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Decolorization and Mineralization of Cationic Dye (Crystal Violet) by Several Photochemical Methods.

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ABSTRACT

The aim of this study is to test the ability of some photochemical processes advanced oxidation processes (AOPs) such as: UV/H₂O₂, UV/S₂O₈²⁻ to eliminate dye in aqueous solution. The efficiency of substrate decolorization and mineralization in each process has been comparatively discussed by decreases in concentration and total chemical oxygen demand content of CV solutions. The obtained results showed that system like: H₂O₂/UV and S₂O₈²⁻/UV were better than direct UV photolysis at 254 nm and acetone/UV at the same wavelength. This improvement seems to be linked to production of OH[•] and SO₄^{•-} radicals issued from the photolysis of H₂O₂ and S₂O₈²⁻, always at this same wavelength. The most efficient method on decolorization and mineralization was observed to be UV/H₂O₂ process. Mineralization efficiency was observed in the order of UV/H₂O₂ > UV/S₂O₈²⁻. Final solutions of AOPs applications after treatment can be disposed safely to environment. The degradation rate is strongly dependent on the initial concentrations of the H₂O₂ and S₂O₈²⁻. The effect of these parameters has been studied and the optimum operational conditions of these processes were found.

Keywords: Decolorization, CV, mineralization, water.

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INTRODUCTION

The effluents produced by the textile industry present a major problem of pollution leading to severe damages to aquatic life (faunas and flora) [1, 2], organic dyes constitute one of the large groups of this effluent. However, the much research has been preformed to develop effective treatment for elimination of this type of pollutants because they are also very resistant to biodegradation. For instance, some conventional methods, such as precipitation, ion exchange [3-4], adsorption or various supports[5-8], membrane techniques, are widely applied to treat aqueous effluent. Nevertheless these traditional methods are limited, for instance physical methods as adsorption are only pollutants transfer towards another phase while chemical oxidation can generate by-products more toxic than the original pollutant.

Advanced oxidation processes (AOP) they are based to generate a very reactive radical OH^\bullet they are able to oxidize rapidly, efficiently and no selectively an elevated number of organic pollutants [9].

The aim of the present work is to analyze the possibility of decolourization of CV by different AOPs such as: $\text{UV}/\text{H}_2\text{O}_2$, $\text{UV}/\text{S}_2\text{O}_8^{2-}$. In this work, we investigate also the effect of some parameters, as on efficiency like: the dose in H_2O_2 , in $\text{S}_2\text{O}_8^{2-}$, in substrate and study of mineralization of dye. These investigations will help to situate the effectiveness of these processes during the fading process.

MATERIALS AND METHODS

Material

Crystal violet (abbreviation CV) was purchased from Fluka chemical company and used without further purification. The hydrogen peroxide (33% Fluka), Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, Prolabo) solutions were prepared with ultra pure water from a Milli pure water. The concentration of solution the substrate is 3mg L^{-1} , The experiments carried in the context of the mineralization of dyes under various conditions have necessitated analytical products include: Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), Prolabo, > 99 %, Silver sulfate (Ag_2SO_4), Sigma-aldrich, mercury sulphate (HgSO_4), Biochem-chemophama, 99 %

Irradiation procedure

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 [10].

The irradiation at 365 nm was carried out in a self-constructed Pyrex photoreactor (diameter of 2 cm) with a cooling water jacket placed in an elliptical stainless steel chamber. A flu-orescent lamp (Philips TLAD 15W/05), which dominantly emits radiation at 365 nm was used. Light intensity ($I = 0.7\text{ mW cm}^{-2}$) was measured using a radiometer type VLX 3W.

