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Solar-Light Induced by Photolysis Process and Comparison of the Several Photochemical Methods Efficiency for Decolorization and Mineralization of Cresol Red Dye.

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ABSTRACT

Degradation of Cresol Red, a well-known non-biodegradable dye, has been studied using photolysis/solar, Acetone/UV and advanced oxidation processes (AOPs) such as: UV/H₂O₂, UV/S₂O₈²⁻. 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 CR solutions. 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⁻ > photolysis/solar. Final solutions of AOPs applications after 60 min treatment can be disposed safely to environment. The degradation rate is strongly dependent on the initial concentrations of the H₂O₂, S₂O₈²⁻ and acetone. The effect of these parameters has been studied and the optimum operational conditions of these processes were found.

Keywords: Decolorization, CR, mineralization, solar irradiation, 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 CR by different AOTs such as: $\text{UV}/\text{H}_2\text{O}_2$, $\text{UV}/\text{S}_2\text{O}_8^{2-}$ and also by the use of a photosensitized component like "acetone". In this work, we investigate also the effect of some parameters, as on efficiency like: the dose in H_2O_2 , in acetone, 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.

EXPERIMENTAL

Material

Cresol Red (abbreviation CR) 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) and Acetone ($\text{C}_3\text{H}_6\text{O}$ $d=0.79$, Labosi) solutions were prepared with ultra pure water from a Milli pure water. The concentration of solution the substrate is $6 \cdot 10^{-5}\text{M}$, 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.

The experiments under solar irradiation were carried out in station of laboratory in Algeria on typical Jun summer days ($T = 40^\circ\text{C}$, $I_0 = 1.521 \text{ mW cm}^{-2}$) the mean value of flux intensity was measured with a radiometer type VLX3W

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 CR is 436 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 Cresol Red

The UV / Visible of the Cresol Red at natural pH (5.18) and in diluted medium ($6 \cdot 10^{-5} \text{ M}$), indicates it is constituted by two bands of varying intensity and located respectively at 436 nm and at 268 nm (Figure.1.)

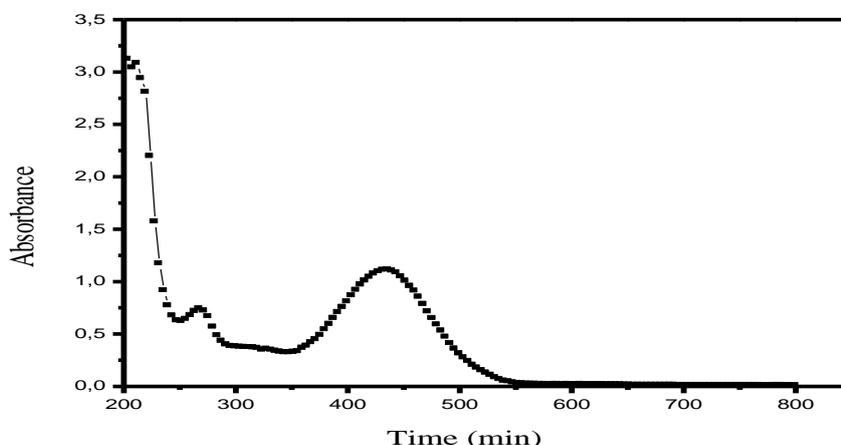
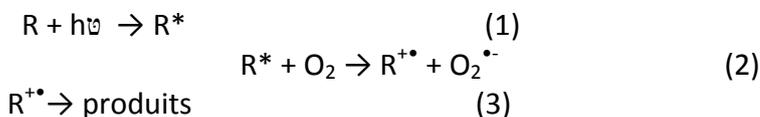


Fig.1. UV-vis spectrum of CR, $[\text{dye}]_0 = 6 \cdot 10^{-5} \text{ M}$

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.)

