Direct Photolysis of an Azo-Dye, Eriochrome Black T

Radia Tafer and Abdelaziz Boulkamh
Laboratoire des Sciences et Technologie de l'Environnement,
Université Mentouri, Route de Aïn El Bey, Constantine, Algérie

Abstract: The direct photolysis of a water soluble organic pollutant, the azo-dye Eriochrome Black T (EBT), was studied. The obtained results indicate that EBT elimination from an industrial effluent may be efficiently achieved by irradiation with an artificial UV light, but mineralization takes much longer times. In a pure aqueous solution, the reaction induces a pH decrease with the probable formation of acidic photoproducts. The reaction rate is affected by many parameters: EBT disappears faster as the solution pH is raised stepwise from 2-12.5, due to the acid-base structural changes accompanying the pH changes. In solutions buffered at pH = 9, the reaction kinetics are apparent first order. The half-life time increases steadily with the initial concentration which points to the growing difficulty to remove the pollutant from an effluent as its concentration rises. Quantum yield, absorptivity and incident light intensity are to be considered for selecting the light source and optimizing the operating conditions: in our experimental devices, a faster decolourisation was obtained at 254 nm than at 365 nm and by increasing the light intensity.

Key words: Photodegradation, eriochrome black T, azo dye, water depollution

INTRODUCTION

Dyes are one of the major classes of organic pollutants in the aquatic environment (Fujishima *et al.*, 1999; Hoffmann *et al.*, 1995). About 1-20% of the total world production of dyes is released in the textile effluents (Houas *et al.*, 2001). These coloured wastewaters cause non-aesthetic pollution and eutrophication and their oxidation, hydrolysis or other chemical reactions taking place in the wastewater phase can generate toxic secondary products, such as the highly carcinogenic aromatic amines (Brown and De Vito, 1993). Consequently, the treatment of these effluents has received increasing attention.

The textile effluents are usually treated by physico-chemical oxidative or active sludge biochemical processes. The latter is often not very efficient because of the resistance of textile dyes to aerobic biological degradation (Chu and Ma, 1998; Sauer *et al.*, 2002; Daneshvar *et al.*, 2003). Physical processes such as adsorption or chemical coagulation have a high capacity to remove some dyes but their main drawback is that they are non-destructive, since they are limited to the transfer of the pollutants from the water phase to the solid phase, thus causing secondary pollution. Indeed, the generation of large amounts of sludge or solid waste result in high operational costs for sludge treatment and disposal (Banat *et al.*, 1996; Nam *et al.*, 2001). The oxidative and biological processes may release chemically or biologically refractory toxic compounds into the environment. Photodegradation seems to be more suitable for dye wastewater treatment.

Among recent studies on the direct photolysis of dyes, we may quote the work of Da Silva and Faria (2003). Who report that UV irradiation at 254 nm was efficient for the decolourisation of Solophenyl Green BLE 155% at 5-50 mg L^{-1} with apparent rate constants ranging, respectively from 0.27-0.042 min^{-1}. According to Zhao *et al.* (2005), decolourisation of Diacryl Red X-GRL can be accomplished by irradiation at 253.7 nm. The substrate disappearance rate depends on temperature, pH, light intensity and oxygen concentration.

The present study aims at improving our knowledge on the efficiency of the direct photolysis process to the removal of azo-dyes from textile wastewaters. Azo-dyes are characterized by the presence of one or more azo bonds (-N = N-) and constitute about half of the textile dyestuffs manufactured worldwide (Zollinger, 1991).

In this first contribution of a series to come we report on the direct photolysis of Eriochrome Black T, chosen as an azo-dye model compound. This substance has been selected because of its acid-base and complexing properties which may strongly affect its photodegradability in the various spent textile wastewaters.

Corresponding Author: Abdelaziz Boulkamh, Laboratoire des Sciences et Technologie de l'Environnement, Université Mentouri, Route de Aïn El Bey, Constantine, Algérie

MATERIALS AND METHODS

Reactants: Analytical grade EBT was purchased from Riedel de Haën. Double distilled water was used for the preparation of solutions. One liter of a borate buffer solution was prepared as follows: 0.1 M NaOH was added slowly to 0.6184 g of boric acid (H_3BO_3, Panreac 99.5%) dissolved beforehand in a few hundred milliliters of water up to pH = 9. The latter was monitored with a pH-meter Hanna instrument equipped with a combined glass electrode to 0.01 units. The final adjustment to the volume was made with water.

