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Evans Blue Removal from Wastewater by Several Photochemical Processes Under Artificial and Solar Light.

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ABSTRACT

The aim of this study is to test the ability of some photochemical processes (photolysis at 254 nm, photoxydation by H_2O_2 /UV, Fenton and photo-Fenton an advanced oxidation system) to eliminate dye in aqueous solution. In this work, the Evans blue (EB) is chosen as molecules models. First, a study conducted with this specie, shows that the dye is readily decolorized by H_2O_2 /UV. These processes are attributed to radical $\cdot\text{OH}$ issued from photolysis of H_2O_2 at 254 nm. By contrast, this decolorization carried out via direct UV photolysis is negligible with artificial light. On the other hand Experiments were conducted in laboratory scale set-up with Fenton and photo-Fenton processes. Best operatory conditions were found to be pH of 3, hydrogen peroxide-to-iron (II) molar ratio of 5:1 artificial (254 nm) and solar light. The UV spectral change of Evans blue has been also studied for both processes. One can conclude that it was easier to destroy the partial $\pi - \pi^*$ conjugated system and $n - \pi^*$ bonding related to OH groups. On the other hand, the rate of decolourization was found to follow first order kinetic in almost cases (except in photolysis). Besides, several parameters were investigated like: pH, dose of H_2O_2 and light effect.

Keywords: Water, Deradation, Evans Blue, Irradiation , Solar light.

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INTRODUCTION

The considerable release of dyes from textile industries, tanneries, printing activities...is a major problem of pollution because they can destroy aquatic life (fauna and flora) and may causes too a great threat to human health as most of these substrates are toxic and carcinogenic [1-3]. Their decontamination is carried out via chemical techniques which have been already developed in the past : biological methods [4-5], ion exchange [6-7] , adsorption on various supports such as :clay, activated carbon and semi conductors [8-12]. Nevertheless, these techniques are inefficient since they may cause problems such as : transfer of pollution from one phase to another for adsorption. An alternative way to these methods, was to use new ones called: "Advanced oxidation Technics" since they could provide a definite solution to this problem by giving a possible mineralization. They are existing as well as in absence of light (Fenton and Fenton-like) as in presence of light (photo-Fenton, photo-Fenton like, UV/ H₂O₂, O₃/UV, semi-conductor /UV...)[13-17],

The purpose of this study is to evaluate and to compare the efficiency of photochemical processes (direct photolysis and POAs such: H₂O₂/UV, Fenton and photo-Fenton) on the elimination of a dye (Evans blue) in homogeneous phase. In this work, we investigate also the effect of some parametres, as on efficiency like: pH, light effect, the dose in H₂O₂. These investigations will help to situate the effectiveness of these processes during the fading process.

MATERIALS AND METHODS

Material

Evans blue (abbreviation EB) was purchased from Fluka chemical company and used without further purification. The hydrogen peroxide (33% Fluka) and salts of iron (II) ((NH₄)₃Fe(SO₄)₂·6H₂O, Labosi 99%) solutions were prepared from ultra pure water from a MILIPORE unit. Besides, the pH was adjusted with NaOH or HCl to reach the desired value. Moreover, the dissolved oxygen (wich was 8 ppm at room temperature) was removed from aqueous solution of Evans blue by bubbling nitrogen gas for about two hours. Then, the reactor was closed (by mean of paraffin) during the irradiation process. The structure of our substrate is represented in Figure.1.

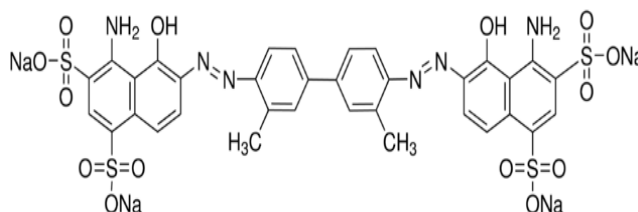


Figure 1: Structure of Evans Blue

Photoreactor and source light

Aqueous solutions were irradiated at 254 nm in cylindrical reactor quartz (100 cm of length and 2 cm in diameter), located on one of the principal axis of the assembly and equipped with three symmetrical externals low-pressure mercury lamps (germicide lamp, Philips TUV 15 W) emitting mainly at 254 nm [18] .

In solar light, aqueous solution of the dye were degraded in presence of H₂O₂ and salt of Fe (II) using a pilot plant containing a reservoir delivery, a pump and an assembly of tubes on Pyrex .They are disposed closely to each other and in a vertical position towards natural light. Samples were withdrawn at regular time and analyzed immediately [19] (Figure.2.)

