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On line spectrophotometric method for the monitoring of colour removal processes

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Abstract

A spectrophotometric method for the monitoring of a discoloration process, based on the calculation, in CIELAB colour space, of colour differences from visible spectra, has been developed. This procedure, simple and rapid, has been tested on standard azo dyes solutions (Trypan Blue and Red Remazol) and an industrial wastewater (paper industry). Advanced oxidation processes, vacuum UV photolysis and photo-oxidation in presence of hydrogen peroxide, have been studied. A discoloration yield (τ) has been defined from colour differences and a minimal value of this parameter (τ_{min}) has been calculated according to the colourless zone (Standard Method 2120C). When τ value reaches τ_{min} value, studied sample is colourless and the treatment process may be stopped. Moreover, the proposed procedure allows to detect any trouble shooting during the discoloration process ($d\tau/dt = 0$ when $\tau < \tau_{min}$). The proposed procedure requires only the acquisition of UV–visible spectra versus time, is easy to implement on line and gives real time information.

Mots-clé : UV–visible spectrophotometry; Colour monitoring; Oxidation process; Discoloration yield

1. Introduction

Coloured industrial wastewater may require colour removal before discharge in the receiving medium. In compliance with regulation, wastewater colour measurement or colour difference determination is needed, in reference to an acceptability level.

Currently accepted spectrophotometric methods are available to determine colour. Standard EN ISO 7887 (Section 3) [1] measures the sample absorbance at three wavelengths in the visible range. Spectral absorption coefficients, α_λ, are defined at 436, 525 and 620 nm which allow to calculate colour removal yield at a specific wavelength.

Standard Method 2120 (Section 3) [2] expresses colour in term of dominant wavelength (hue), luminance and purity (saturation). Chromaticity coordinates, x and y, are calculated from the three stimuli values, X, Y and Z related to red, green and blue light rays. Y is the percent luminance. Located point (x, y) on a chromaticity diagram allows the determination of the dominant wavelength and the purity. The colour space CIE x, y, Y is not uniform.

Another colour space, CIELAB or CIE $L^*a^*b^*$, has been developed by the CIE in 1976, based on the differences of three elementary colour pairs: red-green, yellow-blue and black-white [3]. Hue and chroma are defined by the coordinates a^* and b^* which can have both positive and negative values. The third characteristic, brightness, is

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designated by L^* with scale values ranging from 0 (black) to 100 (white).

Thus, in the approximately uniform CIE $L^*a^*b^*$ space, colour differences can be calculated as a third dimension distance between two samples [7]. This parameter appears to be well fitted for the monitoring of a colour removal process and for the determination of the time after which the process may be stopped.

Various optical measurements may be applied to separate the variables that affect color removal, giving a better understanding of a discoloration process [8,9].

2. Methodology

The proposed methodology is based on the calculation of the trichromatic components (X, Y, Z) according to Standard Method 2120C. Ten visible wavelengths are used for each co-ordinates in the CIE x, y, Y space, with:

$$x = X/(X+Y+Z)$$
$$y = Y/(X+Y+Z)$$

The formulas for the transformation of X, Y, Z to CIELAB approximately uniform space are based on [3]:

$$L^* = 116 \times \left(\frac{Y}{Y_n}\right)^{1/3} - 16 \qquad \text{if } \left(\frac{Y}{Y_n}\right) > 0.008856$$

$$\text{else} \quad L^* = 903 \times \left(\frac{Y}{Y_n}\right)$$

$$a^* = 500 \times \left[\left(f\frac{X}{X_n}\right) - f\left(\frac{Y}{Y_n}\right)\right]$$

$$b^* = 200 \times \left[f\left(\frac{Y}{Y_n}\right) - f\left(\frac{Z}{Z_n}\right)\right]$$

$$\text{with } f\left(\frac{X}{X_n}\right) = \left(\frac{X}{X_n}\right)^{1/3} \quad \text{if} \left(\frac{X}{X_n}\right) > 0.008856 \text{ else}$$

$$f\left(\frac{X}{X_n}\right) = 7.787 \times \left(\frac{X}{X_n}\right) + \frac{16}{116}$$

The same conditions are applied for $f(\frac{Y}{Y_n})$ and $f(\frac{Z}{Z_n})$.

The n index is referred to the chosen reference illuminant.