Irradiation set-up: Three devices were used for the continuous irradiation of EBT solutions. In the first device, solutions ranging from 10^{-5} to 10^{-4} M were irradiated at 254 nm with 3 low-pressure mercury lamps, except for the runs on the intensity effect where we used one, 2 or 3 lamps, respectively. These germicidal lamps were placed along the internal wall of a cylindrical mirror, at equal distance from one another, at the vertices of an equilateral triangle. They surrounded a quartz reaction vessel, set along the symmetry axis, at the center of the cylinder. This reactor was cylindrical (40 cm long and 2 cm internal diameter) and was filled to approximately 2 thirds of its capacity, with 80 mL of the solution to be irradiated.

The 2nd irradiation device was cylindrical with an elliptic base. It was equipped with a fluorescent lamp (Philips TLD 15 W) emitting a continuous light in the spectral region starting at 300 nm and ending at 450 nm, with a maximal emission intensity at 365 nm and a 50 nm width at mid-height. We shall refer to this lamp as the polychromatic lamp. The lamp was set along one of the focal axes and the pyrex reactor along the second focal axis.

The 3rd irradiation device was also cylindrical. It was equipped with 3 black bulbs, i.e. medium-pressure mercury lamps emitting a polychromatic light but allowing predominantly the transmission of the light at 365 nm: About 85% of the transmitted beam energy is at 365 nm, 6% at 334 nm and 2% at 313 nm. In this research, we shall refer to these bulbs as the 365 nm monochromatic lamps. The quantitative determination of EBT was routinely performed by UV-Visible spectrophotometry. The UV-Visible spectra were recorded on a Heλios α_spectrophotometer. The EBT concentration was determined from the absorbance value at the wavelength of maximum absorption, in the visible region of the spectrum where EBT is the only absorbing component (616 nm at pH = 9).

RESULTS AND DISCUSSION

UV-visible absorption spectrum: Figure 1 shows the UV-visible absorption spectrum of a 10^{-4} M aqueous solution of Eriochrome Black T at pH = 9. We observe mainly 2 absorption bands centred, respectively at 344 and 616 nm. The latter is responsible for the blue colour which characterizes EBT at this pH value. The molar absorption coefficients at the wavelengths corresponding to the main absorption maxima as well as the wavelengths of maximum emission of the irradiation devices (254 and 365 nm, respectively) used in this work are gathered in Table 1.

Table 1: EBT molar absorption coefficients at pH = 9 for selected wavelengths

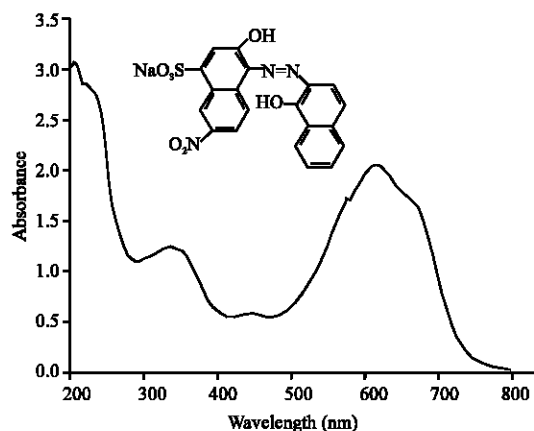| λ (nm)	254	365	344	616
ϵ_($M^{-1}.cm^{-1}$)	15.730	10.190	11.730	20.260

