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Colour elimination through oxidation technologies in leather finishing industry waste waters

D. Prats, P. Varó, C. Yagüe & M. Rodríguez
Department of Chemical Engineering,
University of Alicante, Spain.

Abstract

The leather finishing industries consume great amounts of water and therefore, important producers of liquid effluents. Waste treatment is mostly limited to homogenisation and sedimentation, although in some cases chemical coagulation and sludge digestion is carried out. This is normally insufficient to comply with the existing legislation.

Colour is one of the pollutants common to all these industries. This is a parameter normally difficult to eliminate and furthermore, greater restrictions in the legislation relating to the discharge of industrial residual effluents are being contemplated more and more.

In this present work, ozone and ozone with hydrogen peroxide have been studied in order to determine which of them are more effective in the reduction of the colour present in the waters discharged by the leather finishing industries.

1 Introduction

The discharge of dyes in waste water is one of the biggest problems in the leather- finishing industries. Dye in the water does not allow light and oxygen to pass through and this as a consequence, disfavours the development of micro-organisms and biological treatment.

Dye molecules are formed by one or more chromophore groups, (groups of atoms with unsaturated bonds which give colour to the molecule. There are around 12 types of chromophore groups, the most common being the azo group that includes 60–70% of all the textile dyes produced; this is followed by the group type quinone [1] .

Due to the fact that dyes are resistant to degradation, it follows that only a small amount is eliminated with activated sludge systems [2,3,4] or with different combinations of chemical, physical and biological processes [5-8].

The current tendency is to decrease the concentration of contaminant substances in industrial waste. Consequently, more and more controls are being established regarding the quality of discharged water, which in general makes the pre-treatment of the water necessary.

1.1 Production process in a leather-finishing shoe factory

Leather-finishing comprises a series of treatments to which the tanned leather is subjected to, so as to provide it with the properties required according to each market. In general terms, finishing comprises all the processes following tanning, that is; bleaching, scouring, dyeing, re-tanning and lubrication, treatment of surfaces with pigments and pestilents.

The leather-finishing industries work use a system of production by charges, this enables the waste to be discharged in a discontinuous state.

It has been estimated that the amount of water used by a leather finishing factory with a production of 1,000,000 kgs skins p.a. is approximately 15,000 m^3/year. During the finishing process, an important quantity of water is consumed in the following stages; neutralisation (5.300 m^3/year), dyeing (340 m^3/year), lubrication (1014 m^3/year), fixing (680 m^3/year), final washing (6900 m^3/year) and surface treatment (320 m^3/year)[9].

The processes in which discharge of effluent liquids is produced are draining , neutralization, fixing, final washing, drying and treatment of the surface. Discharged together with the water, are those reactives used that have not been exhausted in the baths.

1.2 Advanced oxydation treatment in the elimination of colour

Much of the literature has characterized the reactivity of ozone toward several single-dye solutions- It has been shown that ozone possesses and excellent decolorizing capability and that the biodegradability of ozone-treated wastewater can be increased [10,11]. However, most of the wastewater from actual dye manufacturing and textile dyeing and finishing factories is composed of mixed-dye- solutions. The ozonation of a mixed-dye solution is considerably more complicated than of a single-dye solution.

Ozone removes the color from textile wastewater by oxidizing or breaking up the complex compounds and chromophores that form dyes used to color natural as when as synthetic fibers and fabrics. The color is removed when the ozone cleaves the –C=C– bonds, the –N=N– bonds and heterocyclic and aromatic rings [12]. Some classes of dyes respond more readily to oxidation by ozone than others. The reactive dyes are degrades to

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the greatest extend and ozonation is moderately successful in treating wastewaters containing sulfur, azonic and basic dyes. However, disperse dyes have poor response to ozone [13].

Ozonization for removal might be a promising process for the following reasons: (1) no chemical sludge is left in the treated effluent; (2) ozonation has the potential to accomplish both color removal and organic reductions in one step; (3) less space is required, and its is easily installed on site; (4) their is less danger, since no stock hydrogen peroxide or other chemical is required on site; (5) its is easily operated; and (6) all residual ozone can easily be decomposed to oxygen and water .

The decomposition rate of ozone is affected by pH, temperature and ozone concentration. During the ozonation process, dyes lose their color by the oxidative cleavage of the chromophores. The cleavage of carbon-carbon double bonds and other functional groups, which have high electron densities will shift the absorption spectra of the molecule out of the visible region.

