NEW WAYS TO IMPROVE COLOURSTRIPPING OF DEINKED PULPS AND DYED EFFLUENTS

Nathalie Marlin, Joaquim Fernandes, Nicolas Bénattar*
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Colour-stripping, dye, hydrogen peroxide, alkaline stage

Abstract
The objective of this study was to improve colour stripping of deinked pulps contaminated by coloured pages. A bleached chemical pulp impregnated with dyes resistant to conventional H2O2 treatment was treated by hot hydrogen peroxide stage. First results showed a strong improvement but depending on the tested dyes better results may be obtained with a hot alkaline stage without H2O2. The singular effect of alkali was studied on dilute dye solution without any fibre. Colour removal was observed only if cellulose was added “as additive” in the dye solution and when suitable conditions were applied: hot temperature (90°C) and high pH (pH 12). This colour-stripping effect may be explained by the reduction of the direct dyes by carbonyl functions liberated during cellulose degradation in strong alkaline conditions.

Introduction
Many industries, like textile, leather and paper industries, include dyes in the production lines in order to get a desired appearance, usually according to customer’s specifications. In the paper industry, the dye is attached on the fibres impairing the paper recycling ability. Paper dyes are highly complex structures. Colour comes from the reflection of light which is not absorbed in the conjugated electronic resonance structure of the dye molecule. The presence of a pi electron cloud of four or more conjugated bonds is required to absorb visible light. All light reflected (i.e. not absorbed) is what gives the dye its colour. The general rule is that increasing cloud size is related to the colour produced. The conjugated part of the dye molecule is known as the chromophore and the part of the molecule that confers the dyeing properties onto the molecule (solubility, charge, affinity for the fibre) is the auxochrome (Kool1).

The chromophore structure contains conjugated links: azoic groups (-N=N-), ethylene structures (-CH=CH-), carbonyl groups (C=O), aromatic structures (C6H5)… Colour results from the movement of electrons relocated on the whole dye molecule.
The auxochrome structure promotes the fixation of the dye molecule onto the fibre and plays also a role in the electronic structure of the dye. It can consist of amine groups (NH2), hydroxyl groups (OH), sulfonic groups (SO3H) and carboxyl groups (COOH). The auxochrome structure also can contribute to the colour due to the presence of free electrons on these groups.

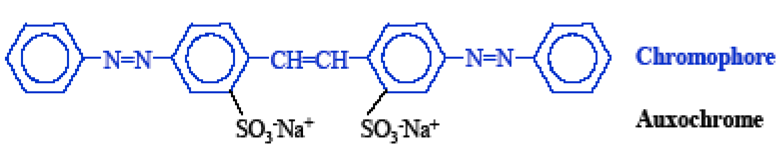


Figure 1. Structure of direct dye Yellow 4 (azo dye)

Production of deinked pulp of high brightness requires efficient colour-stripping treatments since a proportion of mixed office waste papers are contaminated with coloured papers. Coloured papers are mainly made of chemical pulps containing azoic direct dyes. Azo groups transmit electrons between the aromatic ring structures that they link together. This creates a large electron cloud above the molecule that absorbs visible light. To remove colour, the conjugated structure needs to be disrupted. Deinked pulp bleaching frequently uses either an oxidizing agent (hydrogen peroxide for example) or a reducing agent (sodium hydrosulphite) (Lachenal[2], Biermann and Kronis[3], Darlington et al.[4], Sharpe and Lowe[5], Marlin et al.[6]). Hydrogen peroxide is widely used in the treatment of wastewater and dyed pulps, and it is considered as a "friendly" oxidant as the resulting oxidation by-products are water and oxygen. Sodium hydrosulphite is usually applied in complement of peroxide despite its less environmental profile.[a]

Unfortunately, some dyes are resistant to hydrogen peroxide (P stage) or sodium hydrosulphite (Y stage). Consequently, optimization of the treatment of dye-containing pulps and wastewaters is an enormous task, rendered extremely complex by the thousands of dyestuffs commercially available around the world.