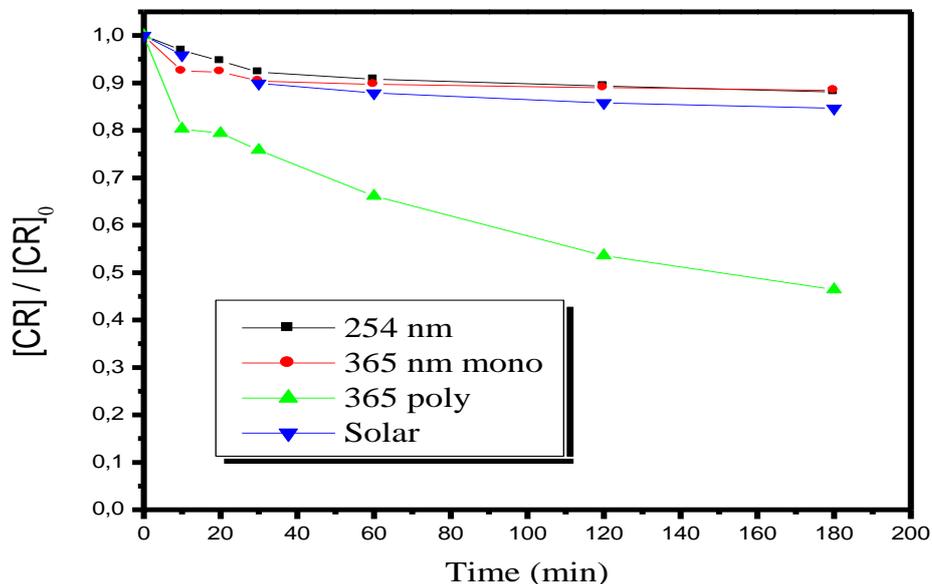


Fig.2. Decolourization of CR by direct photolysis. $[Dye]_0 = 6 \times 10^{-5} M$
Influence of light source

The results obtained show that a very low degradation of the CR ($6 \times 10^{-5} M$) after 3 h of irradiation. Under these conditions, the disappearance rate obtained was 12.1% at 254 nm radiation and 16.2% in solar radiation. However, this rate is nevertheless less than that obtained in 365 nm polychromatic radiations (54.2%). This could be explained on the basis of the incident photon flux emitted and the quantum yield of the lamps.

Acetone /UV process

For the process acetone / UV (254 nm), it is clear that some of the molecules of the CR is transformed by direct absorption of photons (direct photolysis) and the other part is photosensitized by acetone molecules. The performance of this technique is explained by the following mechanism [11-12]:



This mechanism shows both the disappearance of the most intense band at 436 nm of the CR and the other the total preservation of acetone. The latter could be recouped by chemical processes (distillation) for subsequent reuse. The spectrum of acetone is composed of a single absorption band at 264 nm with an absorption coefficient ($\epsilon = 121,6 M^{-1} cm^{-1}$). Figure.3.a.

Before knowing the effect of acetone on the degradation of the dye at 254 nm, it is necessary to study the acetone / CR in the absence of light and a reaction time of 180 minutes. This will allow us to detect possible transformation reactions can occur between these two compounds. As reference to Figure .3.b. and for our experimental conditions (10^{-1} M in acetone and $6 \cdot 10^{-5}$ M of CR), we observed no change in structure on the spectrum of CR in the presence of acetone but only an addition of spectra between acetone and Cresol Red.

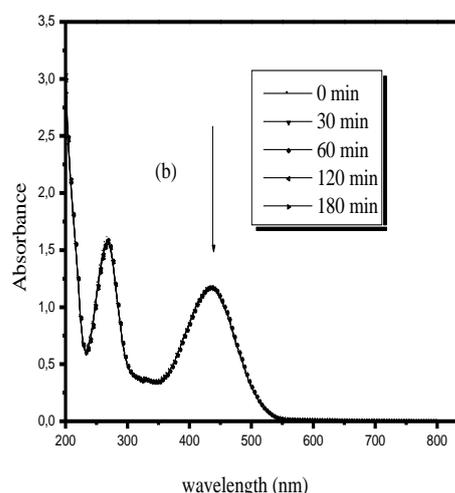
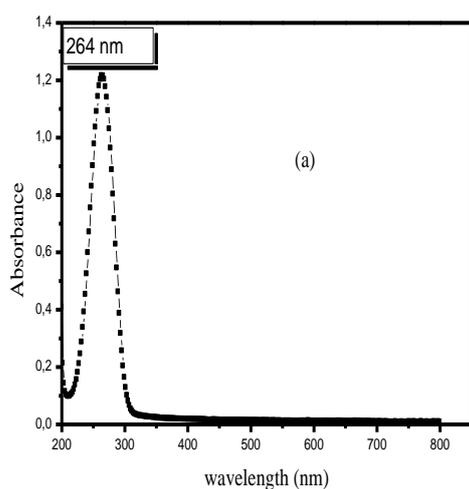
To show the efficacy of this process, we carried out a series of irradiation at 254 nm of solutions containing a fixed concentration in CR ($6 \cdot 10^{-5}$ M) and various concentrations of acetone (10^{-1} M, 10^{-2} M, and 10^{-3} M). Figure.3.c.