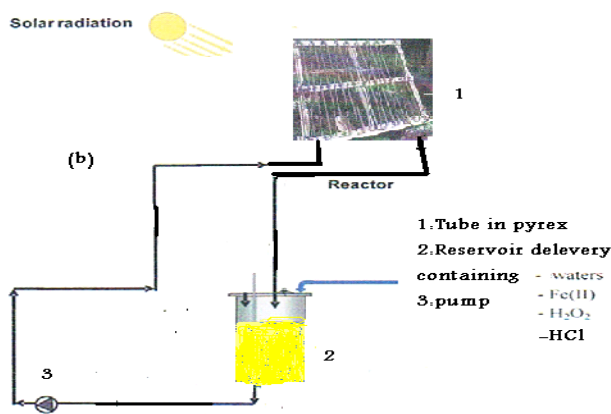


Figure 2: Set up showing the pilot plant solar light. Scheme of the solar reactor

Analysis

The spectral evolution and measurements of the absorbency of all solutions at different times were monitored by UV/Visible spectrometer type "UnicamHelios- α spectronic". HANNA pH meter was used for measurement of pH solutions.

RESULTS AND DISCUSSION

UV-vis spectrum of EB

The UV-vis spectrum of EB is reported in figure.3.a. At natural pH=6.3 one observed mainly three absorption bands, each characterized by a molar absorption coefficient ϵ and located at 230nm, at.320nm and at 604 nm respectively. Moreover, the pH affected the behavior of the substrate mainly in basic medium (pH = 12.1), we observed a deprotonation of the dye molecule. Indeed this high value of pH is responsible of the blue shift and the change in the molar absorption coefficient. By contrast, we observed no shift of all bands in acidic medium (pH<3.5).This could indicate therefore a slight decrease of the absorbance peak of the band located at 604 nm but without any shift, indicating thus no change in the structure Figure .3.b

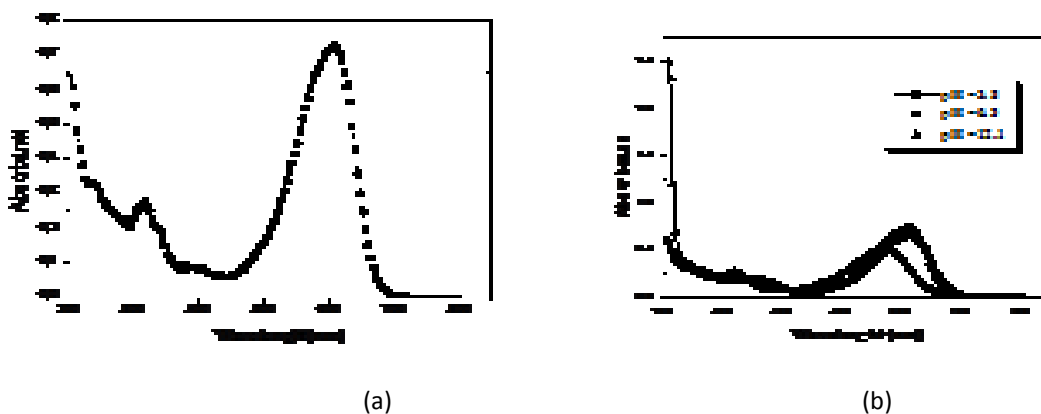


Figure 3: (a):UV /Visible spectrum of the EB (10^{-5} M pH=6.3), (b): Influence of pH.

Direct photolysis of EB under artificial and solar light

Figure.4. present typical data obtained from the photolysis of EB (10^{-5} M) in aerated medium, in solar and artificial light (UV irradiation corresponding to 254 nm). The photodegradation was followed by spectrophotometer at different irradiation time. In artificial light, the results obtained show that this compound undergoes very slow photolysis for the purposed concentration. Whereas, in natural light and on typical summer days, we observe a rapid decolourization process of the dye. Indeed, the elimination rate is

equal to : 30% for artificial light and 4% for solar light, for a reaction time of 120 minutes. This is due to a better absorption of photons by the EB in natural light.