The objective of this work was to understand and to try improve the colour-stripping ability of anionic direct dyes used for chemical pulp dyeing. For that purpose, several colour-stripping treatments were applied on dyed chemical pulps and on the corresponding dye diluted in water, without any fibres.

Part I. Colour-stripping treatments applied on dyed pulps

Experimental

Raw material

Six direct dyes (from BAYER) currently used for the colouration of French folders were chosen (folders contaminate mixed office recovered papers). The structure of the dyes is given in Figure 2. A fully bleached chemical pulp (86% Brightness) was impregnated with a direct dye as follows: the concentrated dye solution was introduced in the fibre suspension after pulping. All paper samples were dyed at 1/6 standard depth of shape (the quantity of dye solution was giving by the dye supplier). After mixing (10 minutes), the resulting coloured pulp was drained and then air dried.

[a] NOTE: Many mills prefer to use hydrosulphite as it can be much cheaper than peroxide, depending on the process and results required.

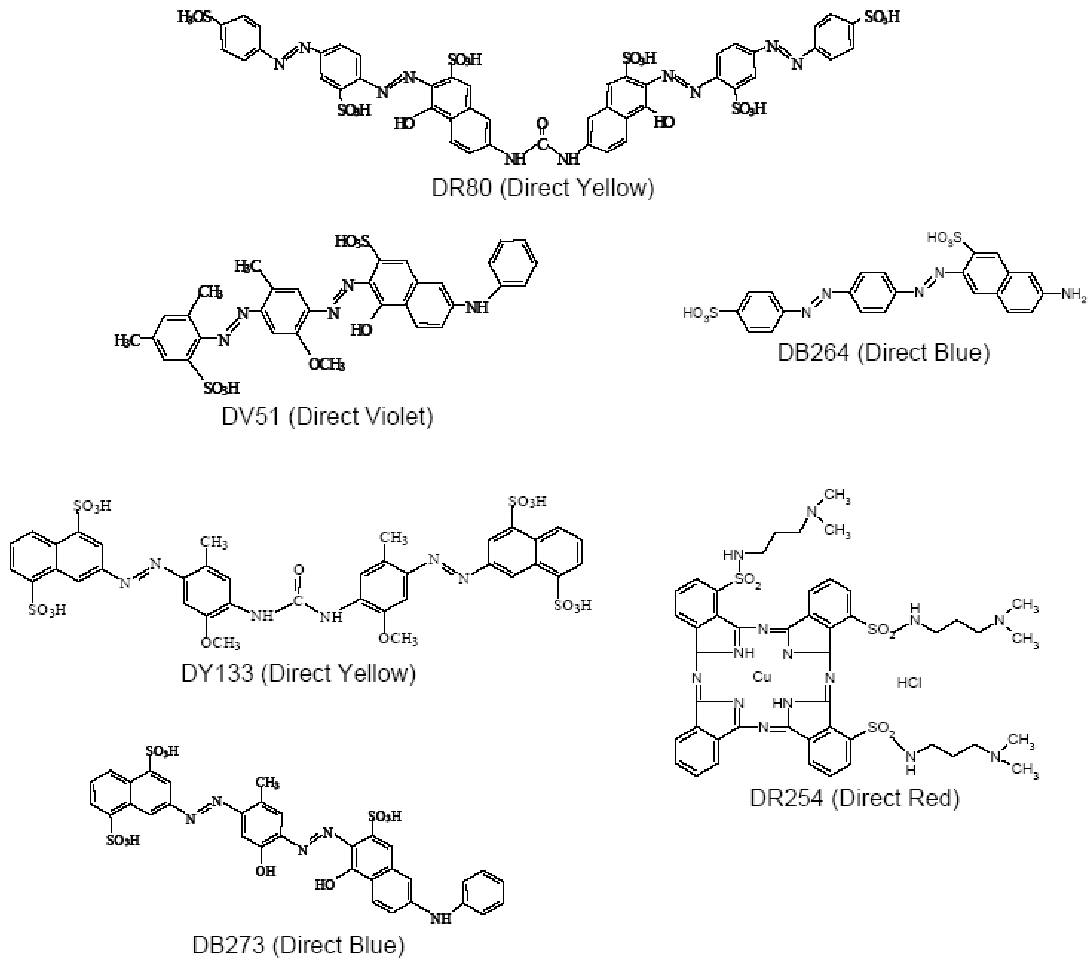


Figure 2. Dye structures

Colour-stripping treatments
Six different coloured pulps were prepared and bleached using conventional P and Y stages. The operating conditions are described in table

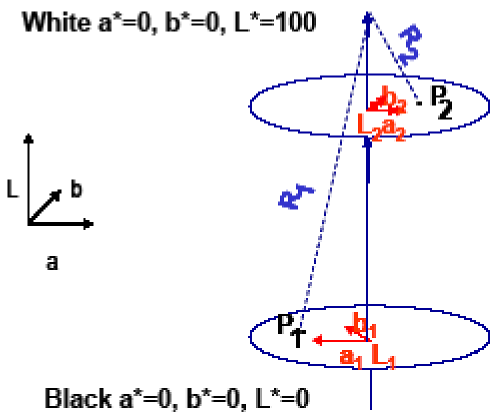
	Time min	Chemicals	T°C	Cp %
P	60	H_2O_2/NaOH= 2%/2%	60	10
