



Acetone photoactivation and implication of methyl radical in the degradation of diazo dye

Soumia Fassi^{1,2}, Rayane Nadjjet Fassi³.

¹Laboratory of Materials Chemistry, Department of Chemistry, Faculty of Sciences, University of Brother's Mentouri, Constantine (Algeria).

²Laboratory of science and technology of the Environment, Department of Chemistry, Faculty of Sciences, University of Brother's Mentouri, Constantine (Algeria).

³Laboratory of pollution and water treatment, Department of Chemistry, Faculty of Sciences, University of Brother's Mentouri, Constantine (Algeria).

The Author's Email: fassisoumia@umc.edu.dz¹, fassirayane@yahoo.com².

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Abstract

This work illustrates the performance of acetone at 254 nm to eliminate Evans blue (abbreviated as EB) diazo dye with relation to various operating parameters, i.e. acetone concentrations, liquid temperature, solution pH and adding of nitrite. The results of this study showed that the photodegradation of EB was accelerated by acetone, probably due to the generation of methyl radical upon UV photolysis of acetone. For the first time, on the influence of acetone concentration. It was found that The EB degradation rate increased with increasing acetone concentration and near complete removal of EB was achieved at acetone concentration of 100 mM and reaction time of 60 min. whereas only 19.5% of removal was achieved under UV alone. The experimental decolorization kinetics data followed the pseudo-first-order reaction model. One observes that sodium nitrite inhibit the elimination of the dye in the acetone /UV system. Thus, these results confirm that methyl radical was probably the main species responsible for the efficient degradation of EB. The solution pH in the interval 3-9 has a minor effect on removal rate of EB. Whereas, at extremely high pH of 11 the enhancement of removal rate of EB was observed. Increasing the temperature intensified the beneficial effect of acetone. The efficiency of substrate mineralization in this process has been discussed by total chemical oxygen demand content of EB solutions. It is possible to conclude that Acetone is a good photosensitized material; the presence of it can completely decolorize EB solutions.

Keywords: Evans blue (EB); Degradation; Mineralization; Acetone photoactivation; Methyl radical.

Introduction

Effluents from the textile dyeing, tanneries, printing activities, etc is a major problem of pollution of water. Estimates indicate that approximately 7.10^5 tons of dyestuffs are produced annually and 280,000 tons of the textile dyes are ended in water basins through textile effluents [1]. Furthermore, dyes are designed to resist bio degradation, are characterized by complicated structure (presence of many aromatic cycles) [2]. Therefore, a proper treatment strategy is required. Conventional treatment technologies for textile wastewater have been investigated such as: coagulation-flocculation, adsorption, and ion exchange. Unfortunately, these techniques are quite ineffective. However, advanced oxidation processes (AOPs) are viable ways to remove persistent and hazardous substances from aqueous-wastes [3]. This effectiveness is related to the production of highly oxidative hydroxyl ($\cdot\text{OH}$). However, UV irradiation alone might not be effective in degrading organic dyes and combination with sensitizer (eg: acetone) is needed to produce highly efficient radicals. Lately, photoactivation of acetone with UV irradiation at 254 nm has become an emerging approach for the removal of organic compounds [4–6]. Moreover, the photodegradation of dyes could be greatly enhanced if acetone was added to the system due to the high triplet energy of acetone (79-82 Kcal/mol), which makes the photosensitization process possible [7].

The main objective of this study is to explore the effect of acetone on the photodegradation of Evans Blue (EB), diazo dye, and to explain reaction mechanism of acetone. The effect of several operating parameters including, acetone concentration, temperature, solution pH and adding of nitrite, will be investigated. The efficiency of substrate decolorization and mineralization has been comparatively discussed

2. Materials and methods

The diazo dye, Evans Blue, (abbreviation EB) and acetone were obtained from Sigma–Aldrich. The structure EB is shown in Fig. 1. The pH of the solutions was adjusted with NaOH or HCl (all from Labosi) to attain desired values. The experiences of degassing EB solutions were performed with nitrogen gas.

Photochemical experiments were carried out in cylindrical reactor in quartz in which low-pressure mercury lamps (germicide lamp, Philips TUV 15 W) emitting mainly at 254 nm. The temperature of the reactor is controlled by thermometer immersed in the reacting medium. The concentration of the dye was determined using a UV-Vis spectrophotometer “Unicam Helios α ” with a cell made in quartz and having a path length of 1 cm at $\lambda_{\text{max}} = 604$ nm. The

gas was introduced in the solution at relatively low flowrate (100 mL/min). Total chemical oxygen demand measurement was carried out with a COD/WTW.CR320.

