A REDUCTIVE APPROACH TO COLOUR REMOVAL OF TEXTILE WASTEWATERS

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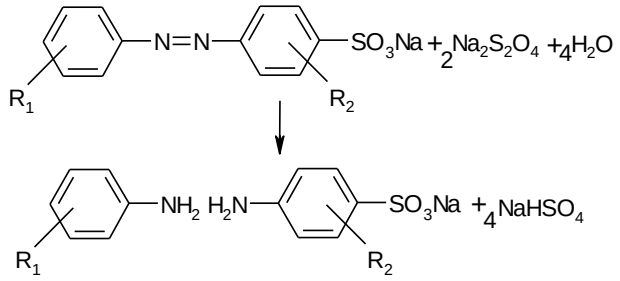
INTRODUCTION

Most of the pollutants contained in the effluents are generated by preparation processes (about 70%). For the remaining 30% dyeing and printing are responsible. The impact of dyes on environment is highly variable, but the colour removal is of great interest.

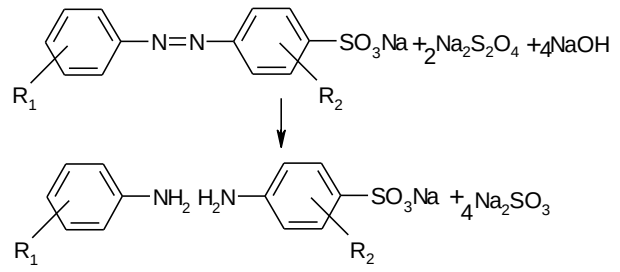
The main principle of colour removal is the same principle that occurs in textile bleaching: the destruction of the dye chromophore. Oxidants are well known in the textile finishing industry as bleaching agents. At a much lesser extend, reductive agents are used (especially for wool). This article tries to investigate if a similar parallel can be drawn in the field of colour removal of wastewater. A common reductive agent that could be used to remove the colour of textile wastewater is sodium dithionite, which has been the standard fugitive dye remover for years.

The colour removing action of the sodium dithionite is a result of its reducing action, which causes the rupture of the azo bond where the dye is broken down into products that have no dyeing capacity.

The way sodium dithionite reacts with azoic dyes in neutral is described by the following reaction:



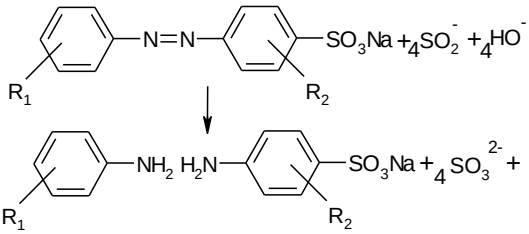
In alkaline medium, the reaction that takes place is showed bellow:



There are opinions that the dithionite ion may be understood as two sulfoxyl (SO2-·) radicals joined by a 2.39 sulphur-sulphur bond, that is significantly longer (and hence weaker) than a typical S-S bonds; thus, $S_2O_4^{2-}$ will easily dissociate into two free radicals SO_2^{-}·:

$$S_2O_4^{2-} \Leftrightarrow 2\ SO_2^{-}\cdot$$

The radicals react with de azo bonds:



In acid medium sulphur dioxide in produced.

1. EXPERIMENTAL

The paper presents a study of the capability of 3 dyes, a direct, an acid and a reactive dye, to be transformed into uncoloured substances using sodium dithionite. The selection of those classes of dyestuffs has been made considering their low capability of adsorption on the activated sludge in a biological plant (especially for the last two).

The influence of pH, sodium dithionite concentration and temperature has been studied.

The dyes used were as follows: Direct Red 80, Acid Red 6 and Reactive Red 45.

1. 1. Discoloration procedure

The wastewater discharged from a typical dye bath was simulated by using different concentrations of dye that are usually encountered in the dyeing effluent. That was realized by adding along with the dye the auxiliaries that would normally be in the residual solution. That means that the direct dyes solution contained 1 g/l sodium chloride, the reactive dye solution contained sodium sulphate (50 g/l) and sodium carbonate (10 g/l), and the acid dyes solution contained sodium sulphate (1 g/l) and acetic acid (to realize a pH=5).

Synthetic dye solutions of known concentration have been prepared by pipetting a

known amount of dye solution of 10 g/l concentration into a 1 liter Erlenmeyer flask, the appropriate quantities of auxiliaries solutions and diluting it with a known amount of tap water in order to obtain the desired concentration.

Samples of 30 ml of synthetic dye solutions were treated with different concentrations of sodium dithionite, at various pH values and temperatures, for durations between 10 and 60 minutes. After the treatment, the sample was vacuum filtered through a 1,0 mm glass microfiber filter, the filtrate was collected in a clean container and analyzed in order to determine the colour removal degree.