Hydrogen peroxide has been incorporated into the ozonation treatment process to enhance its effectiveness. Addition of peroxide lowered the reaction time and increased the efficiency of the decolorization especially with disperse dyes [14].

2 Materials and methods

2.1 Materials

The azo dyes Carbon Derma NBS (Direct Black 168, DB-168), Azul Coracido 2B-175, (Acid Black 241, AB-241), Pardo Coracido CG (Acid Brown 83, AB-83) and quinone dye Pardo Derma D2R (Acid Brown 191, AB-191).Commercial grade dyes obtained from Clariant Iberica, (Spain) a know concentration of the dye was prepared in deionized water and used for all studies. The molecular structure of reactive dyes are elicited in Figure 1, whereas color index and studied λ of the reactive dyes are illustrated in Table 1.

The simulated dye solutions prepared to investigate the effects of dye bath constituents on treatment efficiency were made typical amounts of dye at concentrations normally encountered in real case exhausted dye bath effluents.

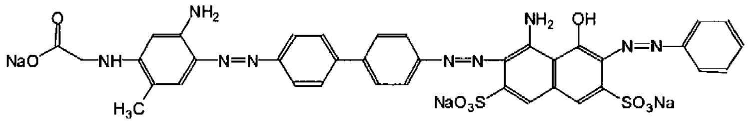
All experiments with ozone were carried out in a 1000 mL contact tower. The ozone was generated from the ozone generator marca Iberozono, model 80, and driven by an air pump with adjustable flow rates. A mechanical stirrer worked with the gas diffuser to achieve sufficient recirculation of the dye solution, so a favorable gas transfer rate was expected [15].

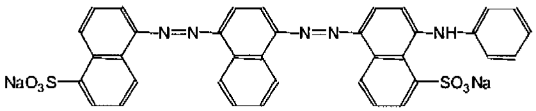
Dye concentrations 40 mg/L and saturated ozone concentrations in excess (by adjusting air-flow rate) were applied to investigate the reaction kinetics of dye ozonation. Samples were collected from the contact tower at times of 0, 5, 15, 60 min, the residual dyes were analyzed by spectrophotometric for quantification. Four initial pHs of 2, 4, 8 and 10 adjusted by sulphuric acid were used to examine the consequence of the initial pHs to the overall reaction rates.

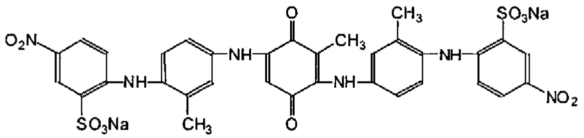
Table 1.Main characteristics of dyes

Dye	Concentration (mg(L)	Color index	λ (nm)
Carbon Derma NBS	40	Direct Black 168	490
Blue Corácido 2B-175	40	Acid Black 24	550
Brown Corácido CG	40	Acid Brown 83	443
Brown Derma D2R	40	Acid Brown 191	381

In the test with O_3/H_2O_2, the procedure followed and the material used was the same as that for O_3; the only difference being that in each experiment, a certain amount of hydrogen peroxide was added (30% p/v) in order to check whether there was an improvement in the elimination of colour. Four amounts of H_2O_2 were studied; 0, 6, 30 y 60 mg H_2O_2/L solution of dye, and aliquot parts of a sample treated with ozone were taken every 5 minutes during a period of 1 hour.


A) CARBON DERMA NBS / DIRECT BLACK 168


B) AZUL CORACIDO 2B-175 / ACID BLACK 24


C) PARDO DERMA D2R / ACID BROWN 191

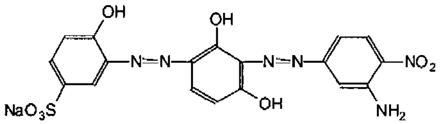

D) PARDO CORACIDO CG / ACID BROWN 83

Figure 1: Dyes studied

2.2 Color measurement

The color of the initial and treated samples was determined by absorbance measurements using a Shimadzu UV-1601 model double-bean spectrophotometer. The light absorbance at the characteristic wavelength of the samples, eg., A_{490} (Direct Black 168), A_{550} (Acid Black 241), A_{443} (Acid Brown 191) and A_{381} (Acid Brown 83), were measurement to follow the progress of decolourization during ozonation. The percent color removal was determinated by using the integrated absorbance of the initial sample, $t=0$, and the integrated absorbance of the sample after being treated for i minutes, $t=i$. Equation 1 shows the formula for percent color removal.

$$\%Color\ Removal = \left(1 - \frac{absorbance_{t=i}}{absorbance_{t=0}}\right) x100 \qquad (1)$$

2.3 Kinetic evaluation

During the application of avanced oxidation processess, decolorization of the reacting samples exhibited decay. Assuming first order reaction kinetics for the synthetic dyehouse effluent matrix, the decolorization rate constant was determinated from slope of the semilogaritmic plot of color versusadvanced treatment time, respectively, in accordance with the kinetic equation;

$$\ln\left(\frac{A}{A_o}\right) = K_d \times t \qquad (2)$$

where K_d stands for the first order decolorization rate constant (in 1/min).

