amine groups (Fig. 6). The four dyes used were AB 25, AG 27, AR 1 and AR 40. As described above, these compound display the best interaction with polymers containing tertiary amine groups. As expected, the overall trend is an increase of the sorption capacity with increasing amounts of amine groups, corresponding to increasing interactions between amine groups and dyes. For AG 27, we note that the sorption increases with the amine group content, then decreases when the nitrogen content is high. This confirms that the crosslinking agent creates a network between the polymer chains which induces a steric effect. As described in the NMR section, we conclude that there is more extensive reticulation in polymers 9 and 10 than in polymers 6, 7 and 8. This could indicate steric restrictions for the sorption at high degree of reticulation. It is not necessary to have high reticulation for obtaining the best results.

For AR 1 and AR 40 dyes, the sorption capacity increases with nitrogen content of the polymers.

Table 2
Comparison between sorption capacity (R in %) of several dyes by six polymers in water (concentration 3×10^{-5} mol l^{-1}) using the batch method

Dye	Polymer 1	Polymer 3	Polymer 5	Polymer 6	Polymer 8	Polymer 10
C.I. Acid Black 48 (AB 48)	66	72.8	77.8	94.2	84.4	92
C.I. Acid Blue 25 (AB 25)	51.6	66	61.1	98.5	98.4	100
C.I. Acid Green 27 (AG 27)	70.5	70.8	72.7	75.9	95	75.2
C.I. Acid Red 1 (AR 1)	2.1	7.2	5	10	91.6	95.1
C.I. Acid Red 40 (AR 40)	2.5	10.3	12	18.8	94.6	97.8
C.I. Reactive Blue 19 (RB 19)	70.5	80.5	84.8	80.5	96.8	95.1
C.I. Disperse Blue 3 (DB 3)	58	67.3	64.2	76.4	66.3	69.2
C.I. Basic Blue 3 (BB 3)	0.3	3	6	2.1	0	0

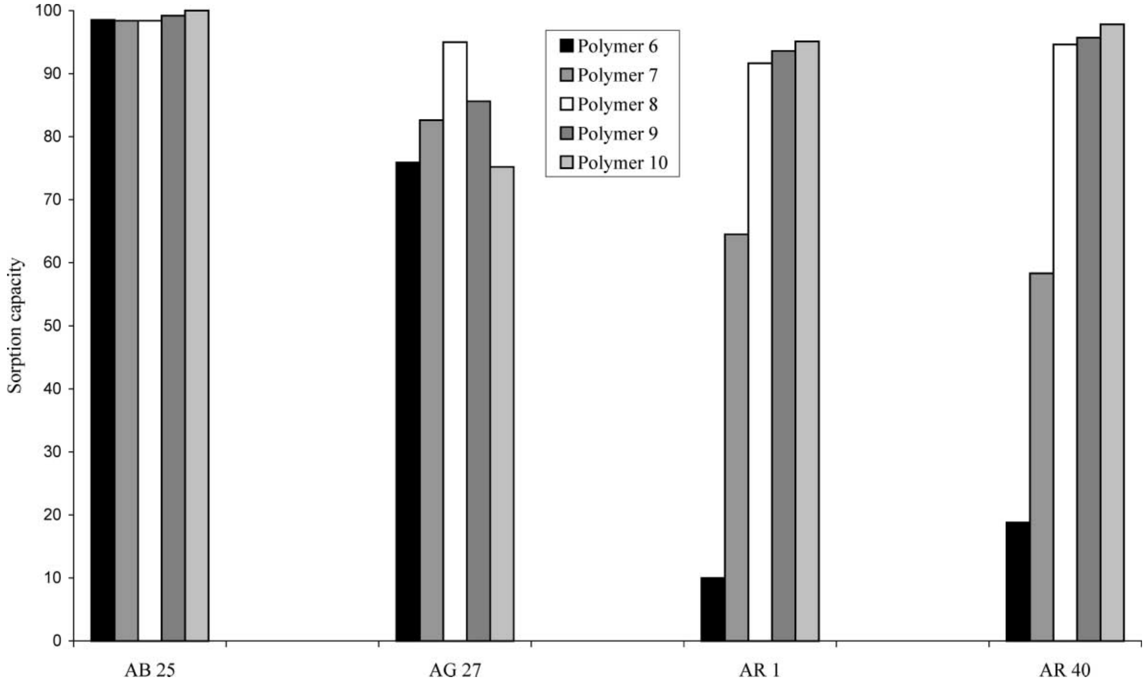


Fig. 6. Influence of the tertiary amine group content on the sorption capacities (expressed in percentage uptake) of several polymers using the batch method (concentration 3×10^{-5} mol l^{-1}).