Colour difference between two samples, ΔE^*, is measured as a distance between two points and is determined by the following equation:

$$\Delta E^* = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2}$$

The aim of the treatment process being theoretically the total discoloration, ΔE^* values are calculated between a sample after a treatment time, t, and a colourless reference (for which $L^* = 100$, $a^* = 0$, $b^* = 0$). This reference sample corresponds to the rectangle central point of the colourless zone according to Standard Method 2120C.

A discoloration yield, τ, is determined as:

$$\tau = \frac{\Delta E_0^* - \Delta E_t^*}{\Delta E_0^*}$$

with:

ΔE^*_0 = colour difference between the initial sample and the colourless reference sample,

ΔE^*_t = colour difference between the sample after treatment time (t) and the colourless reference sample.

When τ value is close to 1, the sample becomes colourless. A minimal value of τ, $\tau_{\min}$, has been calculated so that the treatment process might be thus stopped. This value corresponds to the colour difference between a sample corresponding to the colourless zone limit according to Standard Method 2120C ($x = 0.312$ and $y = 0.321$) and the colourless reference:

$$\tau_{\min} = \frac{\Delta E_0^* - \Delta E_{\min}^*}{\Delta E_0^*}$$

The $\Delta E*_{\min}$ value is 2.642 with C illuminant as reference.

So, $\tau_{\min}$ depends on the distance between the studied sample and the colourless reference. When $\tau > \tau_{\min}$, treated sample is colourless.

A kinetic study allows to detect a potential incident during the treatment process ($d\tau/dt = 0$).

The synopsis of the treatment process is shown in Fig. 1.

3. Experimental

Photolysis and photooxidation have been tested as colour removal processes. Experiments were carried out in a photochemical reactor (irradiated volume = 7.5 mL) formed by a low-pressure mercury lamp (PenRay® UV-P, electrical power = 45 W), emitting at 253.7 and 184.9 nm principally, surrounded by a Suprasil quartz coil (Fig. 2). The photonic flux at 253.7 nm is 1.5 10^{-6} Einsteins s^{-1}.

The UV–visible spectra have been acquired between 200 and 800 nm with a Secomam Anthelie spectrophotometer (Suprasil quartz cell; pathlength = 2 or 10 mm; scan speed = 1800 nm min^{-1}).

Experiments were conducted with synthetic solutions of two azoic dyes, purchased from Aldrich, Red Remazol or Reactive Red 23 (CI: 16202) and Trypan Blue or Direct Blue 14 (CI: 23850). Fig. 3 gives their chemical structure. An industrial wastewater was tested, too.

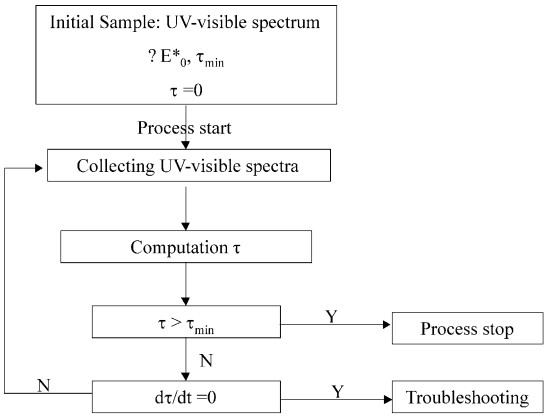


Fig 1. Treatment process synopsis.

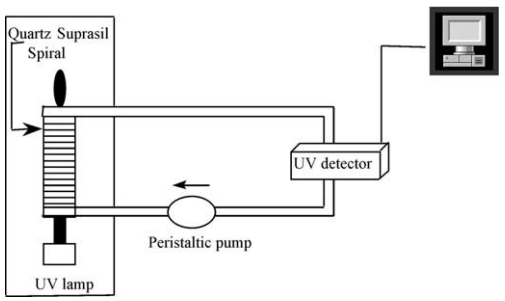


Fig. 2. Photochemical reactor.

4. Results and discussion

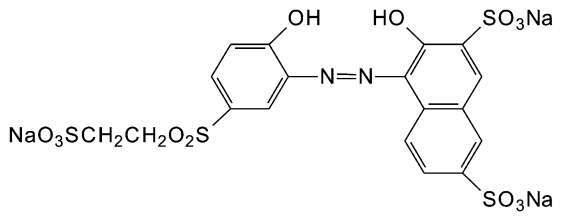
Previous studies showed that UV irradiation [4] and UV/H_2O_2 oxidation process [5,6] can be used to discolour wastewater. These two techniques have been tested with the studied azoïc dyes.

