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A study on the exhaustion of reactive dyes as an influence factor on the colour of reactive dyeing wastewater

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Abstract. One of the most significant pollution factors in the dyeing of textile materials is the colour of wastewater. This feature is particularly pronounced as the dye exhaustion is low. This paper examines the exhaustion of 5 reactive dyes, dyes which are widely used and characterized by modest capacity of exhaustion. The exhaust capacity is analysed in correlation with the value of the liquor ratio and the dye concentration in the dyeing solution.

1. Introduction

The colour of the wastewater from textile dyeing is one of the hardest to solve problems to bring wastewater to conditions that should allow its discharge into a watercourse [1]. The reason for this is the low biodegradability of dyes, which in most cases makes the effectiveness of colour removal in the biological treatment process at most moderate. Various methods, such as oxidative discoloration [2], adsorption [3] or membrane separation processes [4], can be applied to solve the problem, all of which significantly complicating the treatment process. Therefore, it is desirable that the presence of the dye in the wastewater is as low as possible, and this is determined by the exhaustion ability of the dye. Exhaustion refers to process of transferring the dyestuff from the dye bath on to the textile material and can be calculated as the percentage ratio between the amount of dye at the end of the dyeing on the substrate and the amount of dye originally used for dyeing. Of course, as the exhaustion of the dye increases, the colouration degree of the wastewater will be lower, so the wastewater treatment will be considerably simplified. High exhaustion is a condition of successful dyebath reuse, if associated with the use of dyebath auxiliaries that do not interfere with subsequent dyeings. Reusing dyebaths as they are can give water savings up to 90% [5-9]. The speed of dye exhaustion has also important technological significance, as when the exhaustion rates are high, unlevel dyeing can occur. The speed of the dye uptake is influenced by many factors, such as the chemical structure of the dye, its physical properties, the nature of the substrate to be dyed, the dye concentration, the liquor ratio value, the temperature of the dyebath and the nature of dyeing auxiliaries [6, 10-12].

Some of this factors that influence dye exhaustion are studied for 5 reactive dyes. We have chosen this class of dyes as reactive dyes are known for there problems both in what regards their exhaustion capacity and the colour removal from wastewater.

2. Materials and methods

The exhaustion capacity of 5 reactive dyes was analysed. Their names and chemical structures are shown in Table 1.