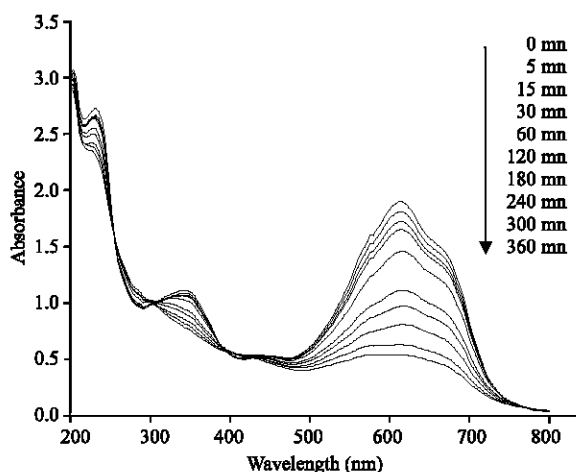Fig. 1: UV-Visible absorption spectrum of a 10^{-4} M aqueous EBT solution at pH = 9

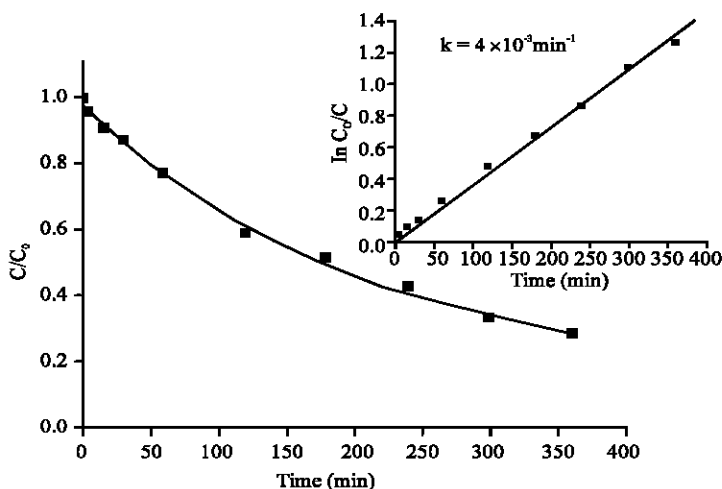Fig. 2: Evolution of the UV-Visible spectrum with irradiation time

Fig. 3: Kinetics of disappearance of 10^{-4} M aqueous EBT at pH = 9, $\lambda_{irradiation}$ = 254 nm, I_0 = 1.66×10^{-7} Einstein. s^{-1}

EBT disappearance kinetics: When a 10^{-4} M aerated aqueous solution of EBT, maintained at pH = 9 with a borate buffer, is irradiated at 254 nm, we observe a progressive decolourisation of the solution, which indicates a slow transformation of the compound. As shown in Fig. 2, this decolourisation is expressed by the decrease of the intensity of the main absorption band, centered at 616 nm. This result clearly indicates that UV light emitted by a germicidal lamp induces the transformation of EBT and that it could be used for the elimination of this dye when it is present in an industrial effluent. On the other hand, we observe a slight initial increase in the 344 nm band intensity, followed by a slow decrease. This band persists for much longer times which points to the formation of some photoproducts that are more persistent than EBT, suggesting that mineralization is more difficult to achieve by direct photolysis.

It appears on Fig. 3 that 72% of EBT, present initially at 10^{-4} M, is degraded in 360 min of irradiation. It also appears on the inset of Fig. 3 that ln (C_0/C), where C_0 represents the initial concentration and C the concentration at the irradiation time t, varies linearly with the latter. We can deduce that 10^{-4} M EBT disappearance follows an apparent first order kinetics that is characterized by an apparent rate constant $k = 6.7 \times 10^{-5} \, s^{-1}$.