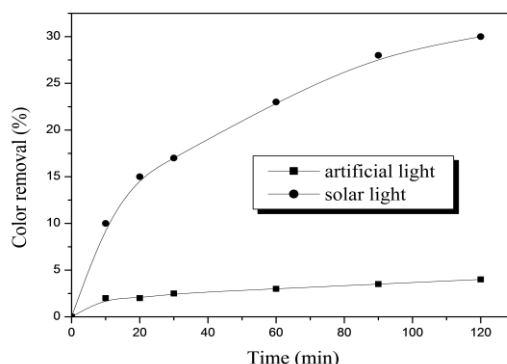


Figure 4: Effect of light on the direct photolysis process of EB, [Dye]₀ = 10⁻⁵ M

Photoxydation of EB by UV/H₂O₂ process

Sensitivity of EB in presence of H₂O₂

Prior to the study of dyes photooxidation by H₂O₂/UV, it is necessary to know if any transformation may occur when we mix each substrate with H₂O₂ took at the highest concentrations which were 10⁻¹ M . The spectral evolution of each mixing is followed during a reaction time (60 minutes) by spectrophotometer scanning from 200 to 800 nm. The results depicted in Figure 5. Showed that no reaction, but only an addition of spectra between both products (EB/H₂O₂).

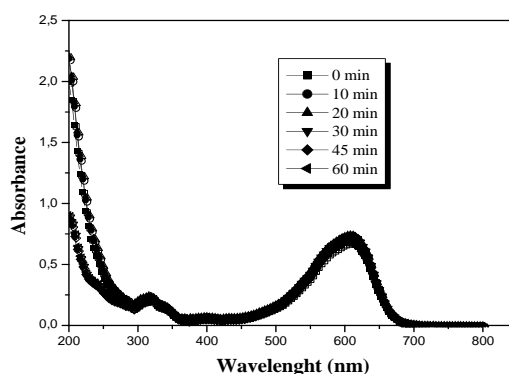


Figure 5: Sensibility of EB in presence of H₂O₂ in absence of light [dye]₀ = 10⁻⁵ M,

Effect of light

Better results are obtained when we combined H₂O₂ with radiation light at 254 nm. Indeed, this combination facilitates the photodecomposition of H₂O₂ into radicals [•]OH (species with a light quantum yield which is almost equal to 1) which are able to react without any discrimination and specificity with most of organic compounds and with a high rate constant: 10¹⁰ M s⁻¹ [20]. Thus, for EB, the bleaching process is total for reaction time of 15 minutes. This can be attributed to the participation of radical [•]OH. Besides, the decolorization rate is increased as the concentration of H₂O₂ increased, involving therefore more radicals [•]OH in the medium (Figure.6.a). However for the highest value in H₂O₂ concentration (10⁻¹ M), we have observed a decrease in the fading rate. This behavior may be due to scavenging effect of into radicals [•]OH by an excess of H₂O₂ [21-22]:



In all experiments, this process is well described by a first order kinetics law with regard of the used concentrations. Initial decolourization rate constants has been computed from the slop of $\ln C_0/C_t$ [vs] time (minutes), where C_0 and C_t are dye concentrations at instant $t=0$ and t respectively Figure .6.b. Also, to get better knowledge of this bleaching process, one can calculate graphically the useful time to reduce to 50% ($t_{50\%}$ called also a half time $t_{1/2}$), the initial dose of the substrate. Results are recapitulated in table (I).At the end of the oxidation process the pH has not varied.

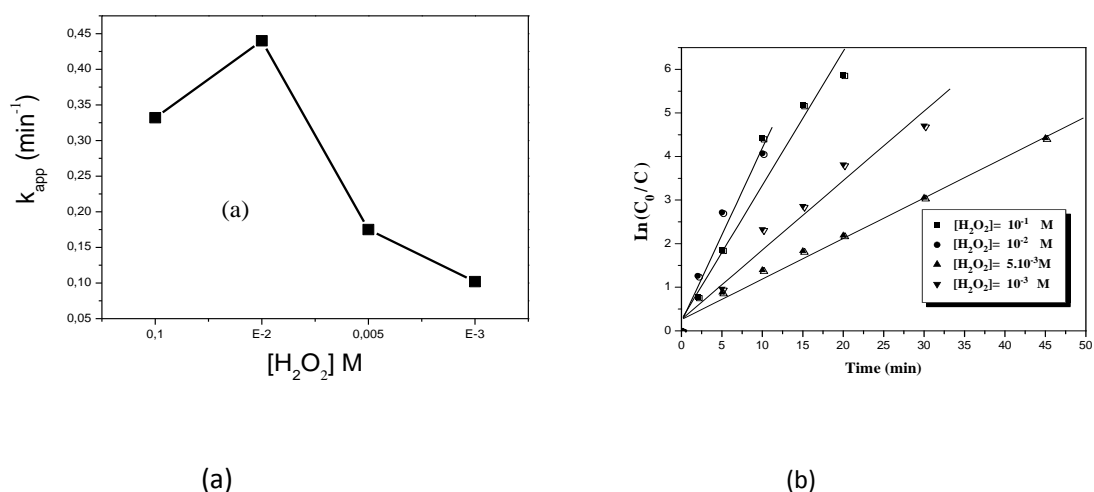


Figure 6: Decolourization process of the dye $[\text{dye}]_0 = 10^{-5}$ M, $\lambda_{irr} = 254$ nm. (a):in presence of H_2O_2 at various concentrations .(b): Kinetics of EB decolourization (linear transform $\ln(C_0/C_t)$ vs t) in UV/ H_2O_2 process.