3 Results and discussion

3.1 O_3 Treatment

As can be observed in Figures 2 to 5, by treating the four dyes with ozone, practically 100% colour elimination is obtained with contact at long intervals of time.

It can be tested that at short intervals of reaction time (5-15 minutes), a greater elimination of colour at basic pHs (8 and 10) is obtained than at acid pHs (2 and 4); nevertheless, in the case of the dye Brown Derma D2R (Acid brown 191) only, it was observed that, both at short and long intervals of time, the best reduction of colour is obtained at pHs. Whereas with the dyes Carbon Derma (Direct black 168), Bluel Coracido 2B-175 (Acid Black 241) and Brown Coracido CG (Acid Brown 83) the best results are obtained at long intervals with acid pHs.

As can be seen from the results, high elimination of colour is obtained using ozone; this is due to the oxydation or break down of the complex compounds and chromophores that form the dyes [16].

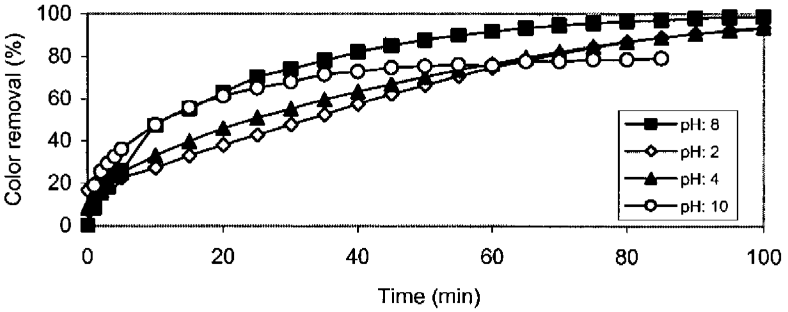


Figure 2: Color removal Carbon Derma NBS with O^3 treatment

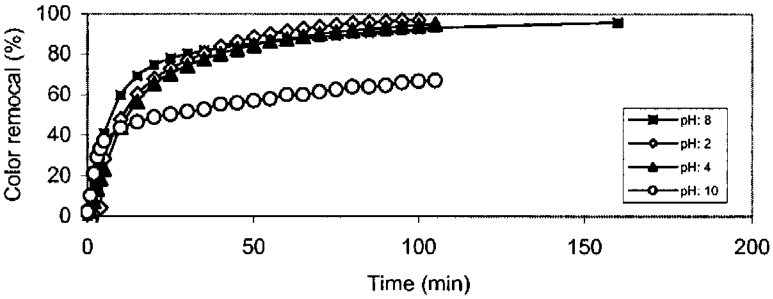


Figure 3: Color removal Blue Coracido 2B-175 with O^3 treatment

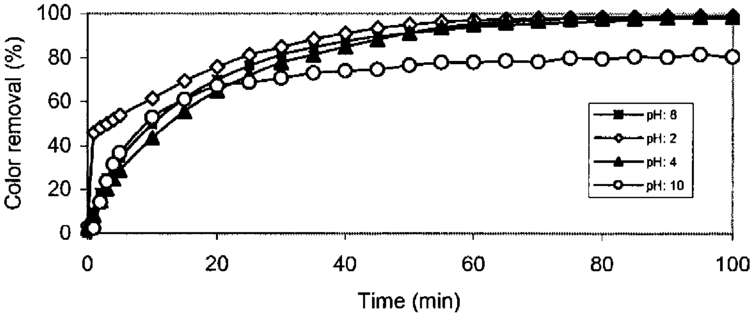


Figure 4: Color removal Brown Coracido with O^3 treatment

The pH of the solution alters the chemical composition of the ozone so, the hidroxile free radicals are formed by the decomposition of the ozone at high pH whereas the molecular ozone remains as the main dye at low pHs [17], this explains the different behaviour of the ozone at different conditions of pH