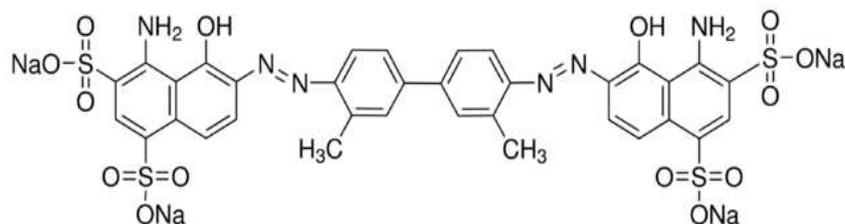


Fig.1. Molecule structures of Evans Blue (EB).

3. Results and discussion

3.1. EB degradation by UV and acetone photoactivation

The performance of the photoactivated acetone process in EB ($[EB]_0 = 20 \text{ mg. L}^{-1}$) removal have been evaluated in absence and in presence of various acetone concentrations (0-100mM). Fig. 2 shows the time-dependent degradation of EB (20 mg/L) at pH ~ 6.3. As seen, under UV alone, the experimental results show that the EB removal reaches 19.5% for a reaction time of 60 minutes. On the other hand, in the presence of acetone, rapid increases in the degradation rate were observed. Note that no EB removal has been occurred with acetone alone in dark conditions. However, the decolorization process increases with increasing of initial concentration of acetone. Consequently, EB decolorized completely for the highest concentration (100 mM) of this reagent in 60 min. We observed also that the decolorization removals of 89%, 53% and 32% recorded within 60 min for, respectively, 10mM, 1mM and 0.5mM of acetone.

This enhancement of the decolorization of EB observed in the presence of acetone concentrations can be described by an apparent first-order kinetics law 1 (figure.2 insertion). The values of rate are summarized in table (I).

Table (I): Values of parameters characterizing the acetone/UV process at 254 nm.

[Acetone] mM	R ²	Apparent rate constants (min ⁻¹)
0.5	0.9485	0.0186
1	0.9830	0.0259
10	0.9746	0.0590
100	0.9518	0.0636

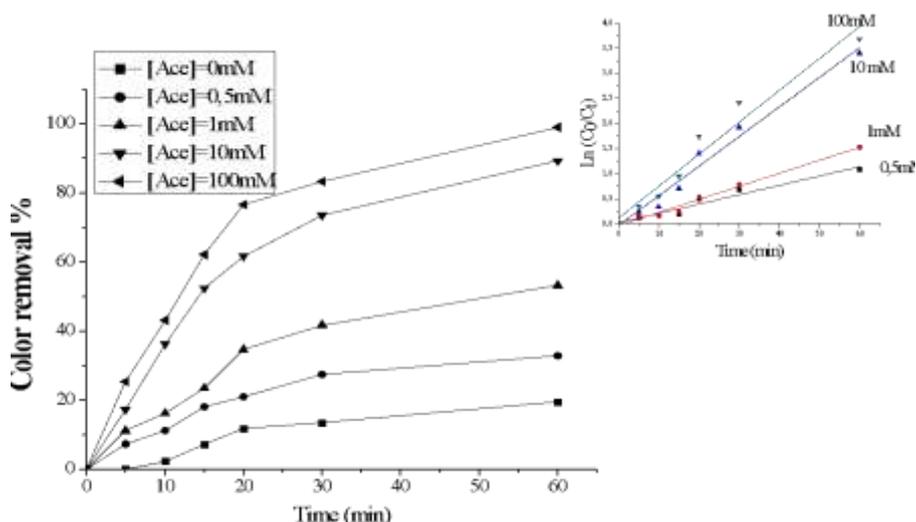


Fig. 2. Effect of initial acetone concentration on the removal kinetics of EB upon UV/acetone treatment (conditions: initial EB concentration: 20 mg/L, initial acetone concentration: 0–100 mM, pH= 6.3, temperature: $25 \pm 1^\circ\text{C}$). The insert represents the kinetics of EB decolourization (linear transform $\text{Ln}(C_0/C_t)$ vs t) in UV/acetone process.