4.1. Photolysis and photoxidation of azoïc dye solutions

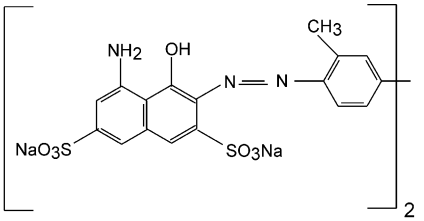
4.1.1. Spectral characteristics

Photolysis tests have been carried out on synthetic aqueous solutions of Trypan Blue (100 mg l^{-1}) and Red Remazol (100 mg l^{-1}). The evolution of visible spectra according to treatment time are presented in Fig. 4.

It can be observed that absorbance in the visible range decreases with treatment time. After 4 min of photolysis, 89% of the coloration (measured by



Red Remazol



Trypan Blue

Fig. 3. Chemical structures of Red Remazol and Trypan Blue dyes.

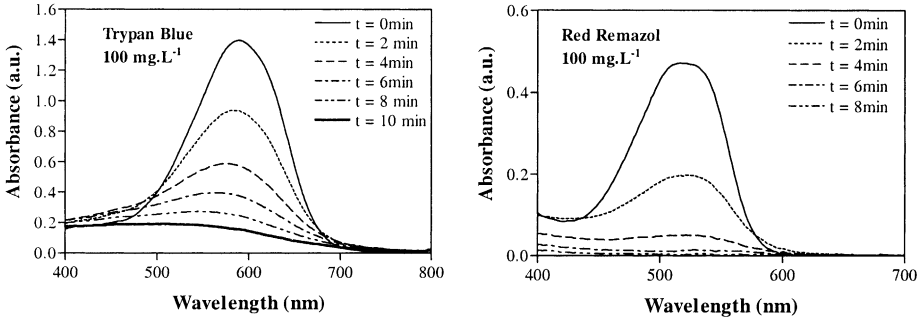


Fig. 4. Evolution of Trypan Blue and Red Remazol visible spectra according to irradiation time during photolysis (water, 100 mg l^{-1}, path length: 2 mm).

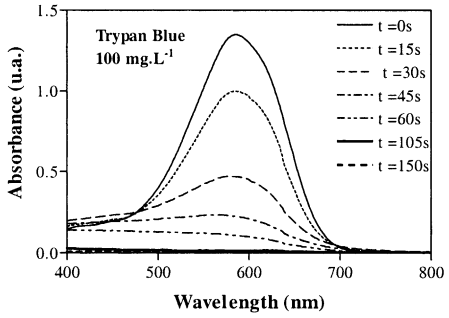


Fig. 5. Evolution of Trypan Blue visible spectra according to irradiation time during photooxidation (water, 100 mg l^{-1}, path length: 2 mm).

Table 1
Colorimetric parameters of Red Remazol solution (100 mg l^{-1}, path length: 2 mm)

L^*	83.84
a^*	41.26
b^*	−4.03
ΔE_0	44.5
τ_{min}	0.9406

the absorbance at 519 nm) is removed for Red Remazol solution. In the same time, only 59% of colour removal is obtained, for Trypan Blue dye ($\lambda = 592$ nm). Moreover, an hypsochromic shift of Trypan Blue absorption peak can be noticed.

The discoloration kinetic of Trypan Blue solution can be improved by addition of hydrogen peroxide (photooxidation). Fig. 5 shows the results obtained with a concentration of hydrogen peroxide of 7.5 10^{-3} mol l^{-1}.

As expected, no more significant absorption is observed in the visible range, after 2.5 min of irradiation.

4.1.2. Kinetic study

For this purpose, L^*, a^*, b^* coordinates in the CIELAB space have been calculated. Colour difference, ΔE_0, and τ_{min} are given, for Red Remazol dye (Table 1).

The monitoring of the photolysis of Red Remazol dye according to irradiation time is shown in Fig. 6. Moreover, a simulation of troubleshooting in the process has been realised: the source of irradiation has been cut off during 15 min.

Total colour removal is obtained after 300 s of photolysis (A). At this time, τ reaches τ_{min} value (0.9406): the treatment process can be stopped. Over this time, the value of τ is still increasing and the value of $d\tau/dt$ is still decreasing. Indeed, small variations on visible spectra still occur but the resulting colour difference is not perceptible by human eye. Studied sample approximates to the colourless reference.