Here again, this confirms strong interactions (ion exchange and hydrogen bonding) between the tertiary amine groups and the functional groups (in particular sulfonic acid functions) present in the dye. These functions have an important role in the mechanism. This can be also supported by the very high sorption capacity of AB 25 which is a monovalent dye containing only one acid sulfonic group ($R = 100\%$). Moreover, the values are identical for the five polymers. Thus, even for the polymers with a low nitrogen content (polymers 6 and 7) sorption is high. However, for the divalent dyes which contain two sulfonic acid groups (AR 1 and AR 40), the low nitrogen content causes the saturation level to be reach rapidly. There are no amine groups available for the interaction. This also assumes that for these two dyes, the dye–dye interactions are weaker.

3.3. Column setup

In a second experiment, we used open columns. We tried to saturate the polymer using a large amount of dye solution. The aim was to confirm that not only do the tertiary amine groups play a role in the sorption, but so also does the polymer network, and others factors such as dye–dye interactions. The sorption capacity of the polymers was found to be independent of the flow rate used in the range 0.4–1.5 ml min^{-1}. The flow rate used was 0.4 ml min^{-1}. The column was filled with 100 mg of polymer. The sorption capacity is expressed in 10^{-5} mol dye sorbed per gram of polymer. The initial concentration (in mol l^{-1}) of the dye is given in each figure legend.

Table 3 represents the sorption capacity using the opening column system for the polymers 3 and 8 versus the eluted volume. The four dyes used are AB 25, RB 19, AR 1 and DB 3. The order of the sorption capacity is the following: AB 25 > RB 19 > DB 3 > > AR 1 for polymer 3 and AB 25 > RB 19 > > DB 3 > AR 1 for polymer 8. These results are in agreement with those obtained by the batch method. For the polymer 3, the sorption capacity shows a large decrease between the first and the last eluted fraction for AB 25, DB3 and

Table 3
Evaluation of sorption capacity by polymers 3 and 8 using an open column[a]

Dye	Polymer 3			Polymer 8		
	V^b = 50	V^b = 150	V^b = 250	V^b = 50	V^b = 150	V^b = 250
AB 25	99	80	64	100	100	100
AR 1	2.5	1	0.75	73	64	59
DB 3	60	16.5	13.4	73	64.4	57.7
RB 19	66	27	16.7	99.6	99	98

[a] Expressed in percentage uptake.
[b] Volume eluted in cm^3.

RB 19. The sorption capacity for AR 1 is very weak and confirms the batch results. This dye does not interact with the polymer network.

For polymer 8, we note an increase in the sorption values for the first fraction in comparison with those obtained by the batch method. This is another confirmation that the polymer network participates in the adsorption mechanism. Once again, AR 1 constitutes an exception: the result shows an important decrease ($R = 73\%$ compared to 91.6%). This difference can be explained by a fast saturation of the polymer network. Moreover, when the eluted volume became large, the sorption capacity decreased: this is due to the saturation of the polymer. With regard to polymer 3, the observation is less severe. In particular, polymer 8 has very high sorption capacity for AB 25 and RB 19 dyes: all the dye passed through the column being adsorbed (R near to 100%). Initially, the colour of dye solution is blue and it became clear after passing through the column. We suppose the presence of hydrophobic dye–dye interactions which cause an accumulation of the solute at the surface of the polymer. For AR 1 dye we found $R = 2.5\%$ using polymer 3 and $R = 73\%$ using polymer 8: this demonstrates the conclusion of the batch tests that the tertiary amine groups play the major role in the sorption process.

The value of the sorption capacity for AB 25 is 100%, thus we can assume that the polymer network is not saturated. For this reason, the influence of increasing dye concentration on the sorption capacity of polymer 8 was investigated using an open column (Table 4). In addition, the same study was carried out on polymer 3. The results are expressed in 10^{-5} mol g^{-1} in order to have the real difference between the sorption capacity for a fixed eluted time. When the concentration increases the amount of dye adsorbed increases as expected for the two polymers. This confirms the participation of polymer network and also the presence of dye–dye hydrophobic interactions. Polymer 8 has a good ability to complex this dye in comparison with polymer 3. That proves again the importance of the dye–dye interaction and the presence of the tertiary amine groups in the sorption mechanism and even the importance of the polymer network.