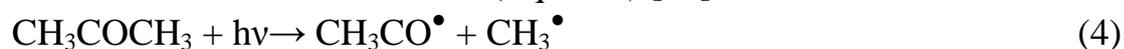
3.2. Mechanism of acetone-induced of EB photodegradation

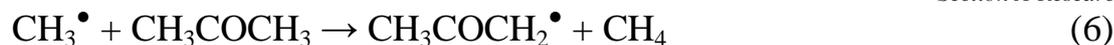
It is well known that, acetone photolysis may enhance the degradation of pollutants through two mechanisms: (i) involvement of methyl radical and (ii) acetone photosensitization. When acetone is excited by UV radiation (254 nm) it could lead to a triplet state: acetone* (79-82 Kcal/mole), as a result a collision between the triplet acetone ($\text{CH}_3\text{COCH}_3^*$) and the substrate molecule (S), which results in the decolorization of the substrate, as shown in equations 1–3.



At the end of the energy transfers, we notice that acetone is regenerated as indicated in equation (2). However, some experimental reports show that irradiation at 253-270 nm decomposes acetone efficiently in aqueous solution [8-9].

Acetone photolysis has been studied by many workers in the pure liquid as well in the gas phase for over 50 years [8,10–13].the identified gaseous products are a methane, ethane and CO, which are formed through methyl radical-induced chain reactions (Eqs. 4-7) [14].





Methyl radical may react with substrates through atom abstraction and addition [15-16].

3.3. Effect of nitrite on the reactivity of Methyl radical

As related by the literature, it appears that photosensitivity is a process which can be considered as a promising route for dye elimination. Acetone photolysis may enhance the degradation of pollutants through involvement of methyl radical. Turkevich and al [17] found that NO_3^- is an efficient scavenger of CH_3^\bullet [17] Additionally, the reaction constant of methyl radical is $2.2 \cdot 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$.

Thus, based on the interesting findings of Turkevich and in order to evaluate the major participation of methyl radical in the degradation of EB upon UV/acetone treatment. EB (20 mg/L) /acetone (100mM) solution was irradiated in presence of nitrite at different concentration. Fig.3. shows the effect of nitrite on the UV-degradation of EB in the presence of 100 mM of acetone. As seen, more than 70% of the degradation was inhibited with 0.5 mM of nitrite whereas with 1 to 50 mM of NaNO_2 , the removal rate was totally inhibited and becomes as that obtained under UV alone. Thus, these results confirm well the major participation of Methyl radical to this process.

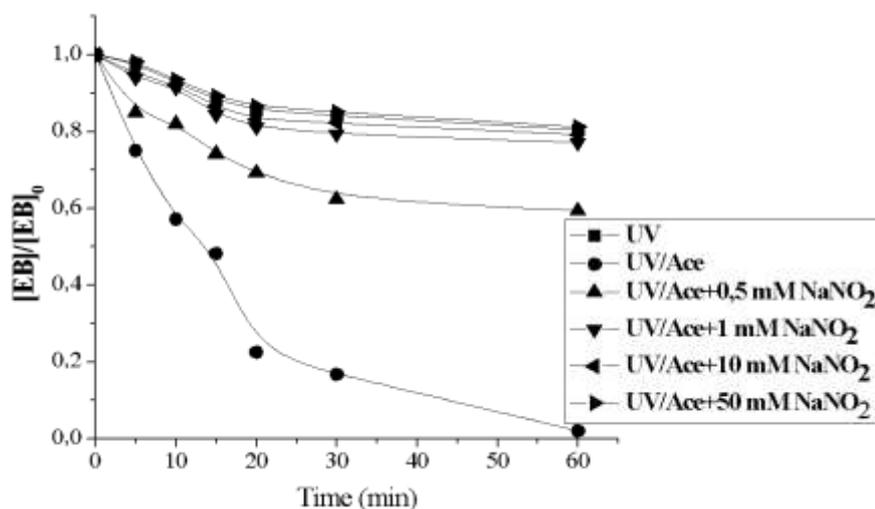


Fig. 3. Effect of nitrite addition on the removal kinetics of EB upon UV/acetone treatment (conditions: initial EB concentration: 20 mg/L, initial acetone concentration: 100 mM, initial nitrite concentration: 0.5-50 mM, pH= 6.3, temperature: $25 \pm 1^\circ\text{C}$).