In case of troubleshooting (B), as expected, the discoloration yield, τ, remains uniform during the lamp stopping (right part). In the same time, its derivative, $d\tau/dt$, tends to zero, showing the relevance of these parameters for the monitoring of a colour removal process.

Concerning Trypan Blue dye solution (100 mg l^{-1}), kinetic study has been realized for photooxidation tests. Two parameters have been taken

into account: the pH of the solution and the concentration of hydrogen peroxide. Fig. 7 collects the results obtained at pH = 4 and 9.

Total colour removal is obtained for the same time of irradiation (nearly 150 s). In the studied range (pH = 4–9), pH seems to have no significant effect on photooxidation: the time after which the process may be stopped remains close to 135 s. A pH value over 9.0 is not interesting because hydrogen peroxide dissociates into hydroperoxyde anion (HO^{2-}) which is an hydroxyl scavenger [6].

On the contrary, hydrogen peroxyde concentration has an impact on the discoloration time. Five concentrations have been tested. Fig. 8 shows the results for two of them: 2.5 10^{-3} and 10.10^{-3} mol l^{-1}.

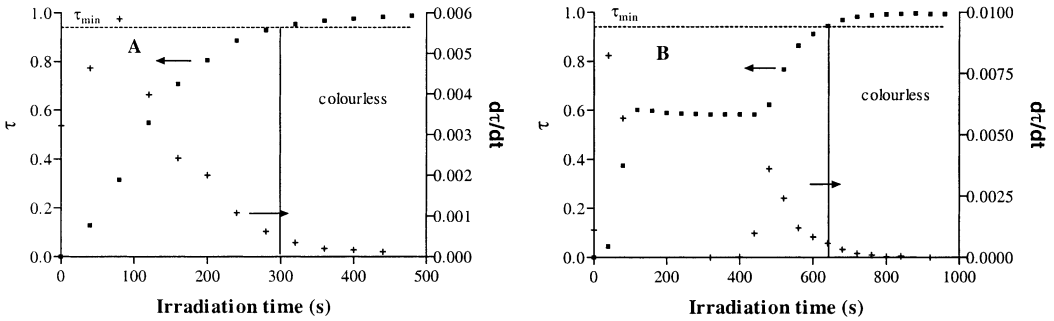


Fig. 6. Monitoring of Red Remazol dye photolysis according to irradiation time, with (B) or without (A) trouble shooting (water, 100 mg l^{-1}, path length: 2 mm).

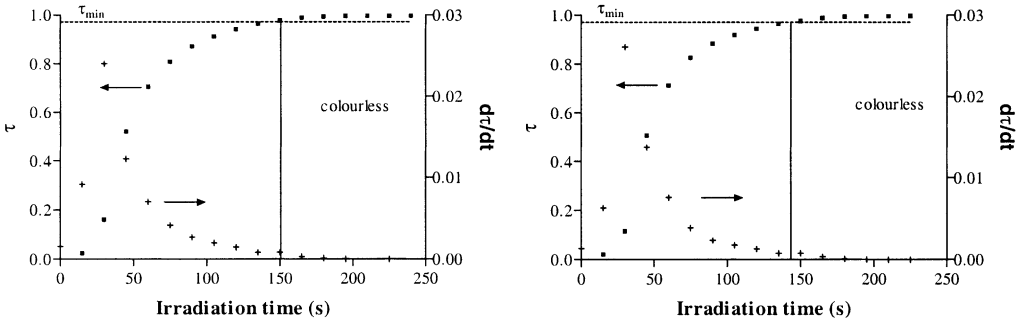


Fig. 7. Monitoring of Trypan Blue dye photooxidation (100 mg l^{-1}) at two pH values (left part: pH = 4; right part: pH = 9).