Table (I): Apparent constants obtained in the process H_2O_2 / UV at 254 nm.

| $[\text{H}_2\text{O}_2]$ M | $t_{1/2}$ (min ⁻¹) | R^2 | Apparent constants (min ⁻¹) | rate |
|----------------------------|--------------------------------|---------|---|------|
| 10^{-1} | 2.5 | 0.97329 | 0.33216 | |
| 10^{-2} | 1.2 | 0.97288 | 0.44078 | |
| 5×10^{-3} | 4.1 | 0.98797 | 0.17502 | |
| 10^{-3} | 5.5 | 0.98137 | 0.10350 | |

Photoxydation of EB by Fenton process

Effect of pH on the elimination of EB by Fenton process

The effect of pH on the degradation of dyes was observed in the pH range 2.0 to 9.0. At pH 3.0 the discoloration of Evans blue and at pH 4.0 the discoloration of amaranth give the best results compared with the other pH's and it has been found that the rate of degradation of dyes increases with an increase in pH Figure,7.

-in very acidic medium (pH<2) the efficiency was low due to a feeble participation of radical OH^\bullet which are scavenged by this medium (reaction 3)



-in basic medium, we observed also a sensitive diminution of the efficiency linked to the formation and precipitation of iron $\text{Fe}(\text{OH})_3$, stopping the formation of radicals OH^\bullet

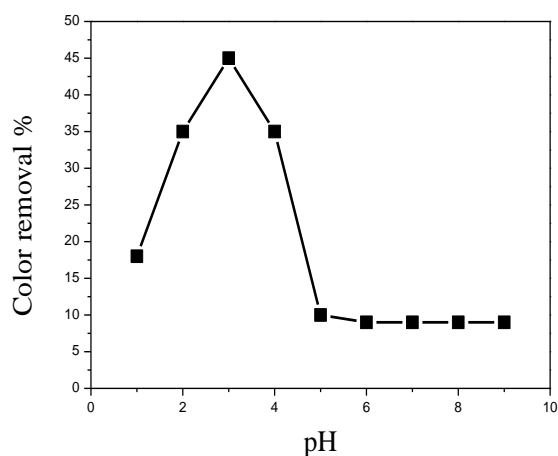
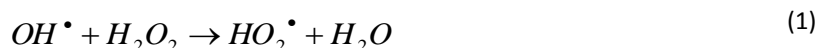


Figure 7: Effect of pH on decolorization process of EB in aqueous medium by Fenton..Initial conditions: C_0 (dye)= 10^{-5} M. C_0 (Fe^{2+})= 10^{-4} M. C_0 (H_2O_2)= $5 \cdot 10^{-5}$ M.

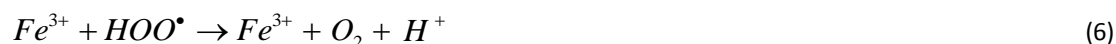
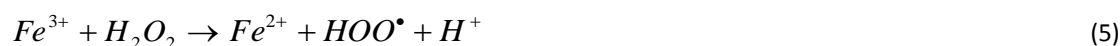
Effect of Amount of Hydrogen Peroxide on the elimination of EB by Fenton process

Amount of H_2O_2 is one of the operating parameters as it is significantly influence the final degradation of dye. The results are graphically shown in Figure 8. It is well known that Fenton reaction is effective at pH=3.0 [23]. Taking into account this value, a set of experiments was performed to obtain best color removal. As it can be seen on Figure.7., we observed a decolorization process reaching a color removal of 45% for a reaction time of 45 minutes. This could be attributed to an effective participation of OH^\bullet to the oxidation of the dye. We observed also an enhancement of this efficiency as the concentration of H_2O_2 increased from 10^{-5} M to $5 \cdot 10^{-5}$ M. Thus, this enhancement might be due to the catalytic production of OH^\bullet and Fe^{2+} . However, for high concentration of H_2O_2 ($[\text{H}_2\text{O}_2] \geq 5 \cdot 10^{-5}$ M), we observed a scavenging effect, of the OH^\bullet by H_2O_2 itself (Eq.1.).