We observe on one hand that the degradation of the CR ($6 \cdot 10^{-5}$ M) by this process improves significantly with increasing concentration of acetone and on the other hand this

This enhancement of the disappearance of CR observed in the presence of acetone concentrations mainly 10^{-1} M, 10^{-2} M and 10^{-3} M can be described by an apparent first-order kinetics law 1(Figure.3.d). The values of rate are summarized in table (I).

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

[Acetone] mol/l	Rate %	R ²	Apparent rate constants (min ⁻¹)
10^{-1}	99.8	0.99113	$2.39 \cdot 10^{-2}$
10^{-2}	96.7	0.98521	$1.57 \cdot 10^{-3}$
10^{-3}	53.3	0.87842	$6.31 \cdot 10^{-4}$



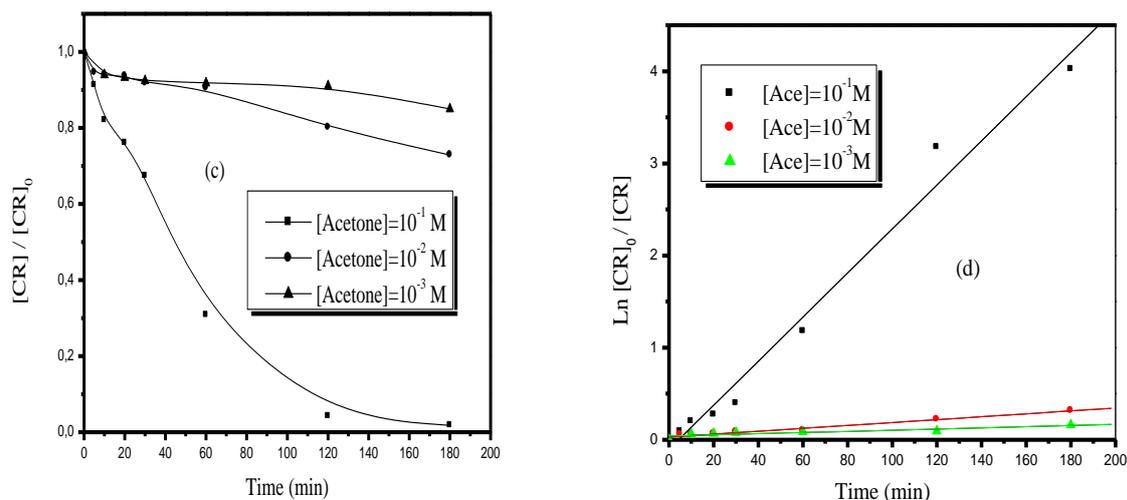


Fig.3. Decolourization of the dye $[dye]_0 = 6 \cdot 10^{-5} M$ by Acetone/UV_{254 nm} process. (a): UV-Vis spectrum of acetone alone ($10^{-2} M$) at natural pH,(b): Sensibility of CR in presence of acetone in absence of light, (c): presence of acetone at various concentration at 254 nm radiation,(d): Kinetics of CR decolourization (linear transform $\text{Ln} (C_0/C_t)$ vs t) in UV_{254nm}/Acetone process.