To support this conclusion, the influence of the amount crosslinking agent on the sorption capacity is showed in Fig. 7. The principal observation is the presence of a plateau for polymer 6 which has a low crosslinked degree. When we increase the crosslinked degree (Table 1), the sorption capacity is higher except for the most crosslinked polymer 10. This fact can be explained by the three following points: (1) the networks of polymers 6 and 7 are saturated and are not accessible for the last eluted fractions, (2) the increase of the crosslinked degree probably induce a more extensive reticulation and more tertiary amine groups which produce better interactions with the dye, (3) it is not necessary to have a high degree of reticulation for obtaining the best results. A strong reticulation can induce a less accessible network, and thus disadvantage the different interactions.

Fig. 8 is an evaluation of the sorption capacity of a mixture of two dyes having the same concentration (AB 25 and AR 1). AB 25 has a blue color and AR 1 a red one. The mixture has a purple colored. They were been chosen because they absorb in two different UV–visible domains. The sorption capacity of these two dyes in the mixture show a decrease for AB 25, but an increase for AR 1. There is a competition between the two dyes: polymer 8 adsorbs AB 25 but also AR1 at the same time. It seems that the presence of AR 1 disfavors the sorption of AB 25. The interaction between AB 25 and AR 1 is stronger than AR 1 with itself. AR 1 partially prevents the adsorption of AB 25, but the presence of AB 25 in the mixture promotes AR 1 adsorption. This example shows

Table 4
Influence of the concentration on sorption capacity by polymers 3 and 8 using an open column

Elution time[a]	Concentration of AB 25[b]	Amount of AB 25 eluted[c]	Amount of AB 25 adsorbed[c] using polymer 3	Amount of AB 25 adsorbed[c] using polymer 8
625	3×10^{-5}	75	48	75
625	9×10^{-5}	225	94	223
625	5×10^{-4}	1250	155	1142.5

[a] In min.
[b] In mol l^{-1}.
[c] $\times10^{-5}$ mol g^{-1}.

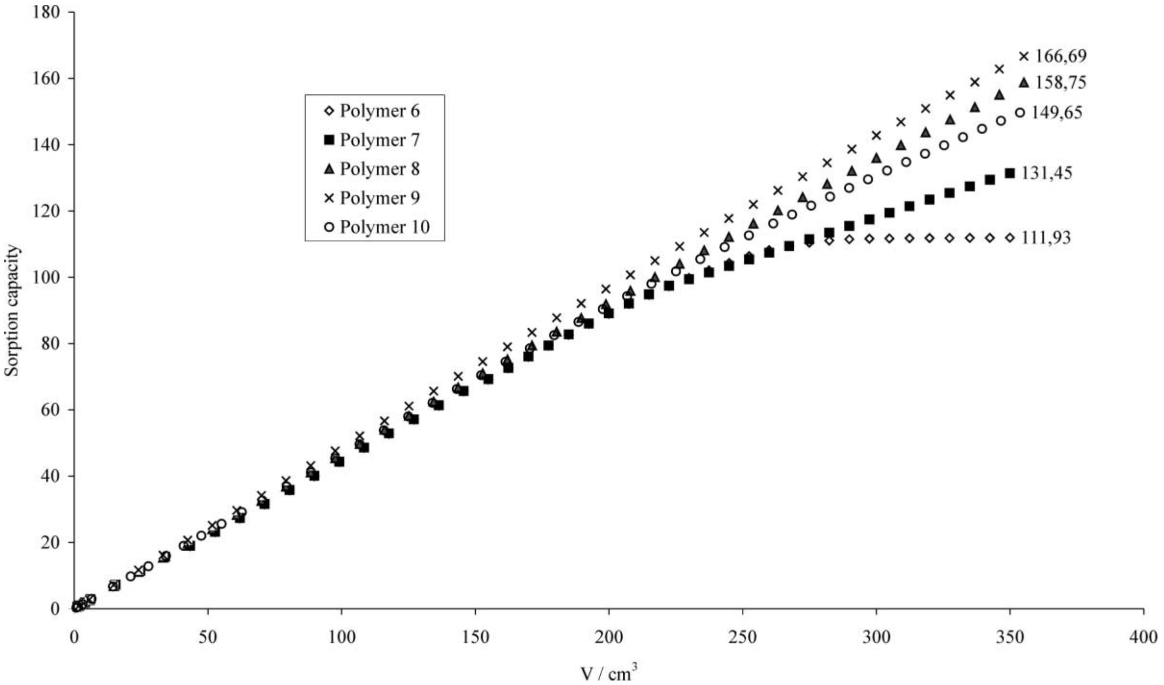


Fig. 7. Influence of the crosslinking agent amount on the sorption capacity ($\times10^{-5}$ mol g^{-1}) versus eluted volume using the open column system (AB 25, concentration 5×10^{-4} mol l^{-1}).