3.4. Effect of initial pH

It is important to point out that during the degradation process; the initial pH plays a role in the photoactivation of acetone on the degradation of EB.

Fig. 4. displays the effect of initial pH on the degradation of EB (20 mg/L) by the UV/acetone process ($[\text{Acet.}]_0 = 100 \text{ mM}$). The obtained results showed that the removal rate of EB was not affected by the pH elevation from 3 to 9, which similar with the results obtained by Chu and Tsu [18] for the degradation of disperse orange11(DO11). However; at extremely high pH of 11 the enhancement of removal rate of EB was observed. This enhancement is likely due to the structural change of the diazo dye by loss of proton, which resulted in ionized form that may absorb UV light at higher extent than its original form [19].

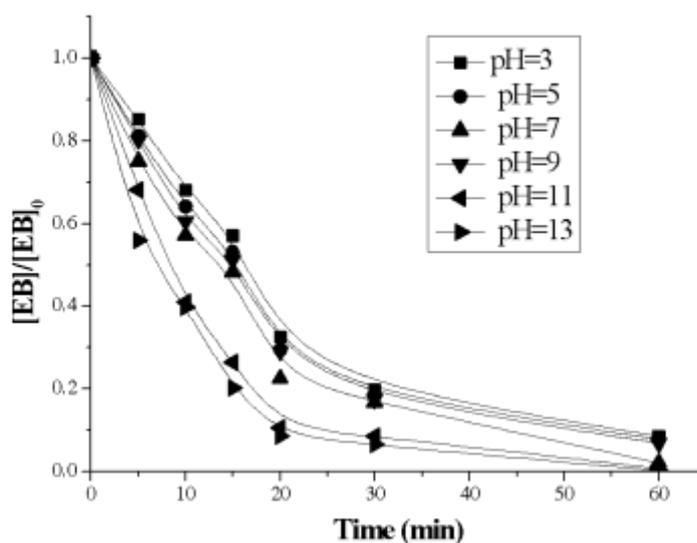


Fig. 4. Effect of initial solution pH on the removal kinetics of EB upon UV/acetone treatment (conditions: initial EB concentration: 20 mg/L, initial acetone concentration: 100 mM, temperature: $25 \pm 1^\circ\text{C}$).

3.5. Effect of temperature

The performance of the photoactivated acetone process in EB removal has been evaluated at different solution temperature. Fig. 5 shows the effect of temperature toward the photodegradation of EB (20 mg/L) by the UV/acetone process ($[\text{Acet.}]_0 = 100 \text{ mM}$). We observe that, the performance of the photoactivated acetone process becomes more efficient at higher temperatures. The Evans blue removal after 20 min increased from 77% at 25°C to 81%, 86% and 92% for, respectively, 35°C , 45°C and 65°C . As a result. This enhancement, could be attributed to the higher production of methyl radical at higher temperature [14]. The photolysis of acetone with the elevation of temperature showed that the yields of methane and ethane increased monotonically [8,10–12]. While ethane is formed through methyl radical recombination (Eq.4), methane was generated via the reaction of CH_3^\bullet

with acetone (Eq.3) [20]. The formation mechanism of these two products was mainly methyl radical-dependent [14].

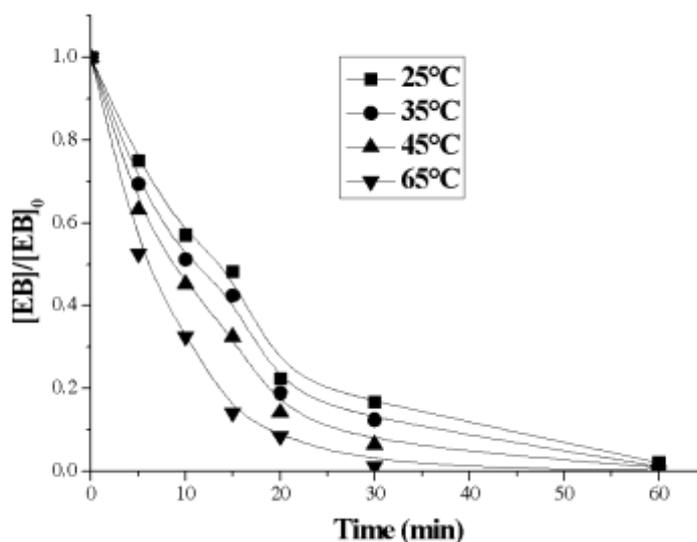


Fig.5. Effect of solution temperature on the removal kinetics of EB upon UV/acetone treatment (conditions : initial EB concentration: 20 mg/L , initial acetone concentration: 100 mM, pH 6.3, temperature: 25–65 °C).