**Table 1**. Chemical structures of the analysed reactive dyes.

Dyestuff name	Chemical structure
Bezactiv violet V-5R (Reactive Violet 5)	
Bezactiv Blau V – R (Reactive Blue 19)	
Bezactiv orange V-3R (Reactive Orange 16)	
Cibacron Rot HE–BB (Reactive Red 120)	
Drimaren Red X–6BN (Reactive Red 243)	
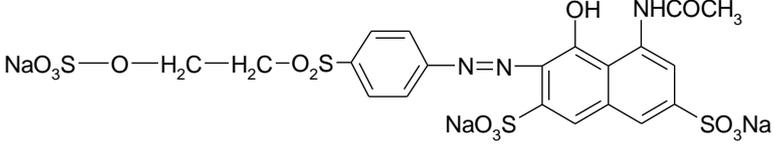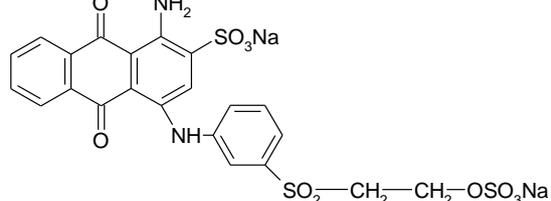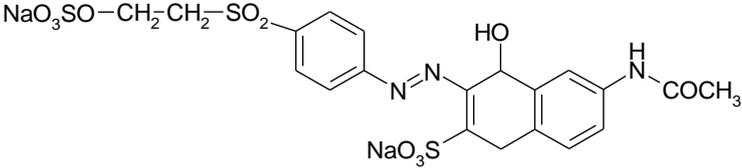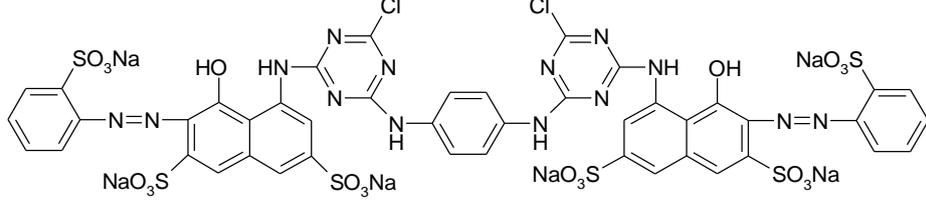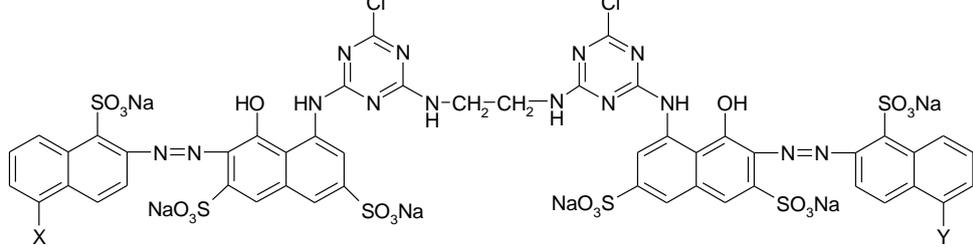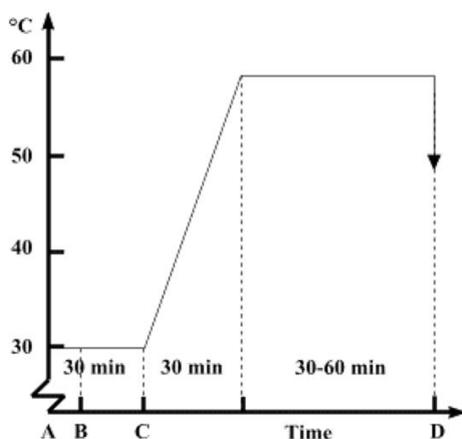
Figure 1. Dyeing diagram for the vinylsulfonic dyes.

The tested reactive colorants are, from a chemical point of view, part of two categories:
• Vinyl Sulphone Dyes - containing vinyl sulfonate group as a reactive radical (Bezactiv violet V – 5R, Bezactiv Blau V ¬ R, Bezactiv orange V-3R)
• bifunctional monochlorotriazinyl - having monochlor-triazine as reactive system (Cibacron Rot HE – BB and Drimaren X – 6BN).

The dyeing process is different for each of the two classes of dyes. The diagram of the dyeing process used to determine the exhaustion capacity is shown in Figure 1 for the vinylsulfonic dyes and in Figure 2 for the bifunctional monochlorotriazinyl dyes, and the composition of the dyeing baths in the two cases is shown in Tables 2 and 3 respectively.
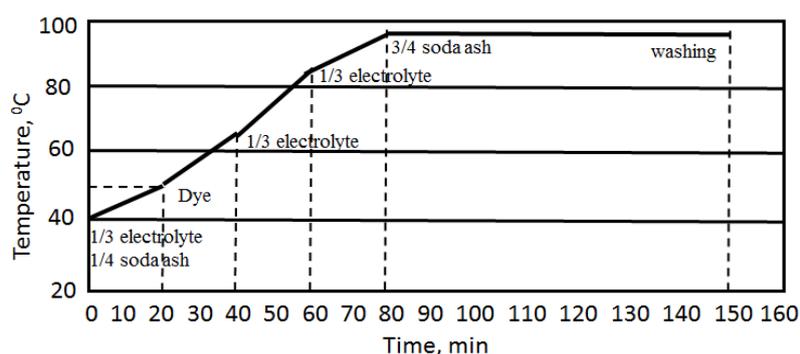
Figure 2. Dyeing diagram for the bifunctional monochlorotriazinyl dyes.

Table 2. Concentration of bath constituents when dyeing with the vinyl sulfone dyes.

Dye concentration	Electrolyte, g/l	Soda ash, g/l	Sodium hydroxide 38° Be ml/l
1%	40	5	2
2%	50	5	2,5
3%	60	5	3

Table 3. Concentration of bath constituents when dyeing with the monochlorotriazinyl dyes.