Time course evolution of pH: The EBT photo-transformation in a pure non-buffered aqueous solution induces a pH decrease of the solution (Fig. 4), which indicates a probable formation of acidic compounds, as reported by some authors (Bali *et al.*, 2004; Georgiou *et al.*, 2002; Neamtu *et al.*, 2002; Rauf *et al.*, 2005).
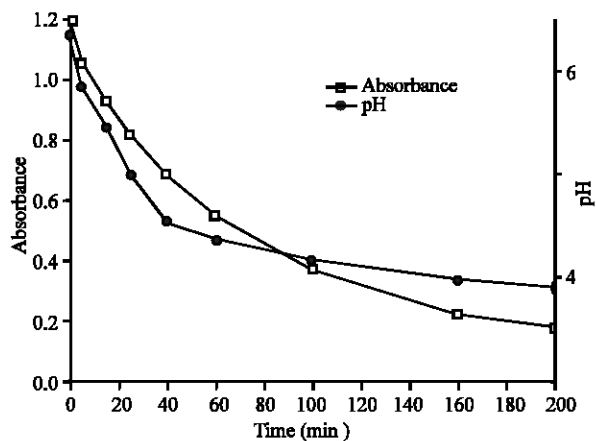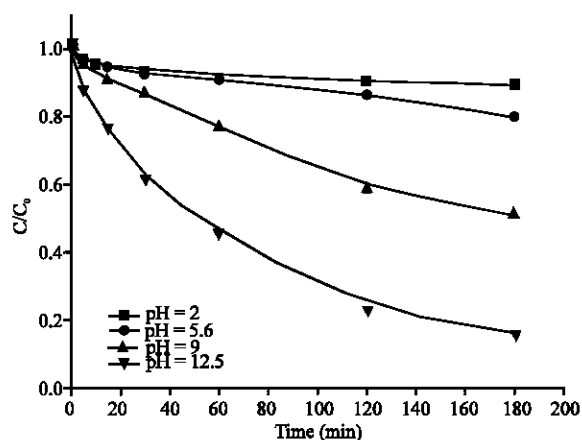

Fig. 4: pH evolution in the course of irradiation

pH effect: To study the effect of pH on the degradation kinetics, the pHs of 10^{-4} M EBT solutions were set with buffers at, respectively 2, 5.6, 9 and 12.5. All solutions were then irradiated at 254 nm in the same device and the concentration changes were monitored by spectrophotometry. The absorbance measurements were carried out in the visible region, at the wavelength of maximum absorption corresponding to each pH.

We observe on Fig. 5 that a pH increase considerably accelerates EBT disappearance: At pH = 12.5, the initial reaction rate is ca 2.5, 4 and 4.5 times higher than at pH 9, 5.6 and 2, respectively. This result indicates that the photochemical behavior of EBT is highly dependant on pH. It can be explained on the basis of the acid-base properties of this compound. Indeed, EBT a is tri-acidic substance, characterized by a relatively strong acidity, that of the sulphonate group (The pKa of sulfurous acid H_2SO_3 is ca 1.9) and 2 weak acidities, those of the

Fig. 5: pH effect on 10^{-4} M EBT degradation kinetics

Fig. 6: EBT degradation kinetics for different initial concentrations; pH = 9; λ_{irr} = 254 nm

Table 2: Apparent first-order rate constants and half-life times for different EBT concentrations

(EBT) (M)	10^{-5}	2×10^{-5}	5×10^{-5}	10^{-4}
k (min^{-1})	2.8×10^{-2}	1.8×10^{-2}	1.2×10^{-2}	4.0×10^{-3}
$t_{1/2}$ (min)	25	38	58	172

phenolic groups, characterized, respectively by pKa_1 = 6.3 and pKa_2 = 11.5. Consequently, in an aqueous solution, it may exist in many different acid-base structures, the predominant one being determined by the solution pH value. We also found experimentally that each structure displays a different UV-visible absorption spectrum. It's finally these differences in structural and absorptive properties that confer to EBT a photochemical reactivity which can considerably differ from a given pH interval to another. The obtained result shows that the tri-basic structure is the most easily photodegraded at 254 nm.

As EBT photoreactivity is affected by pH and as the latter may vary in the course of reaction or be wholly or partly fixed by external agents, any photochemical study should then be performed at a fixed selected pH value, so as to allow the predominance of only one molecular form and to obtain reproducible results. In the following described experiments, we set the solution pH at 9 to insure the predominance of the dibasic structure.

