SORPTION OF TEXTILE DYES ON β–CYCLODEXTRIN-EPICHLORHYDRIN GELS

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ABSTRACT

β–Cyclodextrin (CD), hydroxypropyl β–cyclodextrin (HPCD), poly(vinylalcohol) (PVOH) have been reacted with epichlorhydrin yielding different gels. The sorption capacity of the gels has been tested with acid, direct, mordant and reactive textile dyes as substrates, by the batch method. CD gels were more efficient than HPCD gels. No correlation has been observed between the performances of the CD gels and their respective crosslinking degree. The influence of pH is rather low whilst that of ionic strength is prominent on the sorption rate. The addition of anionic surfactants have either positive (CPA) or negative (SDS) effect on adsorption. The mechanism of sorption of dyes on gels could be physical adsorption in the polymer network and /or a host-guest inclusion complex formation

1. INTRODUCTION

Removal of colour from the effluent of the dyeing industry became ecological necessity ; now the laws impose more and more drastic norms for the content of the effluents in organic pollutants. Amongst the numerous techniques of depollution, sorption on natural sorbents [1] or derivatives [2] has been proposed. Many reports deal with the interaction of dyes with cyclodextrins [3] in solution. For that reason we propose to use cyclodextrin as a heterogeneous system to sorb dyes. Acid, direct, mordant and reactive dyes have been sorbed onto the synthesised gels ; the parameters that have been considered are the pH and the influence of some of the dyeing auxiliaries usually used in the industrial dyeing processes as sodium chloride or surfactants as CPA and SDS.

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2. MATERIALS AND METHODS

Synthesis of the gels : We applied the technology developed by Komiyama et al.[4] with some modifications in order to increase the degree of crosslinking to the minimum required for mechanically stable gels. In a reactor vessel, 160 ml of a 50% wt aqueous sodium hydroxide solution containing 20 mg of $NaBH_4$ was heated to 50° . Meanwhile one hundred grams (88 mmol) of CD (gel CD1 to 3), HPCD (gel HPCD1), a mixture of PVOH and HPCD (gel HPCD2) were then dissolved. A desired amount of epichlorhydrin was added dropwise and the mixture was vigorously stirred (800-1000 rpm). After 2 hours the gel beads appeared. Then 300 ml of acetone were added with stirring and heating was continued for one hour. After cooling, the resin beads were poured into a 1l water beaker, filtered and washed with water and acetone, and dried in vacuum at 60°C for 20h. The ratio CD/epichlorhydrin is 1/10, 1/15, 1/20 for gel CD1, CD2 and CD3 respectively.

Adsorption measurements : 40 mg of gel (diameter between 0.125 and 0.25 mm) and 40 ml of dye solution (1.10^{-5} or 3.10^{-5} M) were put into a stopped erlenmeyer. The mixture was stirred for 24 hours and the absorbance of the supernatant was measured at the corresponding λmax with a UVIKON 930 spectrophotometer. The uptake percentage was calculated as following : (Ao- A)/Ao x 100 = % uptake.

Products : CD and HPCD were a gift from Roquette Freres ; HCl-NaOH-citric acid was used as the pH4 buffer solution and 0.1M borax was used as pH 9.2 buffer. The concentration of sodium chloride (Aldrich) was adjusted to 1M and that of CPA and SDS (Merk) to 2g/l.

3. RESULTS AND DISCUSSION

CD and HPCD gels have been tested for the sorption of Acid Blue 15 at neutral pH (=5.7) (figure 1). The two HPCD gels have a lower sorption capacity than the CD gels. The presence of poly(vinylalcohol) in gel HPCD 2 does not induce any noticeable difference with gel HPCD 1. No direct relation between the initial ratio β–CD/epichlorhydrin and the sorption capacity of the CD gels can be proposed. Gel CD 3 has been used in the following experiments.

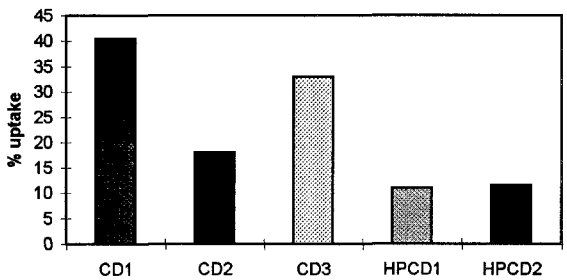

Fig. 1 : Sorption of Acid Blue 15 (10^{-5}M) on CD and HPCD gels at pH 5.7.