H₂O₂/UV process

It was reported by a great number of authors that the combination of UV with hydrogen peroxide (H₂O₂) 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 7)

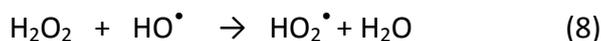


The hydroxyl radical is an oxidizing species that reacts rapidly and non-selectively on most of the organic compounds

Before studying the effectiveness of the process H₂O₂/UV to degrade CR, we tested firstly the reactivity of H₂O₂ about the CR 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 .4.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 • radical generated by the reaction of coupling H₂O₂/UV depend on experimental parameters, in particular, the concentration of hydrogen peroxide. Discoloration of the CR ($6 \cdot 10^{-5} M$) 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 CR ($6 \times 10^{-5} \text{M}$) 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.4.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 8)



The process is correctly described by an apparent kinetic law of order 1 (Figure 4.v.). The apparent constants and half time reactions ($t_{1/2}$) are reported in Table II

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

$[\text{H}_2\text{O}_2]$ mol/l	Rate % 80 min	$t_{50\%}(\text{min})$	R^2	Apparent rate constants (min^{-1})
10^{-1}	96.3	7.8	0.95487	5.38×10^{-2}
10^{-2}	99.5	4.5	0.96768	0,12816
10^{-3}	91.5	14.3	0,9799	4.3×10^{-2}
10^{-4}	74.7	30.6	0.9988	1.76×10^{-2}

