Starch-Modified Filters Used for the Removal of Dyes from Waste Water

Franck Delval,[1] *Grégorio Crini,*[2*] *Joël Vebrel,*[1] *Michael Knorr,*[3] *Gilles Sauvin,*[4] *Emmanuel Conte*[4]

[1] Laboratoire de Chimie des Matériaux et Interface, Université de Franche-Comté, 16 route de Gray 25000 Besançon, France
[2] Centre de Spectrométrie, Université de Franche-Comté, 16 route de Gray, 25000 Besançon, France
E-mail: gregorio.crini@univ-fcomte.fr
[3] Minoterie SAUVIN SA, 39130 Patornay, France
[4] Papeterie de MANDEURE, 25350 Mandeure, France

Summary: The present article proposes the use of starch-enriched flour as low-cost adsorbent of dyes. The adsorbents have been prepared by reticulation of starch-enriched flour using epichlorohydrin as crosslinking agent. These starch-modified filters exhibit interesting properties in terms of sorption rate. Studies concerning the sorption capacity are presented. The influence of the amine groups and the chemical structure of dyes are also studied. The regeneration procedure of the filters is showed and discussed. In order to explain the results, an adsorption mechanism mainly based on physical adsorption and interactions such as hydrogen bonds and ion-exchange due to the nature of the polymer network is proposed.

Keywords: adsorption; dyes; starch; starch-modified filters; waste water treatment

Introduction

Waste waters from paper and textile industries are polluted by dyes. The presence of very low concentrations of dyes in these effluents is highly visible and undesirable. Different treatments[1-6] have been investigated: chemical methods (oxidative processes, Fenton's reagent, photochemical and electrochemical techniques), physical (adsorption, membranes processes) and biological treatments (microbial cultures, fungal degradation) have been used. It is well known that adsorption is one of the most efficient and popular method for color removal from dye waste water. Currently, the most common procedure involves the use of actived carbons as adsorbents but a serious drawback are the expensive costs of activated carbons, in particular for their regeneration. So, many studies have been undertaken to find low-cost

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adsorbents as alternatives to activated carbons. Bentonite, clay, peat, zeolite, saw-dust, maize cob, chitosan and silica beads are significant examples.

In our group, experiments are being to conducted to evaluate the possibility of the use of starch derivatives as sorbents in waste water. In a previous work,[7] we prepared novel low-cost adsorbents containing starch. These polymers have been prepared by polymerization of starch-enriched flour using epichlorohydrin as crosslinking agent. The materials presented high sorption capacities toward phenolic derivatives.[7-9] In order to extend the potential application field of the sorption properties of these materials, we propose the use of these starch-based polymers for the sorption of dyes. In particular, the aim of the present work was to study the sorption properties in relation to different parameters like their chemical composition, or the dye characteristics.

Experimental Part

Synthesis

Details of the crosslinked polymers have already been described.[7-9] The characteristics of the four polymers used in this study are listed in Table 1.

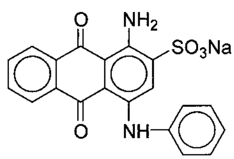
Table 1. Characteristics of polymers.

Polymer	% N[1]	Sp[2]	Ps[3]
Polymer A	0	53	1-2
Polymer B	8.3	280	1-2
Polymer C	9.6	325	1-2
Polymer D	10.7	351	1-2

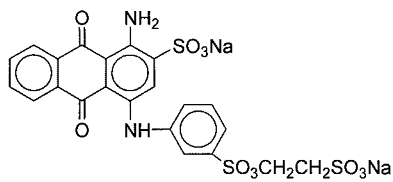
[1] nitrogen content from elemental analysis
[2] specific surface area in m^2/g
[3] particle size in mm