3.6. Mineralization study

It is known that reaction intermediates can be formed during the oxidation of diazo dye and some of them could be long-lived and even more toxic than the parent compounds. Therefore, it is necessary understand the mineralization degree of the diazo dye EB to evaluate the degradation level applied by Acetone/UV process in deionized water. The efficiency of substrate mineralization in the Acetone/UV process has been determined by total chemical oxygen demand (COD). **Fig.6** present the results obtained on COD removal efficiencies of Evans blue dye using acetone photoactivated process .The results obtained from the solutions of the EB (20 mg.L⁻¹) in the presence of Acetone ([10⁻¹M]) and under UV irradiation show that the total mineralization was not achieved. We observed that the maximum COD removal was 68.5% after 240 minutes. Table.1.Shows the concentration of mineralization of Evans blue in deionized water by Acetone/UV process.Taking into account these results, we confirmed that acetone is an excellent photosensitizer not only for decolorization but also for dye mineralization. Nevertheless, the identification of the degradation by-products should be experienced to complete the degradation mechanism of EB.

Table2. COD removal efficiencies of Evans blue dye using Acetone photoactivated process:

Time (min)	30	60	120	180	240
COD (mg.L ⁻¹)	8.13	9.6	10.07	11.26	13.7

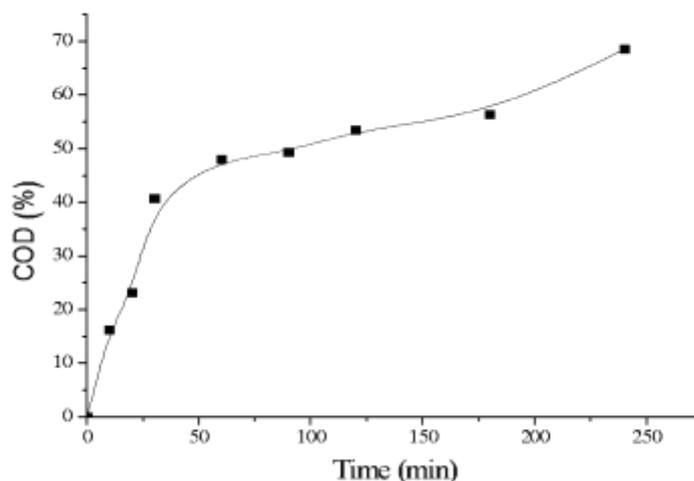


Fig.6. COD removal efficiency of EB in photoactivated acetone process.

Experimental conditions: [EB]=20 mg.L⁻¹; [Ace] = 10⁻¹ M, pH=6.3 and reaction time =240 minutes.

4. Conclusion

In this work, UV/acetone process has been successfully applied for the degradation of EB, as a substrate model of diazo dye. Based on the experimental results of this work, the following conclusions can be drawn:

- 1-The EB degradation rate increased monotonically with increasing acetone concentration. In presence of 100 mM of acetone 98% of EB was removed after 60 min. whereas only 19.5% of removal was achieved under UV alone.
- 2- The decolorization kinetics of EB obey a pseudo-first-order kinetic.
- 3-Radical scavenger tests using sodium nitrite have confirmed that methyl radical was the species responsible for the efficient degradation of EB in UV/acetone process.
- 4-The removal rate of EB was not affected by the pH elevation from 3 to 9. Interestingly, Whereas, UV/acetone system revealed to be more effective in degrading EB in very alkaline pH.
- 5- Increasing the temperature in the interval 25-65°C intensified the beneficial effect of acetone.
- 6- The acetone photoactivated process does not only decolorize the dye solutions but also partially mineralize (68.5%) the diazo dye EB.

From these results it is possible to conclude that acetone photoactivation process may be regarded as a promising innovative process for treating water contaminated with diazo dye pollutants. Nevertheless, the identification of the

degradation by-products should be experienced to complete the degradation mechanism of EB. This task will be conducted in the future.

Acknowledgements

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