Y		$Na_2S_2O_4$=1%		

Table 1. Operating conditions of bleaching stages

Colour-stripping measurement
Colour-stripping efficiency was quantified in term of DRI (Dye Removal Index) using the L*a*b* system according to Sharpe[7]. L*a*b* values were measured on handsheets. The Dye Removal Index (DRI) was developed from the CIE L*a*b* values. L* is a measure of lightness and varies from 0 for absolute black to 100 for perfect white. a* indicates redness and –a* greenness. b*

indicates yellowness and –b* blueness. The unbleached pulp is represented by point P1. The distance in colour space from point P1 to ideal bleach is a straight line R1 as illustrated in figure 2.

After bleaching we will move to point P2 with a distance R2 from the ideal bleach. The amount of colour removal is calculated with the reduction in the distance in moving from point P1 to point P2 as illustrated in the following figure (Figure 3).



DRI calculation:

$$DRI = -100 \frac{R_2^2 - R_1^2}{R_1^2}$$

Figure 3. Dye Removal Index calculation from the CIE Lab colour space

Results and discussion

Conventional P and Y stages were applied on several dyed pulps (direct dyes) to examine the colour-stripping ability of coloured pages coming from mixed office recovered papers. Results are presented in Figure 4.

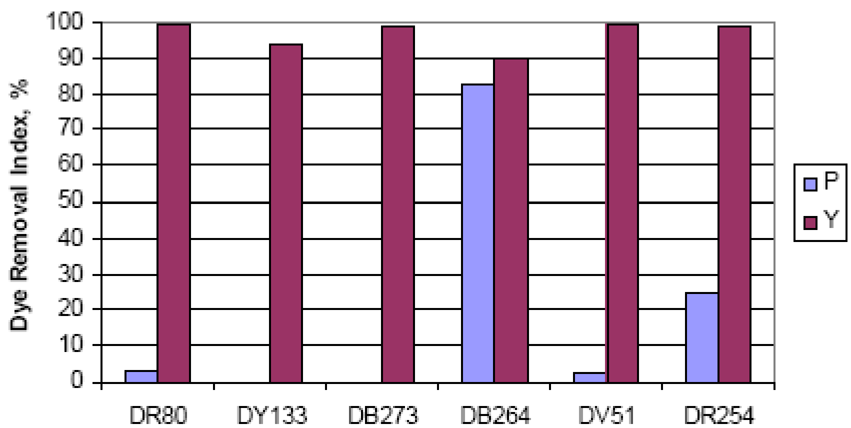


Figure 4. Dye Removal Index after dyed pulp colour-stripping stages carried out at 60°C

