

Application of Sunlight for Treatment of Crystal Violet Dye by Fenton-Like and Photo-Fenton-Like Effect of Operating Parameters

^{1,2}Soumia Fassi* and ²K.E.Djebbar

¹ Laboratory of materials chemistry, Department of Chemistry, Faculty of Sciences, University of brother's Mentouri Constantine (Algeria)

² Laboratory of science and technology environment, Department of Chemistry, Faculty of Sciences, University of brother's Mentouri Constantine (Algeria)

*Corresponding author fassisoumia@umc.edu.dz

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Abstract

The dyes are considered as one of the biggest sources of water pollution. Degradation of these compounds have to be carried out via, AOT's (Advanced Oxidation Technologies) due to their weak biodegradation or their high persistent in different compartments of the environment. The aim of this study is to test direct photodegradation and some advanced oxidation technics (AOTs) in absence of light (Fenton-like) and in its presence (photo-Fenton-like /UV and photo-Fenton-like/Solar) to obtain a total decolorization and mineralization of an cationic dye in aqueous solution: the Crystal Violet (CV).The degradation rate is strongly dependent of hydrogen peroxide dose, pH,potassium monopersulfate concentration and light source. Best operatory conditions were found to be pH of 3, hydrogen peroxide concentration was 0.5mM,oxone concentration was 10⁻¹M and artificial light (254 nm).The reaction efficiencies have been compared for the same system .The obtained results showed that color removal followed the increasing order: photolysis/UV (5.3%) < photolysis/Solar (15.7%) < (Fe(III)/H₂O₂ (19.4 %) < Fe(III)/H₂O₂/sunlight (62.5%) < Fe(III)/ H₂O₂/UV_{254nm} (72.3%) < Fe(III)/ H₂O₂/Oxone/UV_{254nm} (99%) with a reaction time of 30 minutes. The efficiency of substrate mineralization in each process has been discussed by total chemical oxygen demand content of CV solutions.

Keywords: Fenton-like,Photo-Fenton-like,CV,sunlight.oxone.

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Introduction

Textile wastewater is contributing greatly to water pollution. The release of textile wastewater to natural environment is very problematic for aquatic life (1) and human (2).However, several

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treatment processes are available for the removal of this type of pollutants, such as precipitation and biological treatment (3), flocculation (4), coagulation (5), adsorption on various supports (6). However we have observed an efficiency lack because of the pollution transfer from one phase to another leading therefore a further costly treatment. In latter decenies, a promising route to traditional methods is "Advanced oxidation process".

Crystal violet (CV) is widely applied in textile industry as a typical cationic dye. It has also been used as antifungal and antimicrobial agents (2).. CV is a mutagen, mitotic poison and potent carcinogen and is toxic to mammalian cells (2).. Thus, it is necessary to remove such contaminants from industrial effluents to protect the environment and offer people a better quality of life. AOPs are capable of producing of very reactive species either in homogeneous medium: the radicals OH^\bullet . They are able to oxidize rapidly, efficiently and no selectively an elevated number of organic pollutants in wastewater (7).

Among these processes, Fenton-like appear 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 and ferric ions. However, the only disadvantage for both systems, is their use in acidic medium ($\text{pH}=3$) to prevent formation and precipitation of hydroxide. Thus, the mechanism of the oxidation of the pollutant is as shown below; R is an organic binder (8-9).



These resulting hydroxyl radicals then attack organic substrates and cause their chemical decomposition by H-abstraction or addition to C–C unsaturated bonds (10).



Moreover, the combination of light (artificial) to the Fenton-like, could improve the degradation of pollutants. Thus the addition of light to Fenton-like process is beneficial for direct formation of hydroxyl radical.

Recently, other processes have been studied trying to use solar light instead of artificial UV radiation (11).

The aim of the present work is to analyze the possibility of decolorization and mineralization of CV by direct photolysis and by different AOTs such as: Fenton-like, photo-Fenton-like/UV and photo-Fenton-like/Sunlight. The efficiency of substrate decolorization and mineralization in each process has been discussed. The effect of different parameters such as: pH, H_2O_2 dose and light source will be investigated. The effect of additive such as potassium monopersulfate (oxone) was studied.

2- EXPERIMENTAL

2.1. Material

Crystal violet (abbreviation CV) was purchased from Fluka chemical company and used without further purification. The hydrogen peroxide solution (33% Fluka), salts of iron (III) ($\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$, Carlo Erba 99%) and potassium monopersulfate (oxone) solution were prepared from ultra pure water from a MILIPORE unit and at $\text{pH}=3.0$, to prevent formation and precipitation of hydroxyls. Besides, the pH was adjusted with HCl to reach the desired value. The concentration of solution the substrate is 10 mg. L^{-1} and its natural pH is 5.8. The structure of CV is shown in (Fig. 1).