Photooxidation of EB by Photo-Fenton process in presence of artificial and solar light

The Fenton process appears to be very interesting because of their simple implementation which consists on simple equipment and an availability of the used chemical reagents like H_2O_2 , ferrous ions. However, the only disadvantage for this system, is their use in acidic medium (pH=3) to prevent formation and precipitation of hydroxide. Thus, the mechanism of the oxidation of the pollutant is as followed Eqs (4-8) [24-28]:





Moreover, the combination of light (artificial or natural) to the Fenton, could improve the degradation of pollutants since the production of OH^\bullet is greatly increased

The solutions of the dye, prepared under the same experimental conditions were achieved in presence of artificial (254nm) and natural light (solar). The oxidation of the dye was greatly enhanced by light. This enhancement could be attributed to the important production of radical OH^\bullet from different sources like:[29-30]

- The reaction between Fe^{2+} and Fe^{3+} with H_2O_2 .
- The photolysis of H_2O_2 at 254 nm.
- The photoreduction of species resulting from the hydrolysis of Fe^{3+} ($Fe(OH)_2^+$) and Fe^{2+} ($Fe(OH)^+$).

The decolorization process, accruing in solar light, was achieved in typical summer days and under the same experimental conditions. In Figure 9, we observed that efficiency resulting from oxidizing process (photo-Fenton in artificial light) was about 70% in 20 minutes. Whereas in natural light, it was about 88%.The photooxidation of the substrate in natural light involving H_2O_2 and Fe^{2+} , gave good results due to the photoreduction of species like $Fe(III)_{aq}$ or $Fe(OH)^{+2}$, leading thereby, to an important production of radicals OH^\bullet [18].

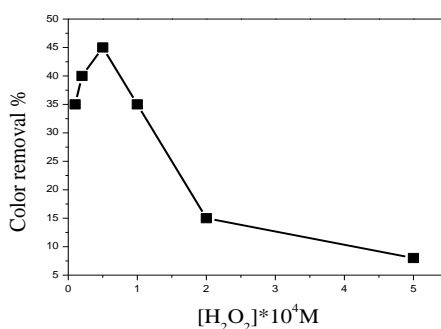
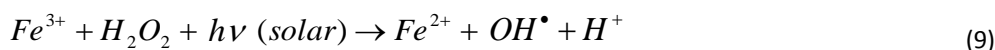


Figure 8: Effect of amount of hydrogen peroxide, condition: $C_0(\text{dye})=10^{-5}\text{M}$, $C_0(\text{Fe}^{2+})=10^{-4}\text{M}$, $\text{pH}=3$.

This enhancement of the disappearance of EB can be described by an apparent first-order kinetics law 1. The values of rate are summarized in table (II).

Table (II): Values of $t_{1/2}$ and apparent rate constants parameters characterizing the different systems:

| Systems | $t_{1/2}$ (min) | R^2 | Apparent rate constants (min ⁻¹) |
|-------------------------|-----------------|--------|--|
| | 20 min | | |
| Fe^{2+}/H_2O_2 | Not reached | 0.9995 | 0.03456 |
| 254nm/ Fe^{2+}/H_2O_2 | 5 | 0.9838 | 0.04981 |
| Solar/ Fe^{2+}/H_2O_2 | 3 | 0.9883 | 0.06661 |

CONCLUSION

The aim of this work is to test some photochemical processes to deplete azo dye, in aqueous homogeneous medium. This substrate is treated by direct photolysis under artificial and solar light. The obtained results indicate that in solar light EB (10^{-5} M) undergoes to a moderate decolorization whereas in artificial light does not (negligible process). A real improvement is observed when this substrate is treated either by $\text{H}_2\text{O}_2/\text{UV}$, Fenton and photo-Fenton (an advanced oxidation process). Based on the obtained results, we observed that optimal value of pH was equal to 3.0 and the most favorable amount of H_2O_2 was 5×10^{-5} M for Fenton and photo-Fenton processes and 10^{-2} M for $\text{H}_2\text{O}_2/\text{UV}$ process. Nevertheless and in these conditions, 38% degradation was achieved for $\text{Fe}^{2+}/\text{H}_2\text{O}_2$. However a better efficiency was obtained comparatively to that in dark solution when artificial and natural light were coupled to this system. The color removal was 70% and 88% for $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}_{254\text{nm}}$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{Solar}$ respectively. In general, photo-Fenton and Fenton, appeared to be suitable for the degradation of the dye since they reinforce the production of radicals OH. These investigations showed that these processes might be used for the treatment of waste water in industrial scale. The application of the Fenton process using solar energy might be interesting in the treatment method of wastewater in industrial applications.

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