From figure 4, it can be seen that different dyes respond differently to colour-stripping at 60°C colour. All the pulps could be efficiently bleached by reduction (Y stage is efficient) but the oxidative P stage is not able to effectively remove colour except in the case of the DB264. As a next step, studies have shown that H_2O_2 is known as a delignifiying chemical when applied at high temperature. Consequently, P stages were performed at 90°C instead of 60°C to examine if color-stripping efficiency could be increased in delignification conditions. Finally, E stages (same conditions as P stage but without H_2O_2) were also performed as control (see Figure 5).

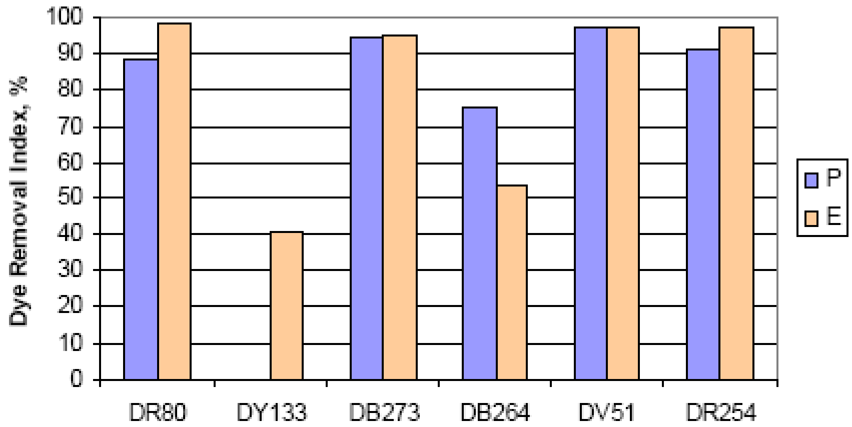


Figure 5. Dye Removal Index after dyed pulp colour-stripping stages carried out at 90°C

As shown by Figure 5, an increase of temperature strongly improved the P stage efficiency except for the DY133 and DB264. P stage has again no effect on the DY133 and higher temperature is detrimental for DB264.

Finally, one interesting result is the effect of NaOH alone. Indeed, an alkaline stage carried out at 90°C is able to colour-strip. In the case of DR80, DB273, DV51 and DR254, colour may be totally removed with soda whereas residual colour was still observed for DY133 after the alkaline treatment.

One exception was the DR264 where soda had a detrimental effect on colour removal but DR264 is not resistant to H_2O_2 (see Figure 4). From these results it could be also concluded that in the case of DR80, DY133 and DR254, dyes, alkaline hydrogen peroxide stage is less efficient than the corresponding E stage. Two explanations may be given:
- the pH decreases after H_2O_2 addition
- or H_2O_2 has a chemical detrimental effect on the colour-stripping reaction

To understand the effect of alkali in colour-stripping efficiency, the DR80 dyed pulp was submitted to various E stages with variable amounts of sodium hydroxide and different temperatures. Results (not presented) showed that a total discolouration may be reached if temperature was equal or above 80°C and if the caustic soda charge exceeded 1% (on oven dried pulp). To our knowledge, the effect of caustic soda on dyed pulp had never been explained. Consequently, for better comprehension some trials were carried out on dilute dye in water without any fibre. This study is presented in part 2.

Part II. Colour-stripping treatments applied on dilute dye, in water without any fibre

Experimental

Dye containing solution preparation

The dyed effluent is prepared by dissolution of 0.1g of the commercial dye solution in 1 liter of distilled water.