1. 2. Colour measurement

The degree of colour removal was found by determining the absorbance of the dyestuff solutions with a spectrophotometer. The cuvettes for the spectrophotometer were clear plastic and held one milliliter of sample. The spectrophotometer compared each sample to a blank containing de-ionized water. The wavelength was selected so as to obtain maximum absorbance (520 nm). The absorbance was converted into concentration using a calibration line.

The evaluation of the efficacy of the treatment has been performed by establishing a colour removal degree, that was calculated using the relation:

$$Colour\ \ removal\ \ degree = \frac{C_{untreated} - C_{treated}}{C_{untreated}} \times 100$$

where:

$C_{untreated}$ represents the concentration of the untreated dye solution;

$C_{treated}$ represents the concentration of the dye solution treated with sodium dithionite;

2. RESULTS AND DISCUSSIONS

To analyse the pH influence solutions of 10 mg/l dye have been treated for 30 minutes at 80^0C with 1 g/l dithionite at different pH value. The results obtained for all the three dyes (figure 1), show that increasing pH values favor the dye degradation.

This confirms the known facts, that the normal potential of the system $S_2O_4^{2-} / 2SO_3^{2-}$ is higher in alkaline conditions then in acid or neutral conditions (-1,12 V against -0,082V, -0,527 mV respectively). It is to emphasize that in the case of the acid dyes the degradations conducted in neutral conditions gave very good result, almost identical to the results obtained in alkaline medium.

The dosage of the dithionite is an important parameter of the colour removal process, which has to be associated with the concentration of the dye in the wastewater. To analyse the influence of dithionite concentration treatments were realized for solutions of 1 to 20 mg/l dye treated for 30 minutes at 80^0C with 0.5 to 6 g/l dithionite at pH 12.

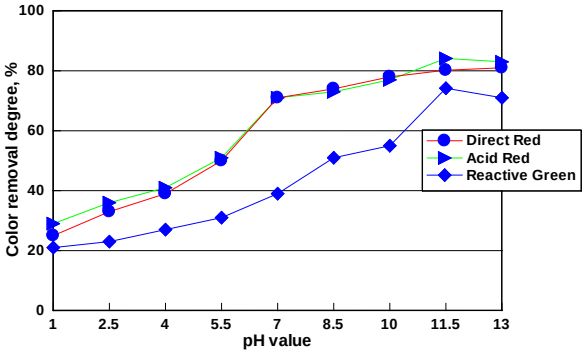


Figure 1. pH influence over discoloration.

The tests prove that the discoloration rate was improved following the increase of the dithionite concentration, especially until 4 g/l, and this effect in extremely pregnant in the case of the reactive dyes wastewater, as it can be seen in figures 2 – 4.

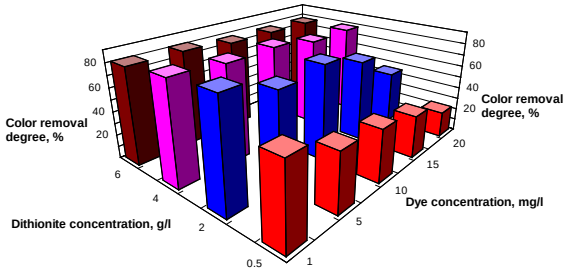


Figure 2. Discoloration degree for Direct Red 80.

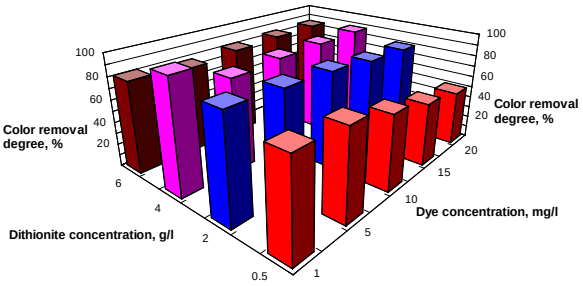


Figure 3. Discoloration degree for Acid Red 6.

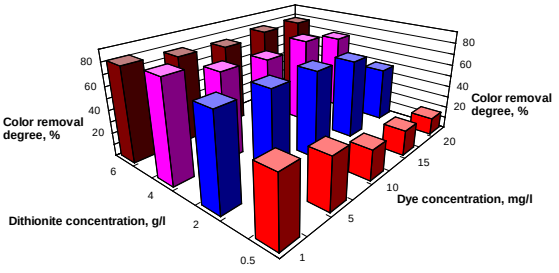


Figure 4. Discoloration degree for Reactive Red 45.

A dosage greater then 4 g/l dithionite does not improve the colour removal, and even worsens it in the case low dyes concentrations.

To analyze the effect of temperature and time treatments were realized for solutions of 10 mg/l dye, 5 – 60 minutes at temperature between 20 and 98^{0}C with 2 g/l dithionite at pH 12.