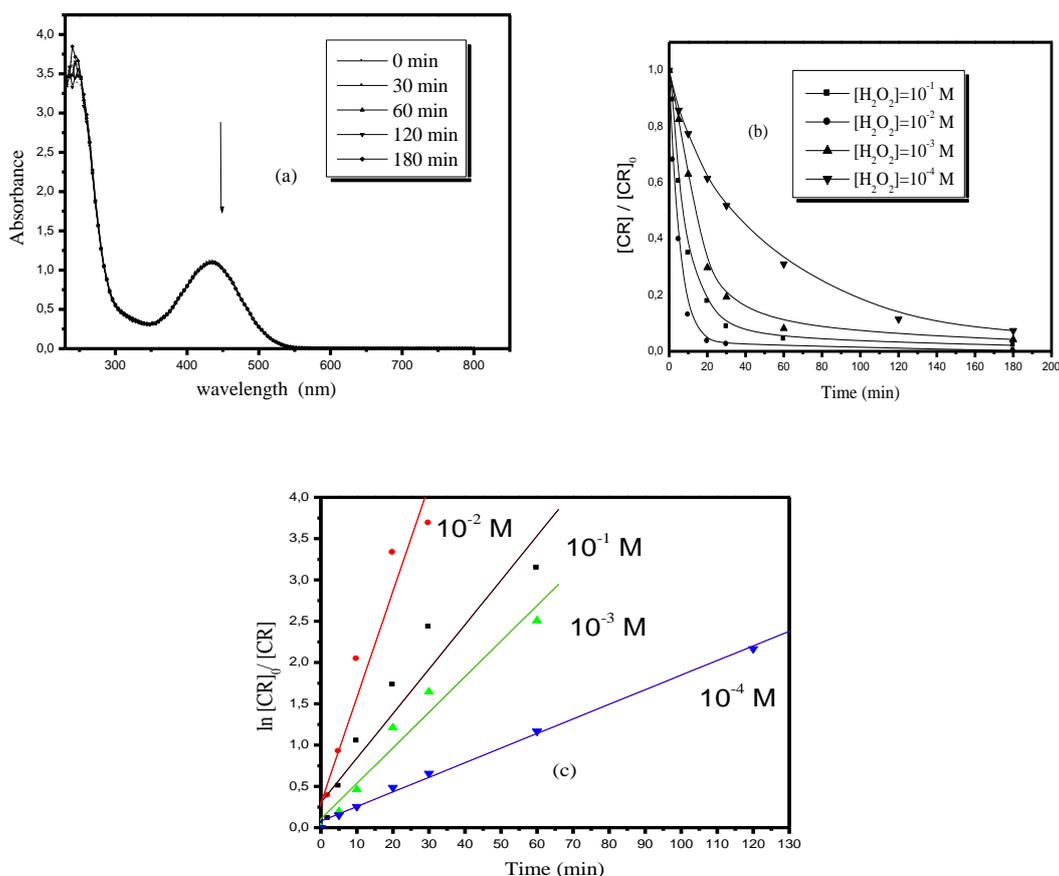


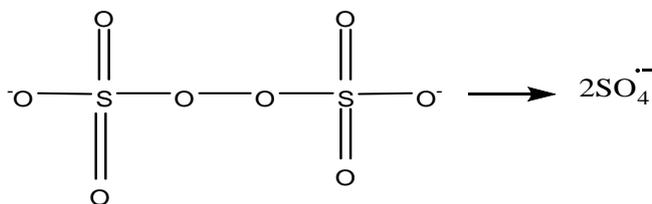
Fig.4. Discoloration of the CR by system $\text{UV}_{254\text{nm}}/\text{H}_2\text{O}_2$ [$\text{CR}]_0 = 6 \times 10^{-5} \text{M}$;
 (a): Sensibility of CR in presence of H_2O_2 in absence of light, (b): Effect of $[\text{H}_2\text{O}_2]_0$ in the discoloration of the CR, (c): Kinetics of CR decolourization (linear transform $\ln(C_0/C_t)$ vs t) in $\text{UV}_{254\text{nm}}/\text{H}_2\text{O}_2$ 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] [Mark *et coll.*, 1990].

Effect of temperature on the oxidation of CR 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 5.a. that the reaction was significantly influenced by temperature The Figure.5.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 cresol red

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.5.b.indicate that the value of the activation energy is found on the order of 187.8 kJ/mol. This result agrees with the literature [21]

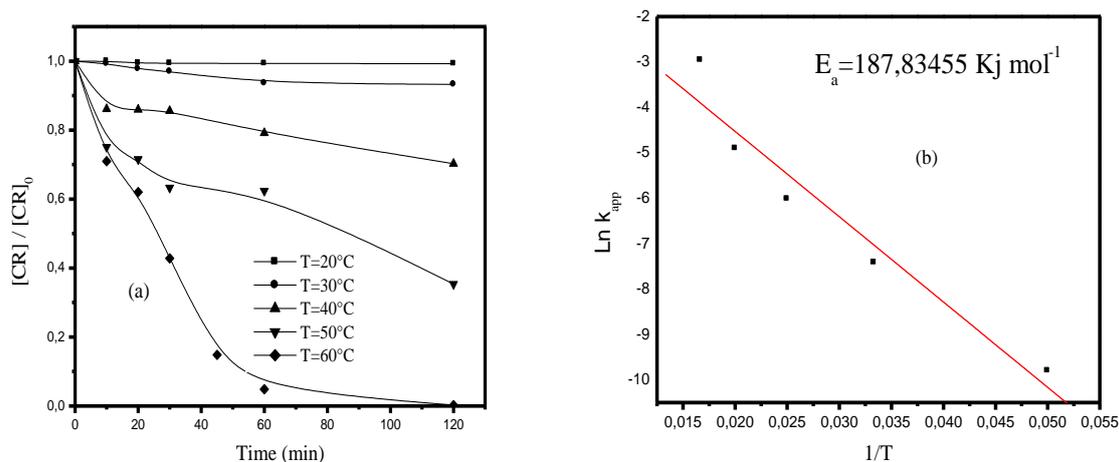


Fig.5. (a):Effect of temperature on the oxidation of CR by persulfate,(b):determination of activation energy using Arrhenius equation. $[CR]=6 \cdot 10^{-5} \text{ M}$, $[S_2O_8^{2-}]=10^{-2} \text{ M}$.

Effect of concentration of persulfate in $S_2O_8^{2-}$ /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 CR ($6 \cdot 10^{-5} \text{ M}$) and various concentrations in $S_2O_8^{2-}$. The Figure.6.shows that the percentage degradation of the dye increased with increasing amount of persulfate ion concentration and achieved 99.57 % degradation within 30 min irradiation time with 10^{-1} M persulfate ion concentration instead of 24.32 % degradation in the presence of 10^{-4} M of persulfate ion at the same time.

