Degradation of Diazo Dye by Acetone Process in Aqueous Solution

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Received: 09/2023 **Published:** 12/2023

Abstract

This work explores and elucidates the effect of acetone at 254 nm to eliminate Evans blue (abbreviated as EB) diazo dye with relation to various operating parameters, i.e. acetone concentrations, solution pH and adding of external gases such as: N_2. 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. 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.. It is possible to conclude that Acetone is a good photosensitized material; the presence of it can completely decolorize EB solutions.

Keywords: diazo dyes,degradation, UV-photolysis, methyl radical.

Tob Regul Sci. ™ 2023 ;9(2): 1666-1673
DOI : doi.org/10.18001/TRS.9.2.103

Introduction

The release of colored wastewater from textile industry is a current problem encountered all around the world, and is especially serious in countries where treatment plants are not available. Organic dyes represent one of the largest groups of these 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 (•OH).However, UV irradiation alone might not be effective in degrading organic dyes and combination with sensitezer (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]. Acetone photolysis has been studied by many workers in the pure liquid as well in the gas phase for over 50 years [7,9–12].the identified gaseous products are a methane, ethane and CO, which are formed through methyl radical-induced chain reactions

The photochemical decomposition of acetone could be a source of methyl radical ,which may be react with substrates through atom abstraction and addition [13-15].

The purpose of this study is to evaluate the efficiency of photochemical systems on the elimination of the diazo-dye (Evans blue, EB) in aqueous solution), and to explain reaction mechanism of acetone. The effect of several operating parameters including, acetone concentration,solution pH and adding of external gases such as: N_2, will be investigated.

2. Materials

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 λ_{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.

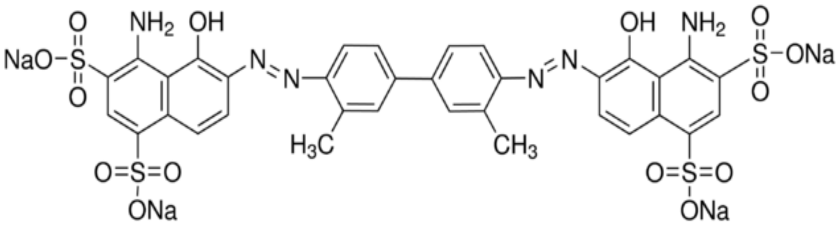

Fig.1. Molecule structures of Evans Blue (EB).

3. Results and discussion

3.1. EB degradation by UV and acetone/UV

The performance of the photoactivated acetone process in EB ($[EB]_o$ = 20 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.

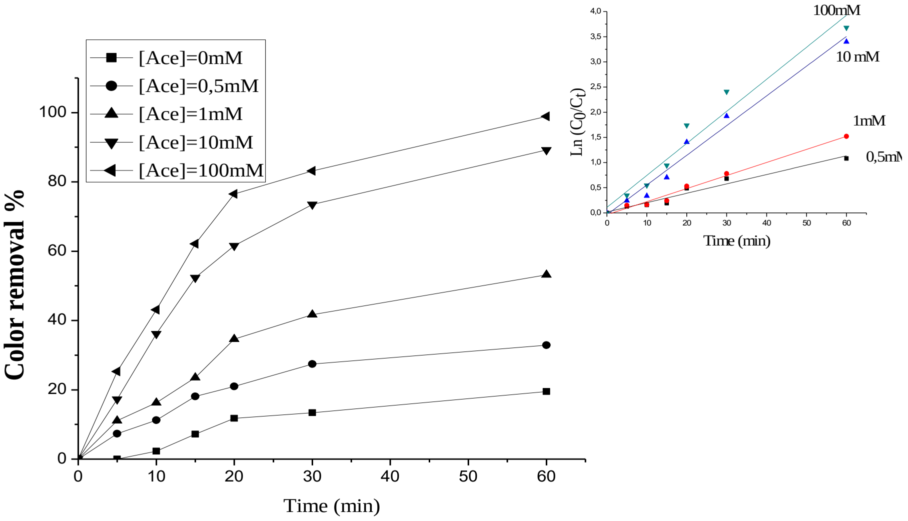

Fig. 2. Effect of initial acetone concentration on the removal kinetics of EB upon UV/acetone treatment (conditions: initial EB concentration: 20 mg/L, initial acetone concentration: 0–100 mM, pH= 6.3, temperature: 25 ± 1°C). The insert represents the kinetics of EB decolourization (linear transform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

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 ([Acet.]0 = 100 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 [16] 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 [17].