Colour-stripping measurement

Colour variation is followed by UV-visible spectroscopy analyses. Absorbance spectra of untreated and treated dye containing solution were recorded from 280 nm to 600 nm on a UNICAM UV500 from Thermo Spectronic.

Dye containing solution treatment Alkaline P stages were carried out with 0.01g of H_2O_2 for 100ml solution to be treated. Temperature was adjusted to 90°C and pH to 12 using NaOH 0.35M. E stage was also performed at 90°C and pH 12 using NaOH 0.35M. If not precise, reaction time was 60 minutes. In the case of microcrystalline cellulose addition, cellulose was added in order to reach 1% consistency. Preparation of oxidized and reduced cellulose Cellulose oxidation was carried out with sodium metaperiodate $NaIO_4$ M/20 at 1% consistency during 2 hours at room temperature. Cellulose reduction used 1% sodium borohydride $NaBH_4$ and 1% sodium carbonate Na_2CO_3 at 10% consistency during 30 min at room temperature.

Results and discussion

Part 1 shows that, when applied on some dyed pulps, an E stage carried out at high alkalinity and at 90°C improved colour-stripping efficiency. To better understand the reactions involved in colour-stripping, trials were carried out on dyes diluted in water without any fibres. Our study focused on the DR80 dye because the corresponding dyed pulp is easily colour-stripped by alkali. Thus P and E stages were applied on the DR80 dyed solution (λ_{max}=526nm) in the same conditions as P and E stages performed on the coloured pulps. Then UV visible spectra were recorded before and after the treatment. Results presented in Figure 6 showed that E stage only slightly degraded colour whereas the P stage had a stronger beneficial effect on colour removal.

These observations were in contradiction with those obtained on the DR80 dyed pulp where alkali was more efficient than alkaline peroxide treatment. The only explanation may be that cellulose plays an active part in the alkaline colour-stripping reaction. To verify our hypothesis, microcrystalline cellulose was added as an additive in E and P stages. Results are also given in Figure 6.

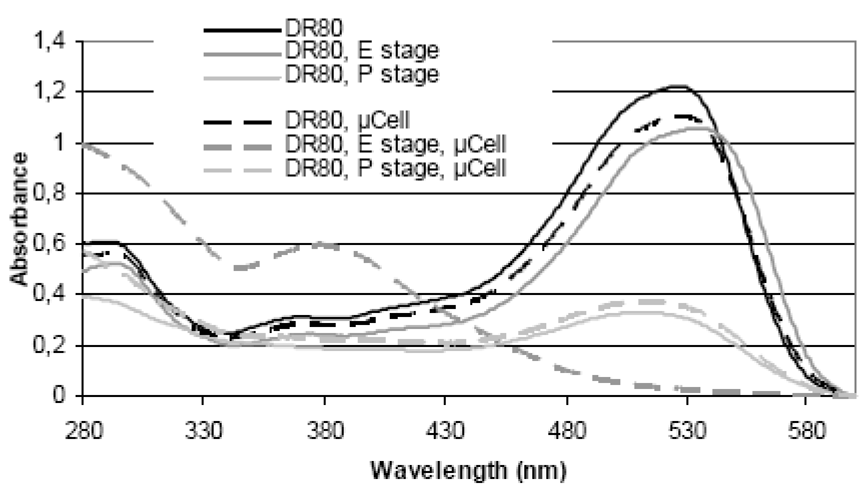


Figure 6. Colour-stripping of the DR80 dye in aqueous solution using P and E stages with or without microcrystalline cellulose addition. [µcell=microcrystalline cellulose]

Addition of microcrystalline cellulose had no effect on H_2O_2 efficiency: signals recorded after P stages with or without cellulose addition are the same meaning that peroxide is still able to remove part of the colour (Figure 6). However, in the E stage, addition of microcrystalline cellulose strongly modified the dyed solution: disappearance of the light absorption at 526 nm (λ_{max}) and increase of the absorption in the near UV light at 380 nm. From this result it may be concluded that the dye in alkaline solution is chemically modified by the addition of cellulose.