Analytical methods

The UV-vis spectra of dye were recorded from 200 to 800 nm using a UV-vis spectrophotometer (Unicam Helios "α") with a spectrometric quartz cell (1 cm path length). The maximum absorbance wavelength (λ_{max}) of CV is 588 nm. Therefore, the residual concentrations of the dye in the mixture and withdrawn at different reaction times, were determined by measuring the absorption intensity at $\lambda_{\text{max}} = 476\text{ nm}$ with and by the use of a calibration curve

RESULTS AND DISCUSSION

Direct photolysis of Crystal violet

The UV / Visible of the Crystal violet at natural pH (5.15) and in diluted medium (3 mg L^{-1}), indicates it is constituted by four bands of varying intensity and located respectively at 212 nm ($\epsilon = 10408\text{ l mol}^{-1}\text{ cm}^{-1}$), at 252 nm ($\epsilon = 4898\text{ l mol}^{-1}\text{ cm}^{-1}$), at 304 nm ($\epsilon = 8245\text{ l mol}^{-1}\text{ cm}^{-1}$) and at 588 nm ($\epsilon = 23532,4\text{ l mol}^{-1}\text{ cm}^{-1}$) (Figure.1.)

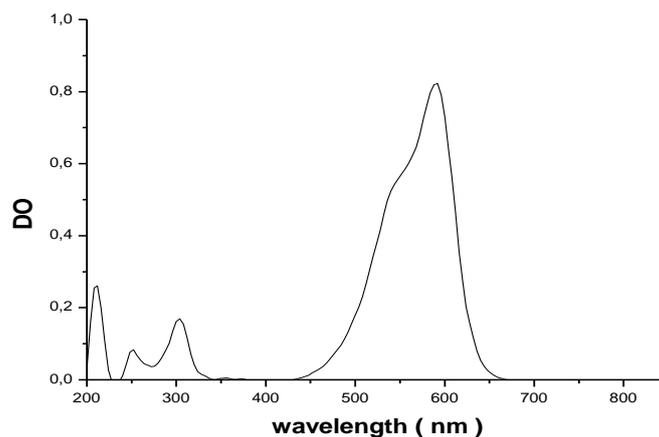
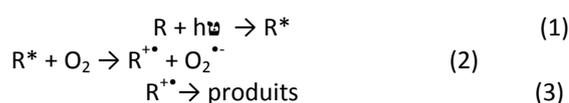


Figure 1: UV-vis spectrum of CV, $[\text{dye}]_0 = 3 \text{ mg L}^{-1}$.

Organic pollutants can be dissociated by direct UV excitation ($\lambda < 250 \text{ nm}$). To do this, pollutants must have a strong absorption for the excitation light and a quantum yield enough. The oxidized compound by the initial photoexcitation reaction (1) reacts with oxygen dissolved in water before being transformed into byproducts (reactions 2 and 3).



Direct UV photolysis experiments by different light source were carried out in dilute medium. The photodegradation was followed by spectrophotometer at different irradiation time (Figure.2.)

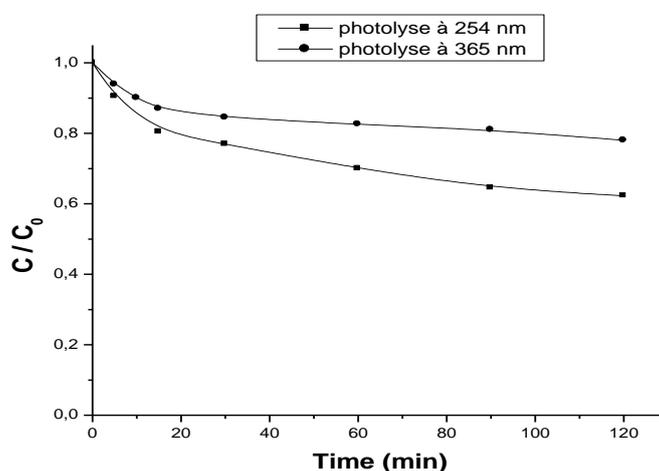


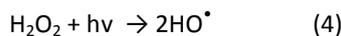
Figure 2: Decolourization of CV by direct photolysis. $[\text{Dye}]_0 = 3 \text{ mg L}^{-1}$. Influence of light source

The results obtained show that a very low degradation of the CV (3 mg L^{-1}) after 2 h of irradiation. Under these conditions, the disappearance rate obtained was 27.6% at 254 nm radiation and 19% in 365 nm. This could be explained on the basis of the incident photon flux emitted and the quantum yield of the lamps.