Dye	1 %	2 %	3 %
Electrolyte, g/l	20	40	60
Soda ash, g/l	5	10	15

All dyeings were performed in an Ahiba lab dyeing machine. After completion the dyeing process, to remove unfixed dye four washes were carried at 1:20 liquor ratio, under the following conditions:

Bath 1 - 98°C for 15 minutes; Bath 2 - 98°C for 15 minutes; Bath 3 - 98°C for 15 minutes; Bath 4 - 20°C for 10 minutes. Finally, all wastewater was collected and the dye concentration in the waste water was determined. The exhaustion has been determined for dyeings at different concentrations (1%, 2%, 3% expressed to textile weight), using in each case three liquor ratios: 1:10, 1:20 and 1:30. The three liquor ratios correspond to the dyeing processes performed on the most common dyeing equipment, as can be seen from Table 4 [7, 13-15].

Table 4. Values of the liquor ratio for various textile dyeing equipment.

Dyeing equipment	Liquor ratio	Dyeing equipment	Liquor ratio
Winch	20:1 – 30:1	Jigger	10:1 –20:1
Skein dyeing machine	30:1	Jet	7:1 – 10:1
Pad – batch	5 : 1		

Determination of the exhaustion was done by spectroscopic analysis of the dyeing baths before and after dyeing (the overall waste baths, i.e. wastewater from dyeing plus wastewater from washing was analysed). Based on the calibration curves for each dye, determined by measuring the absorbance of known dye solutions using a Spectro UV/Vis Dual Beam Labomed UVS-2800 spectrophotometer, the initial dye concentration and residual concentration were determined. Percentage exhaustion was determined using the relationship (1) [8, 16-25]:

$$E = \frac{c_1 - c_2}{c_1} \cdot 100\% \tag{1}$$

Where:

E - dye exhaustion, [%];

c_1 – initial dye concentration in the dyeing bath, [g / l];

c_2 - dye concentration in the dyeing bath and washing water after dyeing, [g / l].

3. Results and discussions

Exhaustion variation according to the dye concentration and the liquor ratio for the three vinyl sulfone dyes is shown in Figures 3-5, and for the bifunctional monochlorotriazinyl dyes in Figures 6-7.
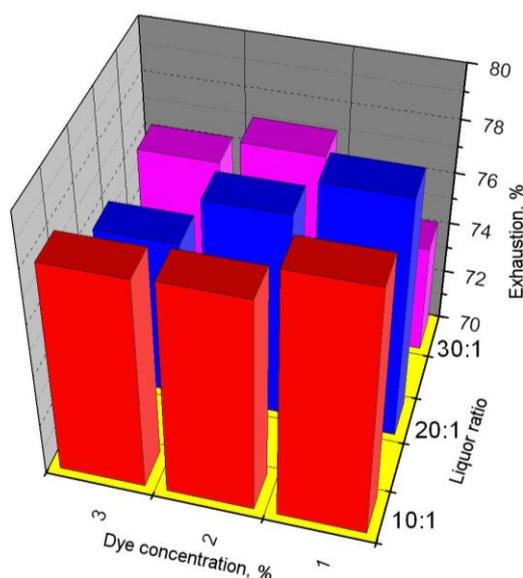

**Figure 3**. Exhaustion variation for Bezactiv Blau V-R.
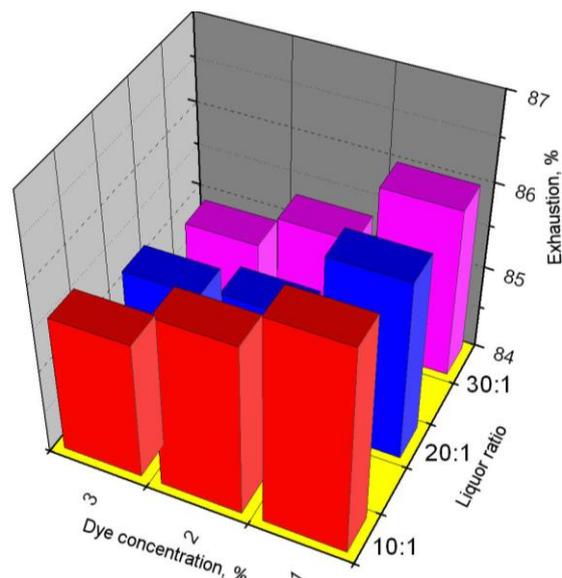
Figure 4. Exhaustion variation for Bezactiv violet V-5R.