Figure 2 reports the results of the study of the influence of pH on the sorption capacity of Gel CD 3 . For most of the studied dyes in this experiment, the good results were obtained either in acidic or (and) in basic medium. A low sorption capacity was observed at the neutral pH. On the other hand, addition of sodium chloride to neutral solutions produces a strong increase of the performance of the gel. In most of experiments reported in figure 2, the capacity of the gel in the presence of NaCl medium reaches the optimum values measured in buffer solution. This observation has led us to conclude that the sorption capacity of the gel depends on ionic strength more than pH. Sodium chloride minimises electrical charge on the surface of the sorbent and increases the adsorption.

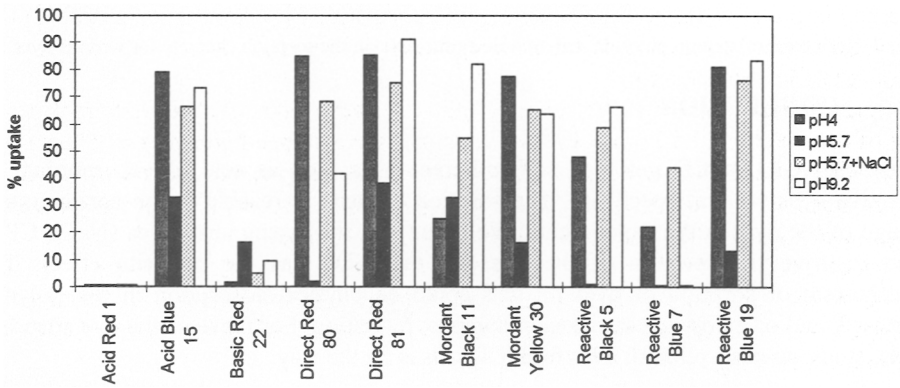

Fig. 2 : pH and salt effect on the sorption capacity of gel CD3 for various dyes (10^{-5}M)

Figure 3 reports experiments where dyes (3.10^{-5}M) have been mixed with auxiliaries in the range of concentration usually used in industrial conditions. NaCl, CPA and NaCl-CPA mixtures have a positive effect on the performances ; however, SDS decreases drastically the sorption. This can be explained by the insulation of the dye molecule inside the surfactant micelle (critical micellar concentration is reached in the conditions of the experiment). Furthermore, SDS is known to form inclusion compounds with β–cyclodextrin. Micellar dissolution and competition with SDS are the reasons of low the sorption of the dye on the gel. In our previous study [5], we found that some of the dyes (DR80, MY30, RB7, RB19) do not have specific interactions with β-CD in the solution (no modification of the visible spectra), but they still can be adsorbed by CD gels. This suggests that the sorption of dyes on gels is not only because of the host-guest inclusion complex formation, but also because of adsorption of dyes in the polymer network.

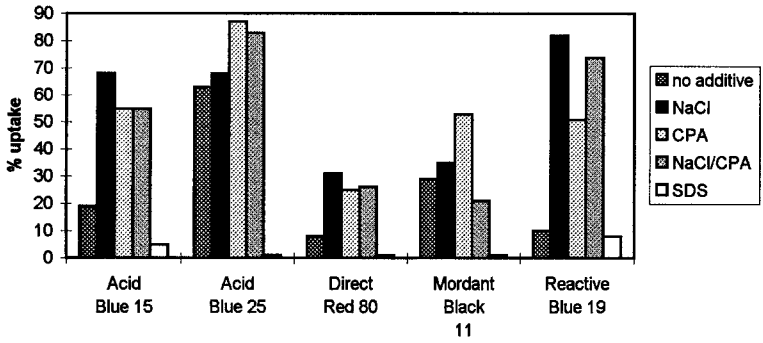

Fig.3 : Influence of sodium chloride and anionic surfactants on the sorption capacity for various dyes.

4. CONCLUSION

We observed that CD gels can sorb different dyes such as acid, direct, mordant or reactive dyes without specificity. The sorption capacity is reliable in the concentration range of the dyes in the experiments. We found that the dyeing auxiliaries (NaCl, CPA) can improve the sorption of the dye and that SDS has the opposite effect. The mechanism of sorption of dyes on gels could be physical adsorption in the polymer network and/or a host-guest inclusion complex formation. For reuse of the dye adsorbed gels, study on desorption of dyes from CD gels is on the way.

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