As it can be observed in figures 5 – 8, the temperature played an important role in the efficiency of the discoloration treatment.

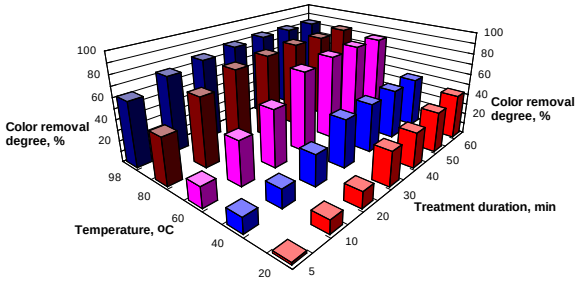


Figure 5. Discoloration degree for Direct Red 80

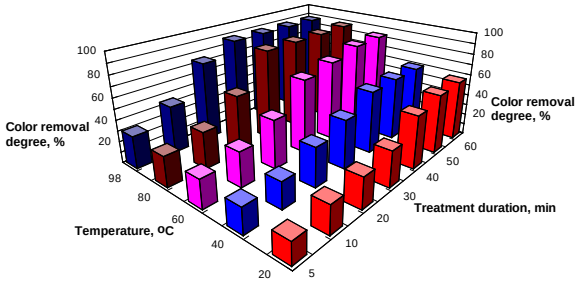


Figure 6. Discoloration degree for Acid Red 6

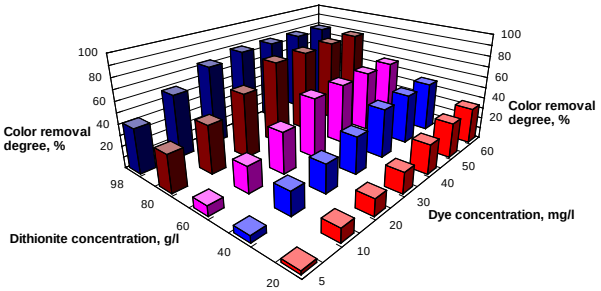


Figure 7. Discoloration degree for Reactive Red 45

At temperatures under 40^{o}C, the colour removal degree is low, and its maximal values are obtained beginning with 75^{o}C; further temperature rises seem to have an insignificant effect.

In what concerns the treatment duration, in the case of the acid dye 10 minutes are enough for obtaining the maximal discoloration effect, but in the case of the other two dyes that we have studied, at least 30 minutes of treatment are required.

In order to compare the reductive treatment with the H_2O_2 treatment, 10 mg/l solutions of the same there dyes have been treated with 1 ml/l H_2O_2 (30%) in the presence of a the Fe^{2+} salt, at a Fe^{2+}:H_2O_2 ratio of 1:20, pH = 10, conditions that proved to be efficient [1]; the results were compared with the best results obtained for the same solutions in the reductive treatment.

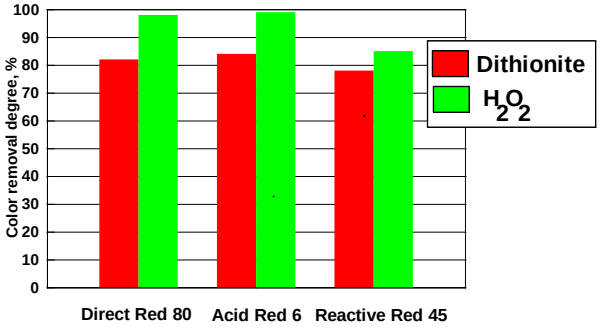


Figure 8. Discoloration degree

Figure 8 shows that the oxidative treatment removes the residual colour to a higher extent, especially in the case of the direct and acid dye, when the colour is practically completely removed.

3. CONCLUSIONS

In some special cases, the use of sodium dithionite may represent a solution for the colour removal of the textile wastewater. The results depend heavily on the pH value, and the needed dithionite concentration is relatively low, depending on the dyestuff concentration. The influence of the temperature is important, and this is why on site treatment is highly recommended.

In all cases, important drawbacks of the sodium dithionite have to be taken into consideration: handling difficulties and potential generation of toxic gases, as the contact with small quantities of water causes spontaneous ignition, and the resulting decomposition causes sulphur dioxide to be released. The solutions may decompose by oxidation when exposed to air to form sodium sulphite and sodium sulphate, that undergo exothermic decomposition if exposed to temperatures exceeding ca. 80 °C for a long period.

Another disadvantage is the COD increase, as each gram of sodium dithionite adds 210 mg O_2 of COD, and the important increase in the sulphate content of the treated wastewater.

References

1. Bertea, A., *Textile Wastewater Decolorization with Hydrogen Peroxide, Bulletin of the Technical University of Iasi, 1996, volume XLII, p. 93 – 97.*

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