Influence of EBT concentration: The influence of EBT concentration on the transformation kinetics was examined. For this purpose, EBT aqueous solutions of different initial concentrations, ranging from 10^{-5} -10^{-4} M, maintained at pH = 9, were exposed to irradiation at 254 nm. Decolourisation kinetics are shown in Fig. 6. It clearly appears that the complete decolourisation takes longer times as the initial concentration increases. As summarized in Table 2, this is expressed by a decrease in the rate constant and a rise of the half-life time. This is an expected result since the incident light intensity is the same in all cases while the number of moles to degrade increases with concentration. It is however useful to note that the reaction rate is higher at $C_0 = 10^{-4}$
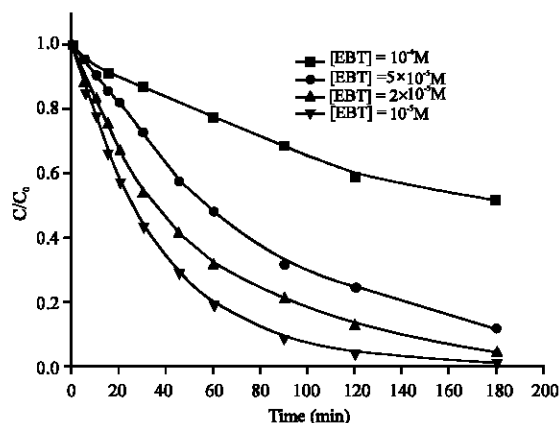
M ($v_0 = kC_0 = 6.7 \times 10^{-9}$ M.s^{-1}) than at $C_0 = 10^{-5}$ M ($v_0 = 4.7 \times 10^{-9}$ M.s^{-1}) due to a higher absorbance of the incident light at the higher concentration: Assuming an average path length of 2 cm, we compute an absorption of almost all photons (>99%) in the former case and ca 50% in the latter case.

Wavelength effect: EBT degradation may also be initiated by UV irradiation at higher wavelengths. However, as we can see in Fig. 7, the substrate disappearance is faster at 254 nm than at 365 nm or in a polychromatic light [300-450] nm peaking at 365 nm. The difference in reactivity of EBT with respect to these various light sources can be explained mainly by the difference in substrate absorptivity, incident light intensity and substrate disappearance quantum yield. For instance, degradation is favored at 254 nm by a higher molar absorption coefficient (ϵ_{254} nm = 15700 M^{-1}.cm^{-1}) than at 365 nm (ϵ_{365} nm = 10200 M^{-1}.cm^{-1}).

Light intensity effect: The effect of incident light intensity on EBT decolourisation has then been considered. For this purpose, 10^{-4} M EBT aqueous solutions at pH = 9 were subjected to irradiation at 254 nm emanating from one, 2 or 3 lamps, respectively, using the same experimental irradiation device. The results are presented in Fig. 8 and Table 3. We can see that the highest degradation rate is achieved by the highest number of lamps. This is in agreement with our
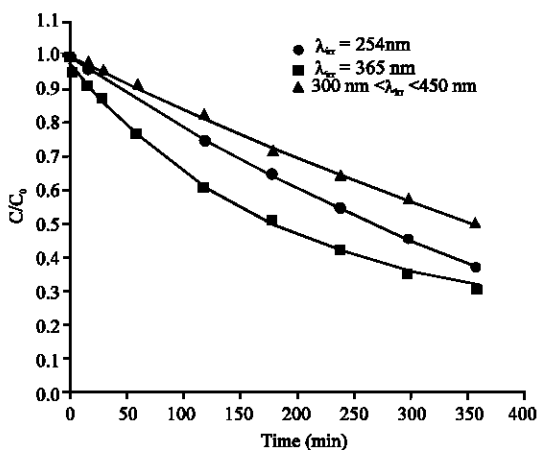
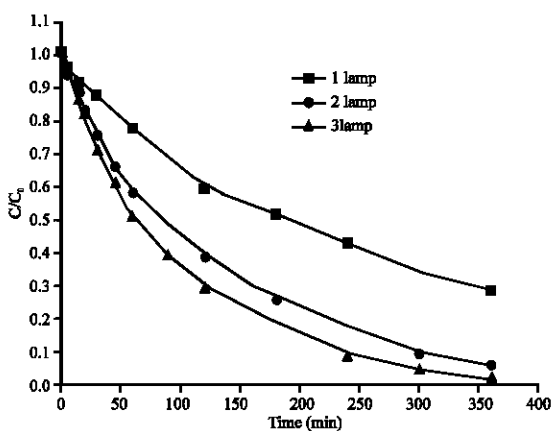Fig. 7: Wavelength effect on 10^{-4} M EBT degradation kinetics at pH = 9

Fig. 8: Incident light intensity effect on 10^{-4} M EBT degradation kinetics at pH = 9

Table 3: Initial rate and half-life times as a function of light intensity

Photonic flow	1 lamp	2 lamps	3 lamps
r_0 (M.min^{-1})	6.5×10^{-7}	8.4×10^{-7}	1.2×10^{-6}
$t_{1/2}$ (min)	172	87	65

expectations, since the light intensity, i.e. the number of photons per unit time, supplied to the solution increases with the number of lamps used.