the role of the dye–dye interaction: the sorption of a given dye may be influenced by the presence of another one. This point needs a more detailed investigation using others dyes and also to correlate the results with the degree of aggregation of the dyes.

In view of the industrial application of these polymers, the reproducibility of the sorption properties is of utmost importance. As the interaction between the dye and the polymer is driven mainly by physical adsorption and interactions with the amino groups, organic solvents are good candidates for the regeneration of the sorbents. The polymers are easily regenerated using ethanol as washing solvent by soxhlet extraction. The sorption capacity values remains unchanged after this treatment. Moreover, after several cycles of sorption-washing, the nitrogen content (obtained

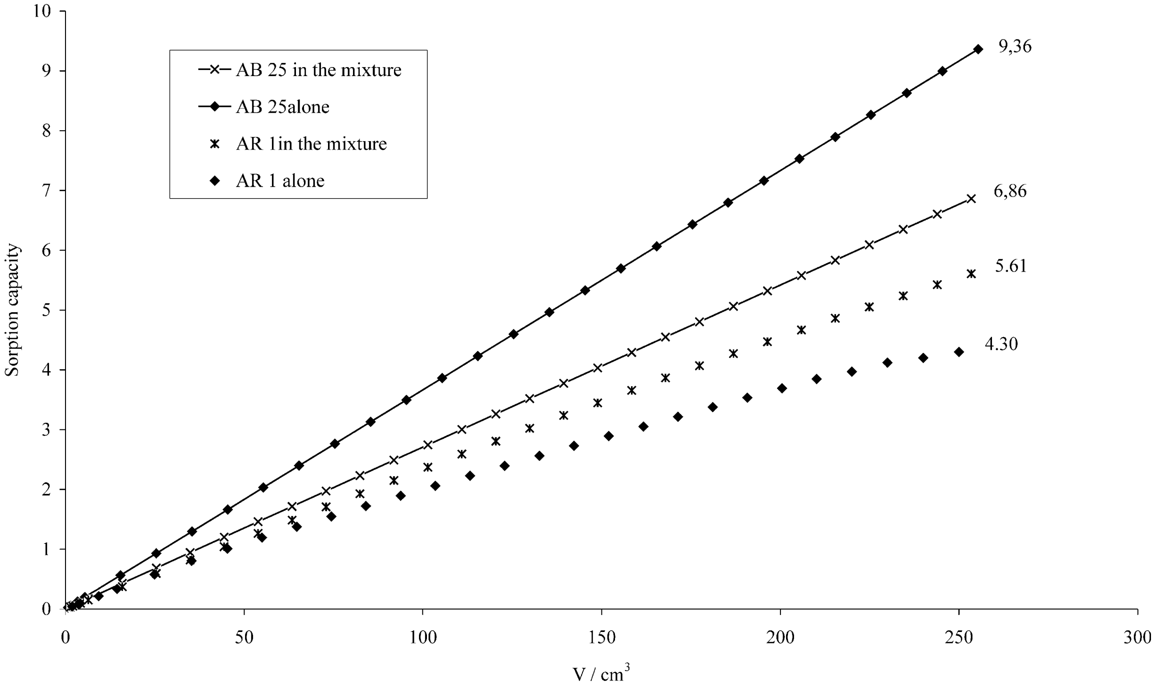


Fig. 8. Sorption capacity ($\times 10^{-5}$ mol g^{-1}) of a mixture of two dyes using polymer 8 obtained by the open column technique (concentration 3×10^{-5} mol l^{-1}).

by elemental analysis) is unchanged (Table 1). These results shows the good chemical stability of the polymers and reproducibility of the values.