Finally, the light pink colour of the cellulose recovered after the E stage certainly means that dye adsorption on the microcrystalline cellulose should not be neglected. Two phenomena may be responsible of the dyed solution colour-stripping: a chemical action in strong alkaline conditions at 90°C and a physical adsorption of the dye on cellulose. Adsorption mechanism of azo dye onto absorbents is well known in the water treatment field (Sankar et al.[8], Van Driessel and Christov[9], Netpradit et al.[10], Bousher et al.[11]). Many absorbents, such as activated carbon, may be used provided that they exhibit high specific area and that sufficient amount is added. Usually adsorption efficiency is reduced by an increase of pH which is not the case in our trials. As shown by Figure 7, colour-stripping occurred at pH 12 whereas no reaction was observed at lower pH (no modification of the absorbance). From that, it may be conclude that adsorption is not the main colour-stripping mechanism.

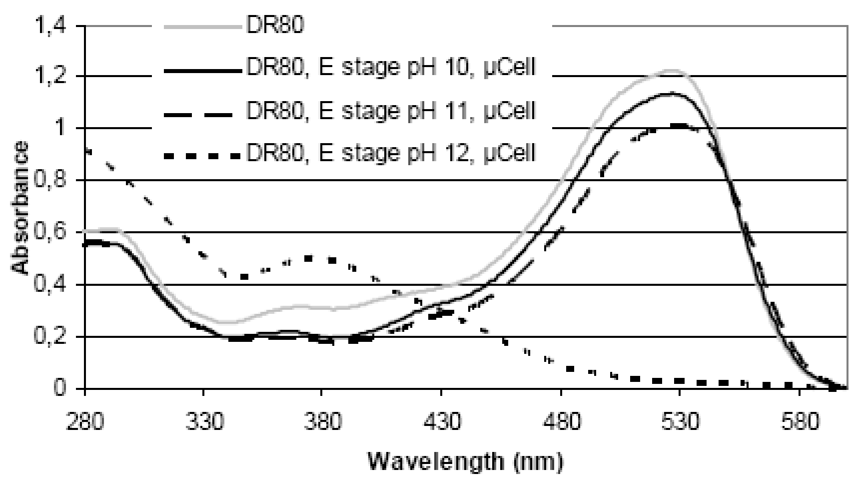


Figure 7. Colour-stripping of the DR80 dye in aqueous solution using E stages at different pH and with microcrystalline cellulose addition

To identify the chemical actions involved in the alkaline colour-stripping with cellulose, oxidized and reduced microcrystalline cellulose were prepared and also tested as “chemical” additive. Results are given in Figure 8.

Figure 8. Addition of oxidized and reduced microcrystalline cellulose in the E stage, comparison with non-modified microcrystalline cellulose. [µcell= microcrystalline cellulose, ox µcell=oxidized microcrystalline cellulose, red µcell=reduced microcrystalline cellulose]

Cellulose is a homopolymer made of D-glucopyranose moieties linked together by 1-4 glycosidic bonds. At one end (C1 position), cellulose exhibits a hemiacetal structure with reducing properties, and at the other end (C4 position) an alcohol structure with nonreducing properties. Oxidation and reduction of cellulose are well-known reactions (Spedding[12], Linderg and Theander[13]).

The periodate oxidation of cellulose is characterised by specific cleavage of the C2-C3 bond of the glucopyranoside ring resulting in the formation of two aldehyde groups per monomer unit in C2 and C3 position. On the other hand, cellulose reduction is usually used to reduce carbonyl functions in C1 position (hemiacetal structure) into hydroxyls.