$\text{H}_2\text{O}_2/\text{UV}$ process

It was reported by a great number of authors that the combination of UV with hydrogen peroxide (H_2O_2) may constitute a simple, inexpensive and effective degradation of organic micropollutants [13]

The decomposition of hydrogen peroxide generates hydroxyl radicals by simple UV irradiation ≤ 300 nm (Eq 4)

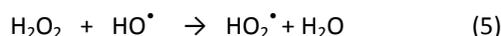


The hydroxyl radical is an oxidizing species that reacts rapidly and non-selectively on most of the organic compounds

Before studying the effectiveness of the process $\text{H}_2\text{O}_2/\text{UV}$ to degrade CV, we tested firstly the reactivity of H_2O_2 about the CV in darkness. The thermal evolution of this mixture was therefore followed during time by spectrophotometric scanning, within a range of wavelength between 200 and 800 nm. The results reported in Figure .3.a., show that the spectrum of our substrate has undergone no change mainly on the structural plan where we have not observed any appearance of new bands (so no formation of new products).

The quantities of HO^\bullet radical generated by the reaction of coupling $\text{H}_2\text{O}_2/\text{UV}$ depend on experimental parameters, in particular, the concentration of hydrogen peroxide. Discoloration of the CV (3 mg L^{-1} .) was followed as a function of irradiation time at $\lambda = 254$ nm for different concentrations of hydrogen peroxide, varying from 10^{-1} to 10^{-4} M. We observe that the degradation of the CV (3 mg L^{-1} .) by this method improves with increasing the concentration of H_2O_2 , however, for the highest concentration (10^{-1} M) H_2O_2 , we find a slowdown in degradation rate Figure.3.b.

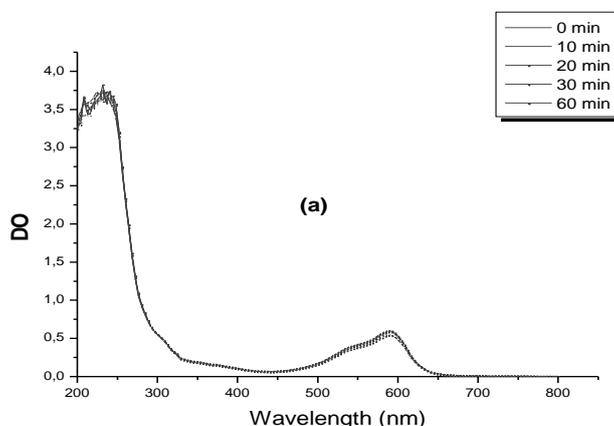
Several authors have reported the self-inhibitory effect of high concentrations of H_2O_2 degradation of dyes and other organic molecules [14-15] It is known that the excess of H_2O_2 acts as a radical scavenger effect creating a self-inhibition which eliminates the effect accelerator. This form could be attributed to the formation of HO_2^\bullet entities which are less reactive than HO^\bullet : (Eq 5)



The process is correctly described by an apparent kinetic law of order 1 (Figure.3.c.). The apparent constants and half time reactions ($t_{1/2}$) are reported in Table 1

Table 1: Values of parameters characterizing the $\text{H}_2\text{O}_2/\text{UV}$ process at 254 n

$[\text{H}_2\text{O}_2]$ mol/l	Rate % 60 min	$t_{50\%}$ (min)	R^2	Apparent rate constants (min^{-1})
10^{-1}	43.2	11	0.95487	0.096
10^{-2}	66.2	2.7	0,96768	0.349
10^{-3}	65.5	5.8	0,9799	0.246
10^{-4}	52.2	6.2	0.9988	0.132