Sorption Tests

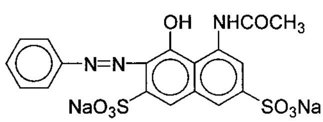
The dyes solutes were commercial products and used without purification (see Figure 1 for the chemical formulae). The sorption capacity is investigated using Acid Blue 25 (AB 25; purity 60 %), Acid Red 1 (AR 1; purity 60 %), Reactive Blue 19 (RB 19; purity 60 %) and Disperse Blue 3 (DB 3, purity 60%). Sorption tests were performed by batch or column techniques. For batch test, 20 mg of polymer was suspended in 4 mL of an aqueous solution of dye (pH = 6.5, distilled water) at a known concentration and stirred with a vortex mixer for 2 hours at room temperature. After centrifugation, the quantification of residual dye concentration was measured by UV-Visible spectroscopy. The adsorption capacity (R) was then calculated and expressed in percentage uptake which represents the ratio between the amount adsorbed dye and the starting amount dye.[10,11] For column tests, 4-cm steel columns were used. The column was filled with 200 mg of polymer. The solutions were moved through the column by a peristaltic pump. Each fraction of 5 ml were collected and analyzed. The experimental conditions were optimized in a previous work.[7]



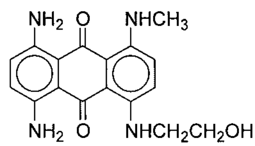
Acid Blue 25
C.I. 62055



Reactive Blue 19
C.I.61200



Acid Red 1
C.I. 18050



Disperse Blue 3
C.I. 61505

Fig. 1. Structure of dyes.

Results

Batch Method

Table 2 shows the sorption of the four dyes on polymers A, B, C and D. Apart from polymer A, polymers B, C and D contain tertiary amine groups (Table 1). The latter polymers display interesting sorption properties for dyes AB 25, RB 19 and DB 3. In contrast, polymer A exhibits lower sorption capacities: in this case, the sorption capacity is based only on the presence of physical adsorption in the polymer network. For polymers B, C and D, the sorption is much better, probably due to the presence of other interactions, such as ion-exchange and hydrogen bonding between the amine groups and the dye. Comparing the values obtained for AR 1 (no affinity for polymer A) and polymer D, an important increase in the sorption capacity (R = 94.6 % instead of R = 7.2 %) is observed, due to the presence of these additional interactions. For AB 25 and RB 19, we see the same effect and we note also that polymer D exhibited very high sorption capacity (R near 100 %). This clearly indicates that the incorporation of tertiary amine groups into the polymer network plays a major role. DB 3 seems not interact with amine groups (R is constant). This finding can be explained by the difference in the chemical structure of this dye, which possesses non-anionic functional groups. According to these results, it assumed that physical adsorption in the polymer network and chemical interaction of the solute dyes via ion exchange and hydrogen bonding are both involved in the adsorption mechanism.

Table 2. Comparison between sorption capacity (R in %) of four polymers in water (concentration $3x10^{-5}$ mol l^{-1}, pH = 6.5) using the batch method.

Dye	Polymer A	Polymer B	Polymer C	Polymer D
AB 25	66	96.2	98.4	100
AR 1	7.2	88.3	91.6	94.6
RB 19	80.5	92.1	96.8	98.9
DB 3	67.3	68.1	66.3	68.3

Open Column

In this technique, we tried to saturate polymer B using a large amount of dye solution. Figure 2 shows the sorption capacity using the open column method of this polymer versus the eluted volume. The results were found to be independent of the flow rate. The sorption capacity shows a decrease between the first and the last eluted fraction for AR 1 and DB 3, due to the saturation of the polymer network. When the eluted volume became too important, the sorption capacity decreased. An increase in the sorption for the first fraction in comparison with those obtained by the batch method is observed for AB 25 and RB 19. All the dye passed through the column being adsorbed quantitatively (R = 100%). Initially, the colour of dye solution is intense and it became clear after passing through the column. This demonstrates the good efficiency of the polymer in waste water treatment. Table 3 represents the sorption capacity versus the eluted volume using different polymers. For polymers B, C and D, we note an increase in the sorption values for the first fraction when the nitrogen content in the polymer increase. This is another confirmation that tertiary amine groups participate in the sorption mechanism. The values for AB 25 and RB 19 for polymers C and D are 100 %. In this case, we can assume that the polymer network is not saturated. These tests (batch and column) gave important information about the potential of this class of adsorbents.