As already shown in Figure 6 and Figure 7, addition of cellulose in the E stage carried out at pH 12 and 90°C had a colour-stripping effect. This reaction takes time, a total discolouration was observed after 80 minutes of reaction. In the case of oxidized cellulose, the colour-stripping reaction was faster, a total discolouration occurred in 40 min. Finally, no chemical reaction seemed to appear with reduced cellulose. From these observations, it may be concluded that the presence of carbonyl functions may assist the alkaline degradation of the dye.

If the presence of carbonyl functions seems to be necessary to colour-strip, strong alkali and high temperature (90°C) are also required for the reaction (see part I). Under these conditions, cellulose is partly degraded by primary peeling. The peeling reaction of polysaccharides involves the elimination of monosaccharide units that form carboxylic acids thus reducing the chain by one monomeric unit at time. As an average about 50 to 60 glucose units are expected to be cleaved by the peeling reaction until a competing termination reaction takes place. The initial step is the isomerisation of a reducing end group to a 2-keto intermediate followed by the □-alkoxy elimination leading to a soluble monosaccharide unit and a shortened polysaccharide chain with a new reducing end group.

In our study 3 kinds of cellulose were used as “additive” in the E stage:
- Cellulose
- Reduced cellulose
- Oxidized cellulose

As the prerequisite for the peeling reaction is the presence of a reducing end group in the polysaccharide chain, the cellulose used in this study will undergo the peeling until the termination reaction occurs. As reduced cellulose is stable in alkaline medium[14], peeling cannot start because the reducing end units of reduced cellulose are totally reduced into hydroxyl groups.

The case of the oxidized cellulose is more complicated. Some doubts have been raised about the stability of oxycelluloses that might undergo a partial hydrolysis in the alkaline medium. A mechanism was first proposed in 1958 by O’Meara et al.[14,15] and was confirmed by Calvini et al.[16,17,18] and Strlic[19]. Some oxycelluloses undergo a □-alkoxy fragmentation leading to cellulose chains splitting and generating some oxidised low molecular-weight soluble fragments containing carbonyl functions. Carbonyl functions are known to have good reduction potentials. Thus our hypothesis is that carbonyl functions liberated during the cellulose peeling and/or during the hydrolysis and peeling of oxycelluloses are able to reduce the dye in alkaline condition.

Oxycellulose degradation would increase the number of reducing functions which may undergo the peeling reaction thus improving the colour-stripping kinetic. Further trials are required to verify this assumption. For example, carbonyl model compounds may replace the cellulose or oxycelluloses as additive in the colour-stripping treatment. Finally, the five other dyes tested, diluted in water, were submitted to the alkaline stage in the presence of cellulose added as an "additive". Depending on the dye, colour-stripping is more or less efficient (see Figure 9) but the results obtained on dye in solution are in agreement with those obtained with the dyed pulp (Figure 5):

- DY133 and DB264 impregnated on the pulp or in aqueous solution are resistant toward alkali even if a slight colour-stripping effect may be observed
- DR80, DB273, DV51 and DR254 impregnated on the pulp or in aqueous solution are totally degraded by the treatment.