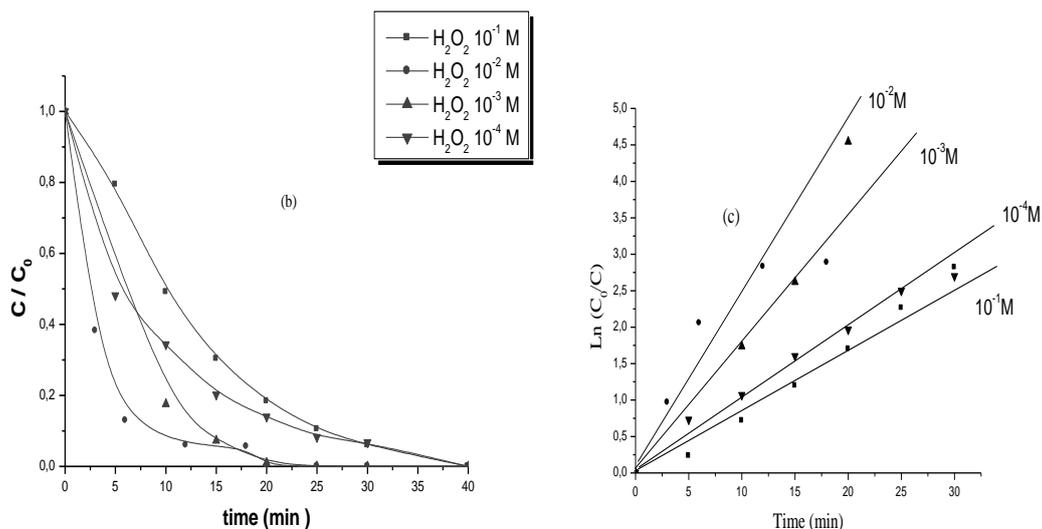


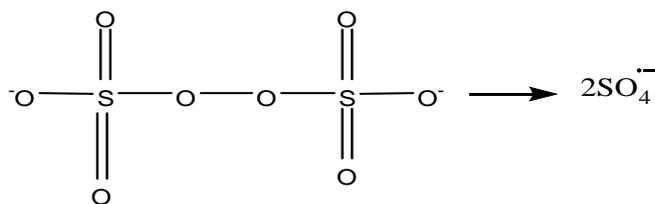
Figure 3: Discoloration of the CV by system UV_{254nm}/H_2O_2 [$CV_0 = 3 \text{ mg L}^{-1}$], (a): Sensibility of CV in presence of H_2O_2 in absence of light, (b): Effect of $[H_2O_2]_0$ in the discoloration of the CV, (c): Kinetics of CV decolourization (linear transform $\ln(C_0/C_t)$ vs t) in $UV_{254 \text{ nm}}/H_2O_2$ process

$S_2O_8^{2-}/UV$ process

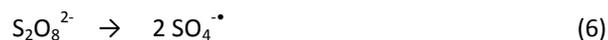
One way of improving the efficiency of oxidation treatment with photolysis is the addition of persulfate in the middle (this is called photolysis often combined). The persulfate ion ($S_2O_8^{2-}$) is one of the most powerful oxidizing agents in aqueous solution. Standard redox potential was determined at a value close to 2 (2.01 V [16] House., 1962], 1.96 V [17] [Mills and Valenzuela., 2004]). This confers a potential oxidizing power similar to that of hydrogen peroxide (1.78 V). The molar absorption coefficient of persulfate was determined at 254 nm ($\epsilon_{254nm} = S_2O_8^{2-}$) = $20 \text{ M}^{-1} \text{ cm}^{-1}$ [18].

Effect of temperature on the oxidation of CV by persulfate

The thermal activation of persulfate in aqueous solution results in the homolytic cleavage of the O-O bond



Bartlett and Cotman 1949 [19] propose the complete mechanism of the decomposition of persulfate in aqueous solution:



It is evident from Figure 4.a. that the reaction was significantly influenced by temperature. The Figure.4.a.gives the effect of the temperature of the solution on the degradation kinetics of the dye. The curves of Figures show that the temperature affects the rate of degradation of the dye. Thus, the increase in the temperature accelerates the degradation of crystal violet

Kolthof and Miller (1951) [20] and Price and Clifton (1996) [21] report that the activation energy necessary for the thermal breakage of the O-O bond for the uncatalyzed reaction is 120 to 140 kJ/mol. This relatively high activation energy indicates that the uncatalyzed decomposition reaction of persulfate will be slow at ambient temperature.