CONCLUSION

EBT in aqueous solution may be degraded by UV artificial light at 254 nm. Its photodegradation is however slow to moderate and induces a pH decrease. It can be accelerated by increasing the light intensity or the solution pH. On the other hand, longer irradiation times are required for its elimination at higher substrate

concentration or when irradiating in the UV-A. The reaction is described by a first order kinetic equation.

REFERENCES

Brown, M.A. and S.C. De Vito, 1993. Predicting azo dye toxicity. Crit. Rev. Environ. Sci. Technol., 23: 249-324.

Banat, I.M., P. Nigam, D. Singh and R. Marchant, 1996. Microbial decolorization of textile-dyecontaining effluents: A Review. J. Bioresour. Technol., 58: 217-227.

Bali, U., E. Çatalkaya and F. Şengül, 2004. Photodegradation of Reactive Black 5, Direct Red 28 and Direct Yellow 12 using UV, UV/H$_2$O$_2$ and UV/H$_2$O$_2$/Fe^{2+}: A comparative study. J. Hazardous Materials, 114: 159-166.

Chu, W. and C.W. Ma, 1998. Reaction kinetics of UV-decolourization for dye materials. J. Chemosphere, 37: 961-974.

Daneshvar, N., D. Salari and A.R. Khataee, 2003. Photocatalytic degradation of azo dye acid red 14 in water: Investigation of the effect of operational parameters. J. Photochemistry Photobiology. A: Chem., 157: 111-116.

Da Silva, G. and J.L. Faria, 2003. Photochemical and photocatalytic degradation of an azo dye in aqueous solution by UV irradiation. J. Photochemistry Photobiology. A: Chem., 155: 133-143.

Fujishima, A., K. Hashimoto and T. Watanabe, 1999. TiO$_2$ Photocatalysis Fundamentals and Applications. BKC Inc., Tokyo, pp: 14-176.

Hoffmann, M.R., S.T. Martin, W.Y. Choi and D.W. Bahnemann, 1995. Environmental Applications of Semiconductor Photocatalysis. J. Chemical. Rev., 95: 69-96.

Houas, A., H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard and J.M. Hermann, 2001. Photocatalytic degradation pathway of methylene blue in water. J. Applied. Catalysis B: Environ., 31: 145-157.

Georgiou, D., P. Melidis, A. Aivasidis and K. Gimouhopoulos, 2002. Degradation of azo-reactive dyes by ultraviolet radiation in the presence of hydrogen peroxide. J. Dyes and Pigments, 52: 69-78.

Nam, S., V. Renganathan and P.G. Tratnyek, 2001. Substituent effects on azo dye oxidation by the Fe^{III}-EDTA-H$_2$O$_2$ system. J. Chemosphere, 45: 59-65.

Neamtu, M., I. Siminiceanu, A. Yediler and A. Kettrup, 2002. Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/H$_2$O$_2$ oxidation. J. Dyes and Pigments, 53: 93-99.

Rauf, M.A., S. Ashraf and S.N. Alhadrami, 2005. Photolytic oxidation of Coomassie Brilliant Blue with H_2O_2. J. Dyes and Pigments, 66: 197-2005.

Sauer, T., G.C. Neto, H.J. José and R.F.P.M. Moreira, 2002. Kinetics of photocatalytic degradation of reactive dyes in a TiO_2 slurry reactor. J. Photochem. Photobiol. A: Chem., 149: 147-154.

Zhao, W., Z. Wu, H. Shi and D. Wang, 2005. Photochemical and photocatalytic degradation of an azo dye in aqueous solution by UV irradiation. J. Photochemistry Photobiology. A: Chem., 171: 97-106.

Zollinger, H., 1991. Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments. VCH Publishers, New York.