4. Conclusions

Crosslinked polysaccharides containing tertiary amine groups are synthesized and characterized by IR and NMR techniques. These polymers derived from an industrial by-product are effective adsorbents for the removal of dyes from aqueous solutions. It would be interesting to use these polymers as sorbents for the economic treatment of effluent containing dyes. The study shows that the presence of amino groups and the nature of the dye influence the sorption capacity. Physical adsorption in the polymer network and chemical interaction of the solute dyes via ion exchange and hydrogen bonding are both involved in the sorption process. The sorption mechanism is also due to the presence of dye–dye interactions. Experiments with mixtures of textile dyes also show that the sorption of a given solute may be influenced by the presence of another.

Acknowledgements

We gratefully acknowledge the financial support of Agence de l'Environnement et de la Maîtrise de l'Energie (ADEME).

References

[1] Dutta S, Basu JK, Ghar RN. Studies on adsorption of *p*-nitrophenol on charred saw-dust. Sep Purification Technol 2001;21:227–35.

[2] Juang RS, Tseng RL, Wu FC. Role of microporosity of activated carbons on their adsorption abilities for phenols and dyes. Adsorption 2001;7:65–72.

[3] Hachem C, Bocquillon F, Zahraa O, Bouchy M. Decolourization of textile industry wastewater by the photocatalytic degradation process. Dyes and Pigments 2001;49:117–25.

[4] Sismanoglu T, Pura S. Adsorption of aqueous nitrophenols on clinoptilolite. Colloid Surfaces A: Physicochem Eng Aspects 2001;180:1–6.

[5] Rodriguez I, Llompart MP, Cela R. Solid phase extraction of phenols. J Chromatogr A 2000;885:291–304.

[6] Doong RA, Chang SM, Sun YC. Solid phase microextraction for the determining the distribution of the sixteen US EPA polycyclic aromatic hydrocarbons in waters samples. J Chromatogr A 2000;879:177–88.

[7] Manoli E, Samara C. Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. Trends Anal Chem 1999;18:417–28.

[8] Puig D, Barcelo D. Determination of phenolic compounds in water and waste water. Trends Anal Chem 1996;15:362–75.

[9] Huck CW, Bonn GK. Recent developments in polymer based sorbents for solid phase extraction. J Chromatogr A 2000;885:51–72.

[10] Hennion MC. Solid phase extraction: method development, sorbents and coupling with liquid chromatography. J Chromatogr A 1999;856:3–54.

[11] Delval F, Crini G, Janus L, Vebrel J, Morcellet M. Novel crosslinked gels with starch derivatives. Polymer–water interactions. Applications in waste water treatment. Macromol Symp 2001;166:103–8.

[12] Delval F, Vebrel J, Pont P, Morcellet M, Janus L, Crini G. Sorption properties toward aromatic compounds of insoluble crosslinked polymers containing starch derivatives. Polym Recycling 2000;5:137–43.

[13] Janus L, Crini G, El-Rezzi V, Morcellet M, Cambiaghi A, Torri G, et al. New sorbents containing beta-cyclodextrin. Synthesis, characterization and sorption properties. React Funct Polym 1999;42:173–80.

[14] Crini G, Janus L, Morcellet M, Torri G, Morin N. Sorption properties toward substituted phenolic derivatives in water using macroporous polyamines beta-cyclodextrin polymers. J Appl Polym Sci 1999;73:2903–10.

[15] Crini G, Bertini S, Torri G, Naggi A, Sforzini D, Vecchi C, et al. Sorption of aromatic compounds in water using insoluble cyclodextrin polymers. J Appl Polym Sci 1998;68:1973–8.

[16] Simkovic I, Laszlo JA, Thompson AR. Preparation of a weakly basic ion exchanger by crosslinking starch with epichlorohydrin in the presence of NH_4OH. Carbohydr Polym 1996;30:25–30.

[17] Simkovic I. One-step quaternization crosslinking of starch with 3-chloro-2-hydroxypropylammonium chloride/epichlorohydrin in the presence of NH_4OH. Carbohydr Polym 1996;31:47–51.

[18] Gough BM. Interaction of wheat starch and epichlorohydrin. Starch 1967;8:240–3.

[19] Kuniak L, Marchessault RH. Study of the crosslinking reaction between epichlorohydrin and starch. Starch 1972;4:110–6.

[20] Rayford WE, Wing RE. Crosslinked cationic and anionic starches: preparation and use in heavy metal removal. Starch 1979;31:361–5.

[21] Holmberg L, Lindberg B, Lindqvist B. The reaction between epichlorohydrin and polysaccharides. Carbohydr Res 1994;262:213–21.

[22] Casu B, Reggiani M. Infrared spectra of amylose on its oligomers. J Polym Sci Part C 1964;7:171–85.