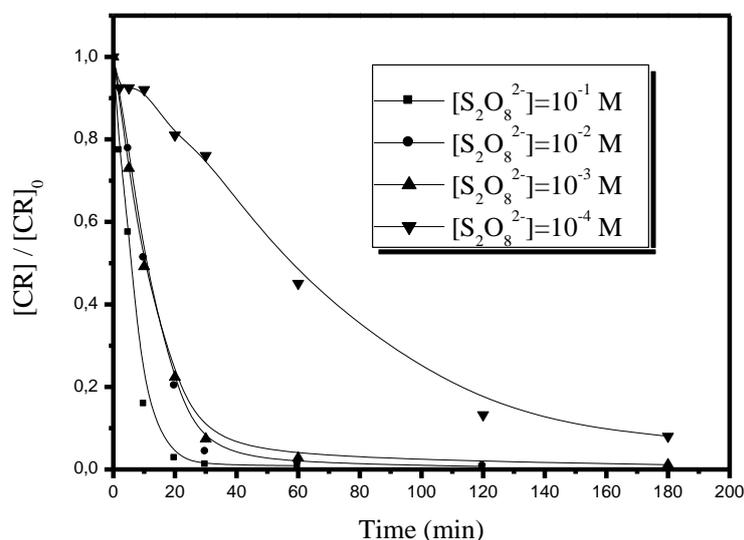


Fig.6. Effect of initial $S_2O_8^{2-}$ concentration on the degradation of CR. $[dye]_0 = 6 \cdot 10^{-5} \text{ M}$
 $\lambda_{irr} = 254 \text{ nm}$

Mineralization of CR 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 CR in the middle of the solar and 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 CR with 39% at 9 hours.

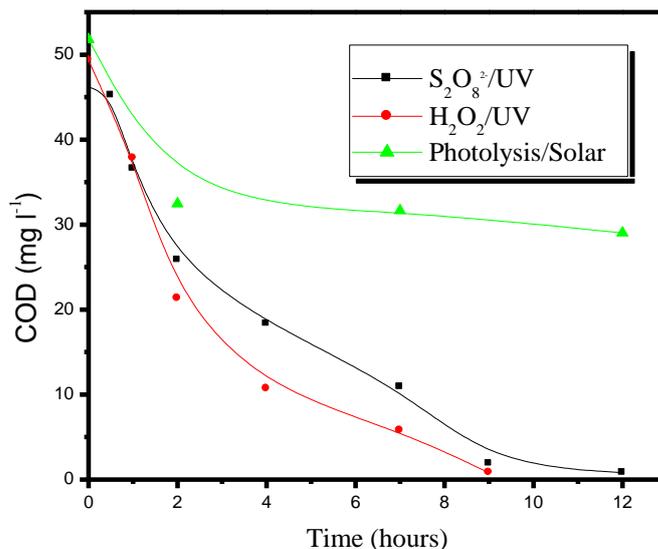


Fig.7. Evolution of COD as a function of irradiation time for different photochemical processes: photolysis solar, H_2O_2/UV_{254nm} and $S_2O_8^{2-}/UV_{254 nm}$.
 $[CR]= 6 \cdot 10^{-5}M, [H_2O_2]=[S_2O_8^{2-}]=10^{-2}M$

CONCLUSION

This study has confirmed that the performances of Acetone/UV, H_2O_2/UV_{254nm} and $S_2O_8^{2-}/UV_{254 nm}$ methods are significantly superior to the oxidative ability of photolysis solar process in the degradation of CR

The system using acetone/UV provided (concentration of acetone 0,1 M) better results than direct UV photolysis, in the decolouration process of the CR, demonstrating

therefore the important role played by the sensitizer. Indeed, the color was removed completely after an irradiation time of 180 min. However this efficiency was not sufficient by comparison to that obtained by AOT 's. in this condition, the bleaching process was totally reached at 30 min for $S_2O_8^{2-}/UV_{254\text{ nm}}$, which represents then the best performance. From the results obtained in this work, it can be confuted that the influence of parameters (light source, $[H_2O_2]$, temperature, $[S_2O_8^{2-}]$) have great effects on the degradation rate and degradation efficiency for the removal of CR.

Application of $S_2O_8^{2-}/UV_{254\text{ nm}}$ and $H_2O_2/UV_{254\text{ nm}}$ for wastewater treatment and using solar energy as source of irradiations a cost-effective technology can be suitable treatment method for in industrial applications.

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