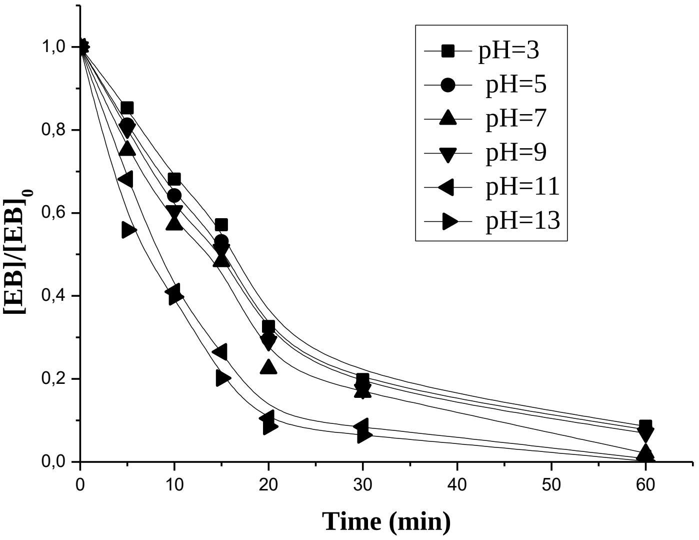

Fig. 4. Effect of initial solution pH on the removal kinetics of EB upon UV/acetone treatment (conditions: initial EB concentration: 20 mg/L, initial acetone concentration: 100 mM, temperature: 25 ± 1°C).

3.3.Effect of nitrite

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 [15] found that NO_3^- is an efficient scavenger of CH_3▪ [15] Additionally,the reaction constant of methyl radical is $2.2.10^7$ $M^{-1}.s^{-1}$.

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 irradiate 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.

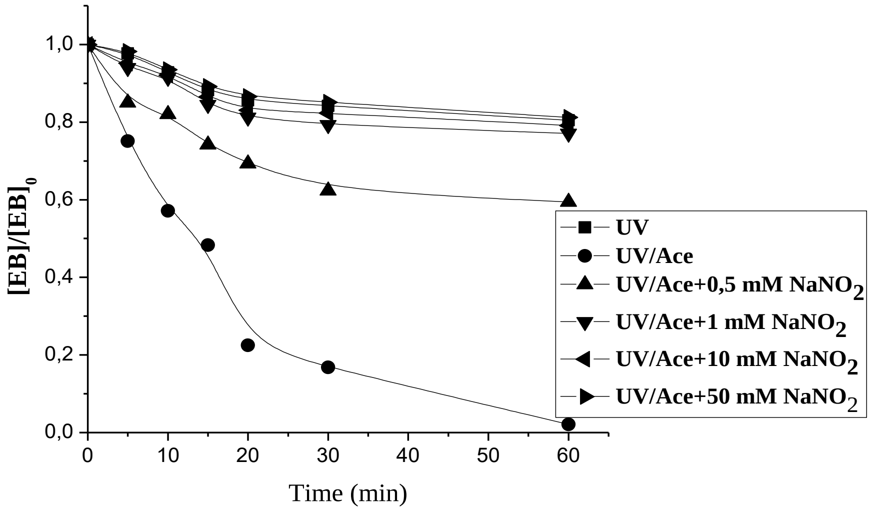

Fig. 3. Effect of nitrite addition on the removal kinetics of EB upon UV/acetone treatment (conditions: initial EB concentration: 20 mg/L, initial acetone concentration: 100 mM, initial nitrite concentration: 0.5-50 mM, pH= 6.3, temperature: 25 ± 1°C).

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^{-1}M]) 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.

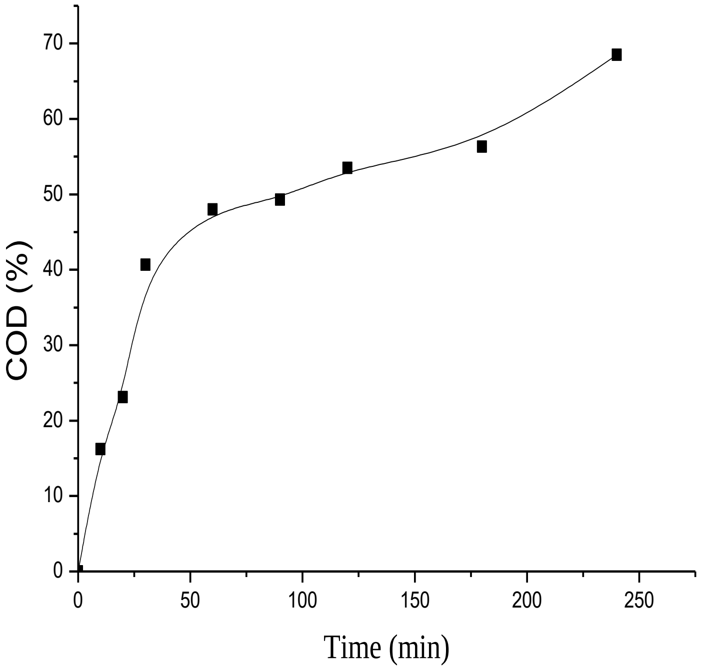

Fig.6. COD removal efficiency of EB in photoactivated acetone process. Experimental conditions: [EB]=20 mg.L^{-1}; [Ace] = 10^{-1} M,pH=6.3 and reaction time =240 minutes.

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- 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

The financial support by the Ministry of Higher Education and Scientific Research of Algeria is greatly acknowledged.

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