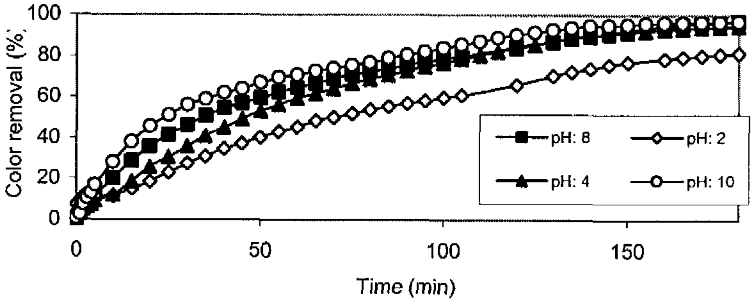


Figure 5: Color removal Brown Derma D2R with O^3 treatment

3.2 O_3 /H_2O_2 Treatment

In accordance with the results obtained and shown in Figures 6 - 9, a general tendency towards a greater colour reduction can be observed at short periods of time (4, 5 minutes), with high concentrations of hydrogen peroxide; reaching reductions of between 36-52% for the dyes Carbon Derma NBS, Blue Coracido 2B-175 and Brown Coracido CG and 19% for the dye Brown Derma D2R (which is much more difficult to break down).

This tendency is reversed after 5 minutes reaction time; a greater reduction of the colour is obtained with low concentrations of H_2O_2, with colour reductions close to 90% after 1 hour of treatment for the dyes Carbon Derma NBS DB-168 (Direct Black 16), Blue Coracido 2B-175 (Acid Black 241), and Brown Coracido CG (Acid Brown 83), whereas for the dye Brown Derma D2R (Acid brown 191, AB-191) a reduction of only 40% is obtained.