For this, we measured the activation energy experimentally and by the application of the law of Arrhenius, the results obtained are presented in Figure.4.b.indicate that the value of the activation energy is found on the order of 137.8 kJ/mol. This result agrees with the literature [21]

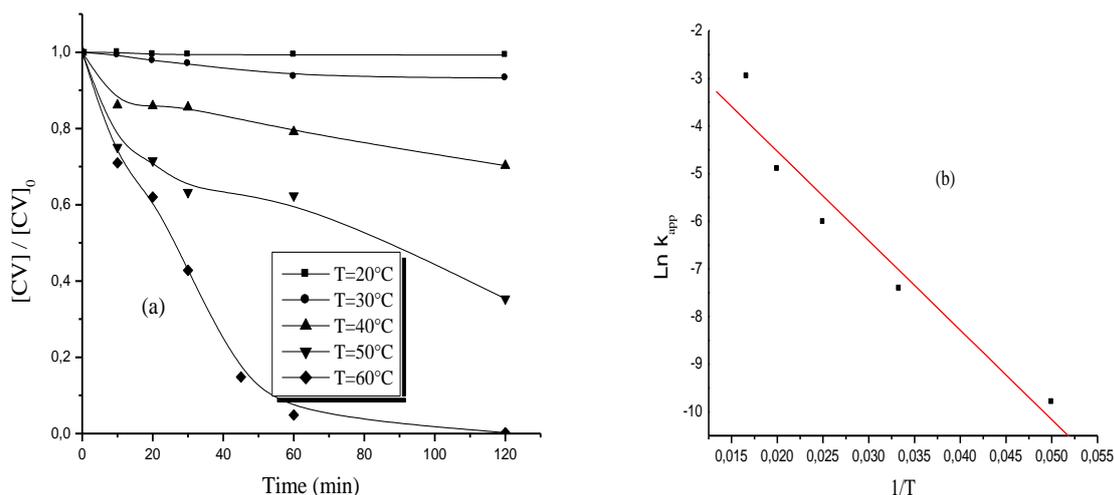


Figure 4: (a): Effect of temperature on the oxidation of CV by persulfate,(b):determination of activation energy using Arrhenius equation.[CV]=3 mg L⁻¹, [S₂O₈²⁻]=10⁻²M.

Effect of concentration of persulfate in S₂O₈²⁻/UV process

To show the efficacy of this process, we conducted a series of irradiation at 254 nm of solutions containing a fixed concentration in CV (3 mg L⁻¹) and various concentrations in S₂O₈²⁻.The Figure.5.shows that the percentage degradation of the dye increased with increasing amount of persulfate ion concentration and achieved 99.7 % degradation within 45 min irradiation time with 10⁻² M persulfate ion concentration instead of 73.2 % degradation in the presence of 10⁻⁴ M of persulfate ion at the same time.