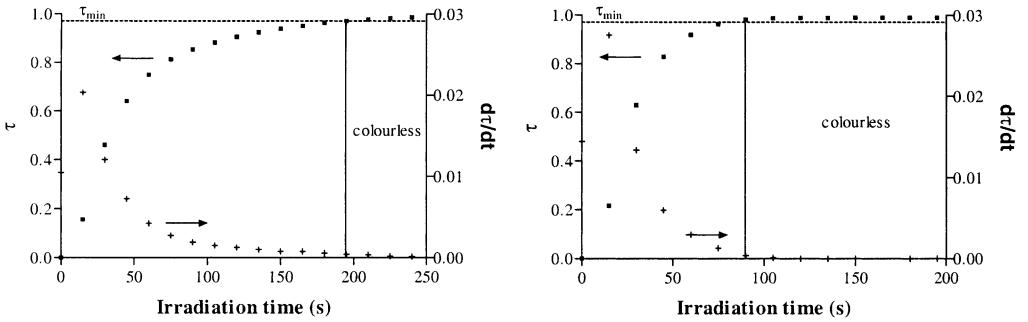
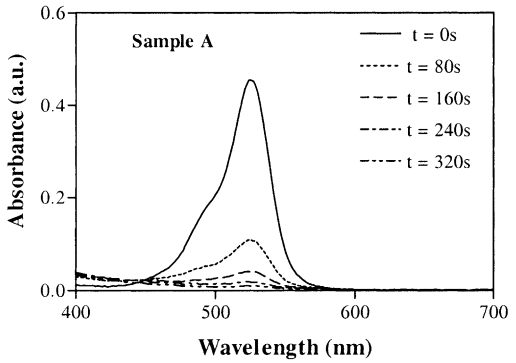


Fig. 8. Monitoring of Trypan Blue dye photooxidation (100 mg l^{-1}, pH = 6) at two hydrogen peroxide concentrations (left part: 2.5 10^{-3} mol l^{-1}; right part: 10.10^{-3} mol l^{-1}).



Colorimetric parameters :

$L^* = 90{,}95$

$a^* = 30{,}17$

$b^* = -8{,}69$

$\Delta E_0 = 32{,}67$

$\tau_{min} = 0{,}9191$

Fig. 9. Evolution of sample A visible spectra according to irradiation time (water, path length: 2 mm) and colorimetric parameters.

Table 2 collects the data for the studied concentrations.

It can be observed that the initial concentration of hydrogen peroxyde has an important impact on the discoloration kinetic. As the hydrogen peroxyde concentration increases the photooxidation efficiency is improved. A maximum is obtained with a 10^{-2} mol l^{-1} hydrogen peroxide concentration value.

4.2. Photolysis of industrial wastewater

The same experiment has been conducted on an industrial waster, sample A, coming from a paper industry which colours paper pulp for specific applications. The resulting coloured wastewater is pretreated by aeroflottation. Fig. 9 presents the evolution of spectral characteristis during photolysis and colorimetric parameters of sample A, after filtration.

Discoloration of sample A is rapidly achieved by photolysis (240 s) as shown in Fig. 10. The proposed procedure seems to be also fitted to the discolouration of industrial wastewater.

Table 2
Discoloration time of Trypan Blue photooxidation (100 mg l^{-1}) according H_2O_2 concentration

$[H_2O_2]$ (mol l^{-1})*10^{-3}	Discoloration time (s)
2.5	195
5	120
7.5	105
10	90
20	90

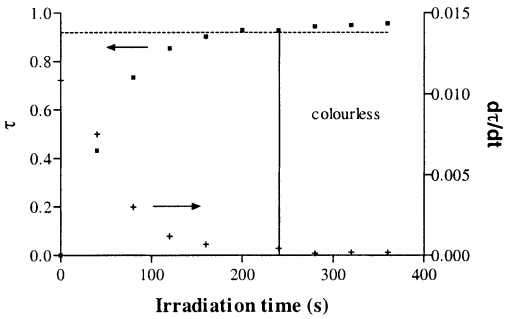


Fig. 10. Monitoring of sample A photolysis.

5. Conclusion

A new method for the monitoring of a discoloration process, based on the calculation of colour differences from visible spectra, has been developed. This procedure, simple and rapid, allows to monitor any colour removal process and requires only the on line acquisition of visible spectra versus treatment time.

The absorbance in the visible range is measured at 10 wavelengths, taking into account potential any spectral modification during the treatment. This makes the method more robust than EN ISO 7887 Section 3 standard which uses only three wavelengths.

The proposed procedure allows to point out any troubleshooting during the colour removal treatment and to stop the process when the treated sample becomes colourless.

For highly coloured samples for which absorbance in the visible range may lead to saturation, the actual procedure has to be adapted. Nevertheless, most discharge waters are not very concentrated.

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