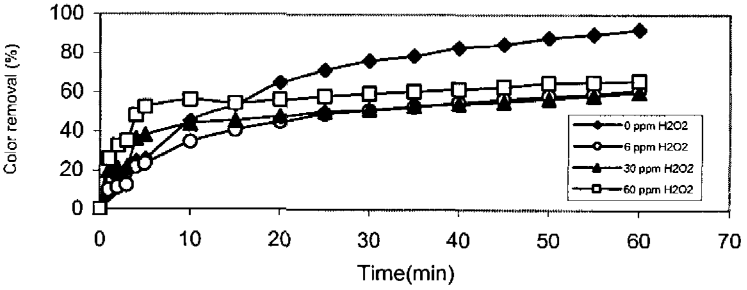


Figure 6: Color removal Carbon Derma with O^3/H_2O_2 treatment

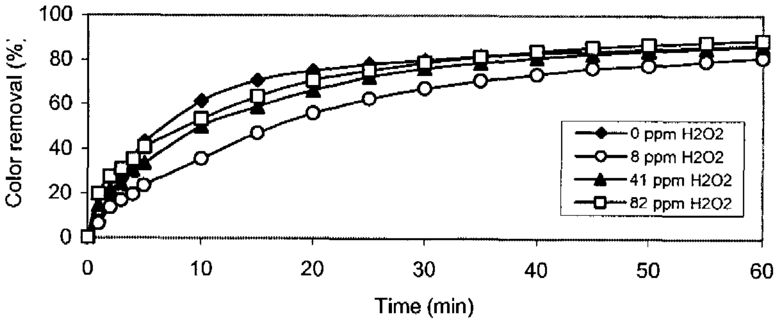


Figure 7: Color removal Blue Coracido with O^3/H_2O_2 treatment

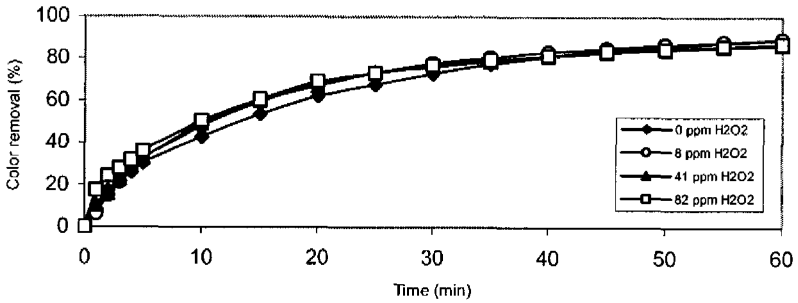


Figure 8: Color removal Brown Coracido with O^3/H_2O_2 treatment

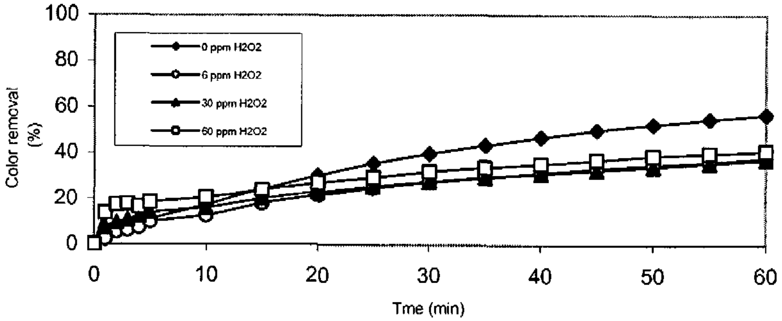


Figure 9: Color removal Brown Derma with O^3/H_2O_2 treatment

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Treatment with ozone permits reductions close to 100% to be obtained, both for the dyes in the chromophore group and the azo group. Treatment with ozone and hydrogen peroxide does not improve the results obtained from treating water only with ozone at long intervals, nevertheless it does allow greater reductions of colour at short intervals of time (5-15 minutes).

References

[1] Vandevivere, P.C., Bianchi, R. & Verstraete, W. Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies. *J. Chem. Technol. Biotechnol.*, **72**, pp. 289-302, 1998.

[2] Shaul, G.M., Dempsey, C.R., Dostal, K.A. & Lieberman, R.J. Fate of azo dyes in the activated sludge process. *Proc. of the 41st Purdue University Industrial Waste Conference*, 603-611, 1985.

[3] Paga, U. & Taeger, K. Development of a meted for adsorption of dyestuffs on activated sludge. *Wat Res*, **28**, pp. 1051-1057, 1994.

[4] Panswad, T. & Luangdilok, W. Decolorization of reactive dyes with different molecular structures under different environmental conditions. *Wat. Res.*, **34(17)**, pp. 4177-4184, 2000.

[5] Arslan, I. & Balcioglu, I.A. Effect of common reactive dye auxiliaries on the ozonation of dyehouse effluents containing vinylsulphone and aminochlorotriazine dyes. *Desalination*, **130**, pp-61-71, 2000.

[6] Chinwetkitvanich, S., Tuntoolvest, M. & Panswad, T. Anaerobic decolorization of reactive dyebath effluents by two-stage UASB system with tapioca as a co-substrate. *Wat* Res, **34(8)**, pp- 2223-2232, 2000.

[7] Lin, S.H. & Lin, C.M. Treatment of textile waste effluents by ozonation and chemical coagulation. *Wat. Res*, **27(12)**, pp. 1743-1748, 1993.

[8] Lin, S.H. & Liu, W.Y. Treatment of textile wastewater by ozonation in a packed-bed reactor. *Environ. Technol.*, **15**, pp. 299-311, 1994.

[9] Yagüe, C. *Eliminación de color en aguas de industria de curtición de piel mediante tecnología de oxidación.* (Doctoral thesis). Alicante: Universidad de Alicante. 2001.

[10] Beltrán, F., Encinar, J. & .Garcia-Araya, J. Oxidation by ozone and chlorine dioxide of two distillery wastewater contaminants, gallic acid and epicatechim. *Wat. Res.*, **27**, pp. 1023, 1993.

[11]Gähr, F.,Hermanutz, F, & Oppermann, W. Ozonation an important technique to comply with new German laws for textile wastewater treatments. *Wat Sci Tech*, **30**, pp. 255-263, 1994.

[12]Strikland, A & Perkins, W. Decolorizartion of continuos dyeing wastewater by ozonation. Textile Chemist and Dolorist, **27(5)**, pp.11-15, 1995.

[13]Churcheley, J. Removal of dyewaste colour from sewage efluent the use of a full scale ozone plant. Wat. Sci. Technol, **30(3)**, pp. 275-284, 1994.

[14]Glace, W & Kang, J. Advanced oxidation proceses. Description of a kinetic model for the oxidation of hazardous materials in aqueous media

with ozone and hydrogen peroxide in a semibath reactor. Ind Eng Chem. Res. **(28)**, pp. 1573-1587, 1989.

[15] Lin, S & Yen, K. looking to treat wastewater? Try Ozone. Chem Eng, **100(5)**, pp. 112-116, 1993.

[16] Lin, S. & Liu, W. Continuous treatment of textile water by ozonation and coagulation. J.Environ. Eng., **120(2)**, pp.437-446, 1994.

[17] Liakou, S., Kornaros, M. & Libertaos, G. Pre-treatment of azo dyes using ozone. Wat Sci Technol, 36(2-3), pp.155-163, 1997.