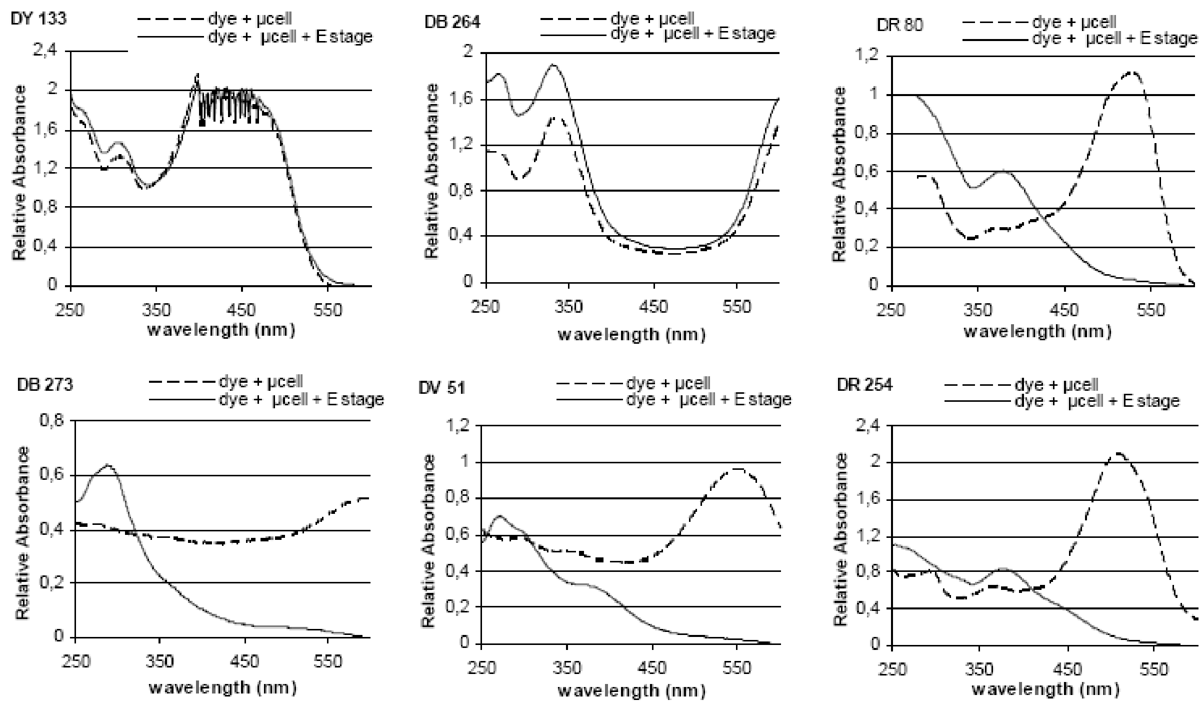


Figure 9. Colour-stripping of the tested dyes in aqueous solution using the E stage with microcrystalline cellulose addition. [µcell= microcrystalline cellulose]

DR254 dye is made of copper and an organic ligand and its structure cannot be compared to other dyes studied. DR80, DB273, DV51, DY133 and DB264 are linear organic molecules containing the same main functions. They are consequently comparable. After a examination of dye structures, it can be observed that dyes containing phenolic functions (DR80, DB273, DV51) are easily degraded by the alkaline treatment with cellulose whereas the other dyes (DY133 and DB264) are resistant. One explanation may be that phenolic functions of the dyes are reduced by the carbonyl functions of cellulose in strong alkaline medium.

Further trials with other dyes are needed to conclude on the colour-stripping mechanism involved and to evaluate the colour-stripping ability of dyed pages according to the dye formula with the aim of applying the suitable bleaching treatment.

Conclusion

Coloured pulps are usually treated by conventional P and Y stages to reach high level of brightness but some of them are resistant to hydrogen peroxide bleaching. Our study showed that, depending on the dye, hot alkaline or hot alkaline peroxide stages are able to improve the poor colour-stripping efficiency of dyed pulps.

The singular effect of alkali was studied in detail. Alkali, applied on dilute dye solution without any fibre, had no effect on colourstripping. Colour removal was observed only if cellulose was added in the dye solution and when suitable conditions were applied: hot temperature (90°C) and high pH (pH 12). Moreover it has been shown that colourstripping is mainly due to a chemical reaction.

Using oxycelluloses and reduced cellulose as additive, it may be conclude that carbonyl functions play an active role in colour-stripping but only phenolic dyes are efficiently degraded. Our hypothesis is that carbonyl type reducing groups (liberated during cellulose degradation) are able to reduce phenolic dyes in strong alkaline conditions. Further study needs to be completed to confirm this theory.

ENDS