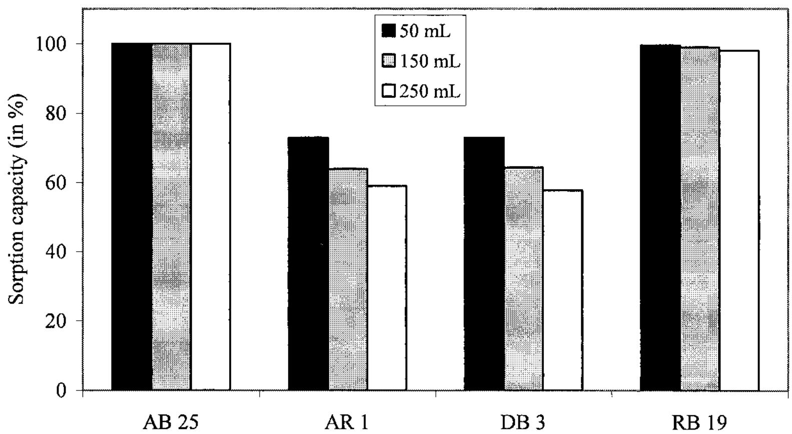


Fig. 2. Sorption capacity of polymer B for four dyes using the column method (flow rate 0.4 ml min^{-1}).

Table 3. Evaluation of sorption capacity by four polymers using an open column.[a]

Dye	Polymer A			Polymer B			Polymer C			Polymer D		
	50[b]	150[b]	250[b]	50[b]	150[b]	250[b]	50[b]	150[b]	250[b]	50[b]	150[b]	250[b]
AB 25	99	80	64	100	100	100	100	100	100	100	100	100
AR 1	2.5	1	0.75	73	64	59	80	75	71	83	77	72
DB 3	60	16.5	13.4	73	64.4	57.7	82	76	65	90	82	71
RB 19	66	27	16.7	99.6	99	98	100	100	99	100	100	100

[a] expressed in percentage uptake
[b] volume eluted in ml

Regeneration Procedure

For the regeneration procedure, we choose AB 25 which reached a sorption capacity of 100% after passing 250 mL of a dye solution. The polymer is easily regenerated using a water/ethanol (40/60) mixture as washing solvent. Figure 3 shows that the adsorbed dye is completely recovered after passing 15 mL of washing solution. Using this technique, it is possible to concentrate the dye adsorbed by the polymer.

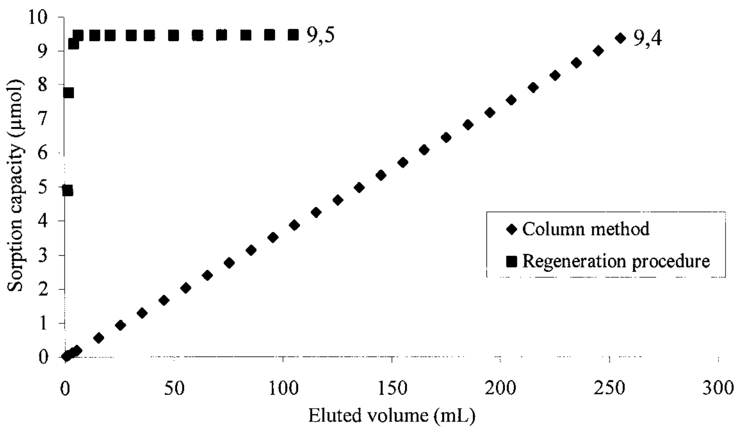


Fig. 3. Sorption and desorption capacity of polymer B using AB 25 as pollutant.

Conclusion

Polymers derived from low-cost starch-enriched flour are effective adsorbents for removal of dyes from solutions. The results indicate that these materials have high sorption capacity. This study shows that the presence of amino groups influence the sorption capacity. The polymers are easily regenerated using an appropriate water-ethanol mixture. The mechanism of sorption implies both physical adsorption in the polymer network and/or the formation of hydrogen bonds and ion-exchange interactions due to the presence of tertiary amine groups.

Acknowledgements

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