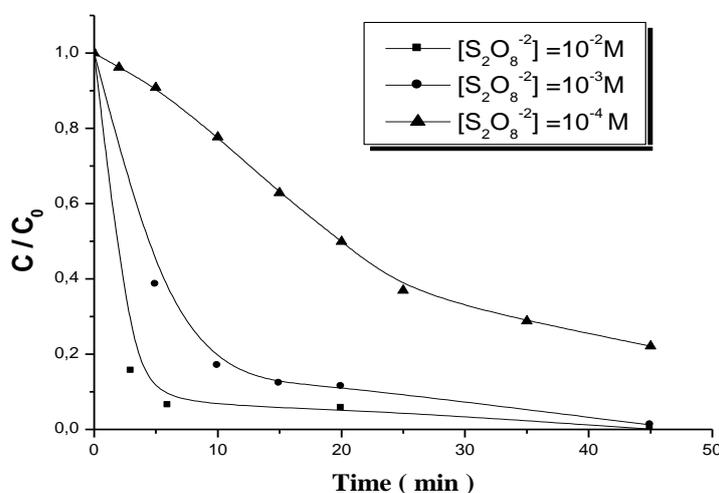


Figure 5: Effect of initial S₂O₈²⁻ concentration on the degradation of CV. [dye]o = 3 mg L⁻¹ λirr =254 nm

Mineralization of CV using several photochemical processes

To verify whether the dye undergoes a total mineralization, we followed the variation of the chemical oxygen demand (COD) of reaction mixtures in function of time. To this effect we used a COD-meter. The principle of measurement is based on the colorimetric dosage of the excess dichromate which would not be governed with organic matter. Appropriate calibration possible to determine the COD value of the sample.

The monitoring of the degradation of CV in the middle of the artificial chemical oxygen demand can be a serious indication of the mineralization of the dye. The results presented in Figure .6. show that the mineralization is almost complete by the processes $S_2O_8^{2-}/UV$ and H_2O_2/UV . This is attributed to the formation of OH radicals, which are very reactive

The fastest mineralization was obtained with H_2O_2/UV oxidation process with 98% efficiency. Mineralization with $UV/S_2O_8^{2-}$ system was also observed to be efficient (96% mineralization) photolysis/solar treatments were found to be less efficient methods on mineralization of CV with 39% at 9 hours.

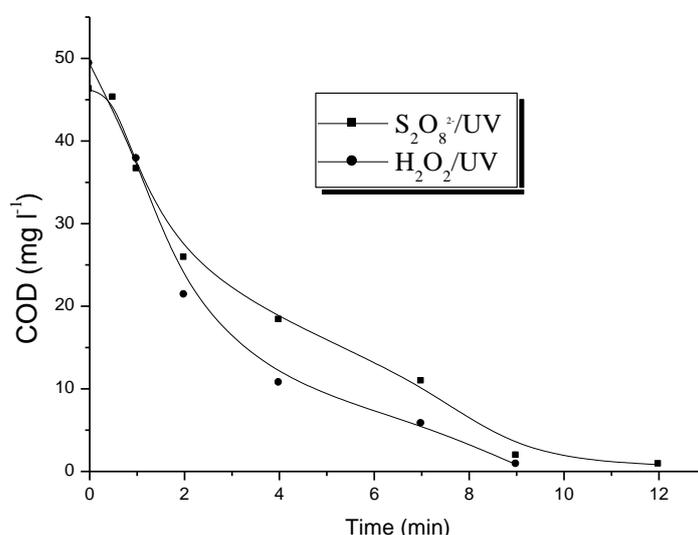


Figure 6: Evolution of COD as a function of irradiation time for different photochemical processes: photolysis, H_2O_2/UV_{254nm} and $S_2O_8^{2-}/UV_{254 nm}$. $[CV]= 3 \text{ mg L}^{-1}$, $[H_2O_2]=[S_2O_8^{2-}]=10^{-2}M$

CONCLUSION

This study has confirmed that the performances of H_2O_2/UV_{254nm} and $S_2O_8^{2-}/UV_{254 nm}$ methods are significantly superior to the oxidative ability of photolysis process in the degradation of CV. The bleaching process was totally reached at 45 min for $S_2O_8^{2-}/UV_{254 nm}$, which represents then the best performance. From the results obtained in this work, it can be concluded that the influence of parameters ($[H_2O_2]$, temperature, $[S_2O_8^{2-}]$) have great effects on the degradation rate and degradation efficiency for the removal of CV.

Application of $S_2O_8^{2-}/UV_{254 nm}$ and H_2O_2/UV_{254nm} for wastewater treatment is a cost-effective technology can be suitable treatment method for industrial applications.

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