It can be noted that the exhaustion values are contained in a wide interval of values ranging from 70.4% to 97.2%. In the case of the vinyl sulphone dyes, and especially at high liquor ratio values and at the lowest concentration, relatively low exhaustion values were recorded - between 78 and 85%, but even at lower liquor ratio the exhaustion does not exceed 86.4%, which means the passage of an important amount of dyestuff into the wastewater.

The influence of the dye concentration in the bath on the exhaustion is less prominent at low liquor ratio, but at higher liquor ratio a significant decrease in the exhaustion value can be observed when the dye concentration is higher.
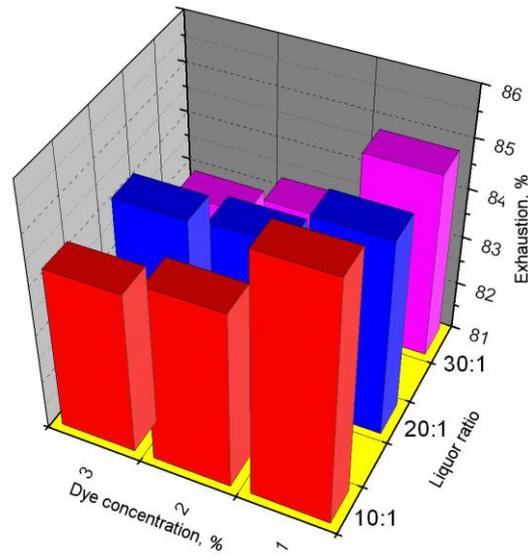
Figure 5. Exhaustion variation for Bezactiv Orange V–3R.
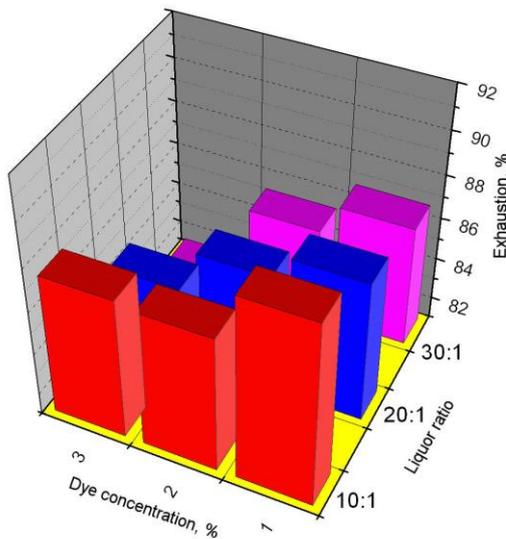
Figure 6. Exhaustion variation for Cibacron Rot HE–BB.
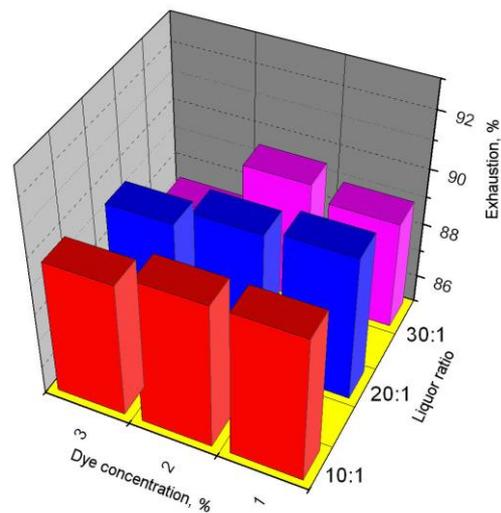
Figure 7. Exhaustion variation for Drimaren Red X–6BN.

Higher extinction values were found in the case of the two bifunctional reactive dyes (Reactive Red 120 and Reactive Red 243), which reach maximum extinction values of 90%, but even in this case the dye concentration that ends in the residual bath is significant, justifying a treatment phase if recirculation is desired.

4. Conclusions

The colour of textile wastewater is a serious problem, difficult to solve. As the amount of dyestuff in wastewater is dependent on the exhaustion of dyes, in the paper the exhaustion capacity 5 reactive dyes were analysed. The exhaustion was studied in relation to the dye concentration in the dyeing bath and the liquor ratio of the bath, revealing the dependence between these parameters and the structural characteristics of the analysed dyestuffs.

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