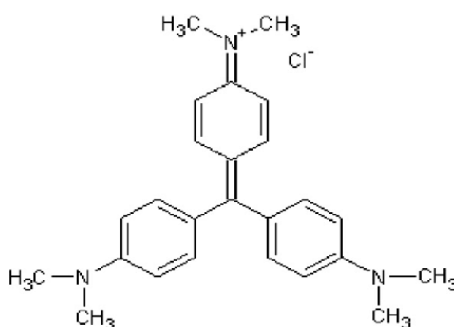


Fig.1. Structure of Crystal violet

2.2. Photo-reactor and source light

2.2.1. Artificial source light

Aqueous solutions were irradiated at 253.7 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 (12) . The reactor is surrounded symmetrically by these lamps. The temperature of the reactor was maintained between 18 and 20 °C by the use of an air flow provided by a Ventilator. The entire system is placed in a cylindrical enclosure.(Fig.2).

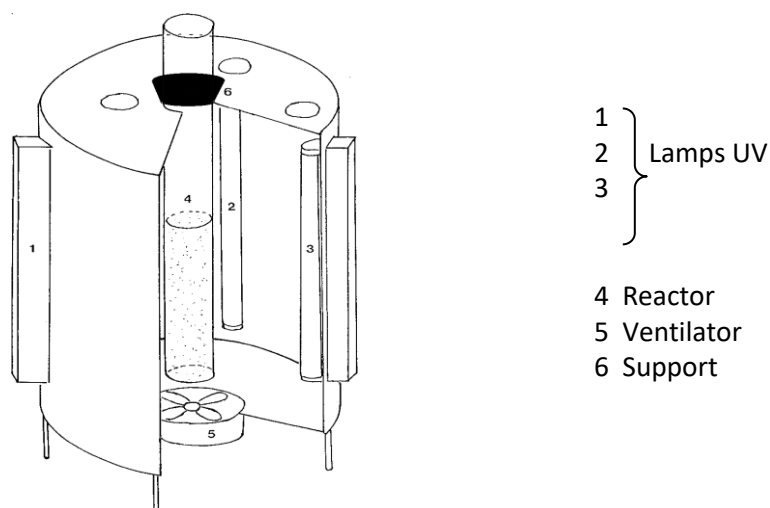


Fig.2. Scheme of the used device

2.2.2. Description of the used Photoreactor in sunlight

Solar light experiments were performed during sunny day of Jun at University of Constantine – Algeria. The temperature of the reactor during those experiments rose from approximately 36 to 38°C. The intensity of the incident light inside the photoreactor, measured was 0.92 W. cm⁻², using solar light radiometer PMA2100. In solar light, aqueous solution of the dye were degraded in presence of H₂O₂ and salt of Fe (III) using a pilot plant containing a reservoir delivery, a pump, and an assembly of tubes on Pyrex. They are located closely to each other and in a vertical position towards natural light. Samples were withdrawn at regular time intervals and analyzed immediately (13) (Fig.3).

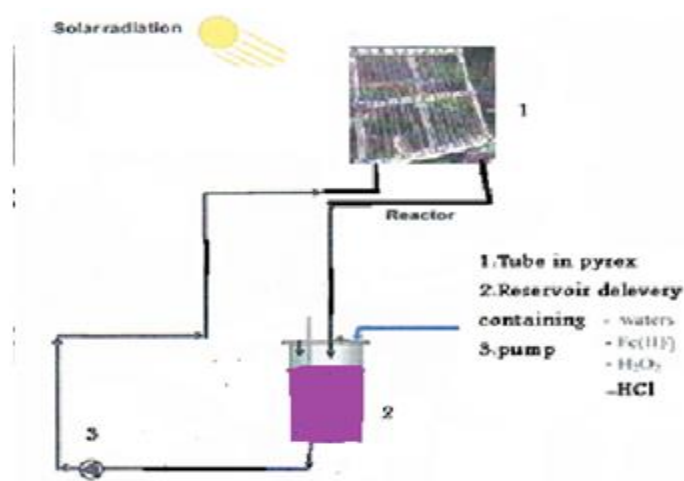


Fig.3. Set up of pilot plant solar light, scheme of the device (1: tube in pyrex, 2: dye solution, 3: pump).

2.3. Analysis method

CV dye was analyzed on UV-Visible spectrophotometer in Fenton-like or photo-Fenton-like reaction. After every 5 to 10 min of reaction time, 3 mL of CV dye solution was taken out from photoreactor and was then analyzed by UV-Visible spectrophotometer in the spectral range from 200 to 800 nm. The change in color of CV dye in the reaction mixture at different time intervals was obtained by measuring absorbance at 588 nm and by computing the residual concentrations of substrate. Total chemical oxygen demand measurements were carried out with a Skalar Formacs COD/WTW.CR320.

3. Results and discussion

3.1. Direct Photodegradation of Crystal violet under artificial and sunlight

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The direct photodegradation of CV was carried out in batch method reactor, at pH 5.8, at concentration of 10 mg. L⁻¹ and at 254 nm and sunlight. **Figure.4** presents typical data obtained from the photolysis of CV ([CV]₀ = 10 mg. L⁻¹) in aqueous solution. In artificial light, the results obtained show that this compound undergoes slow photolysis for the purposed concentration. Whereas, in natural light and on typical summer days, we observe a rapid decolorization process of the dye. However, photolysis/Sunlight process has a better decolorization capacity than photolysis/UV process. Indeed, the elimination rate is equal to: 10.1% for artificial light and 30% for solar light, for a reaction time of 150 minutes. This is due to a better absorption of photons by the CV in natural light.

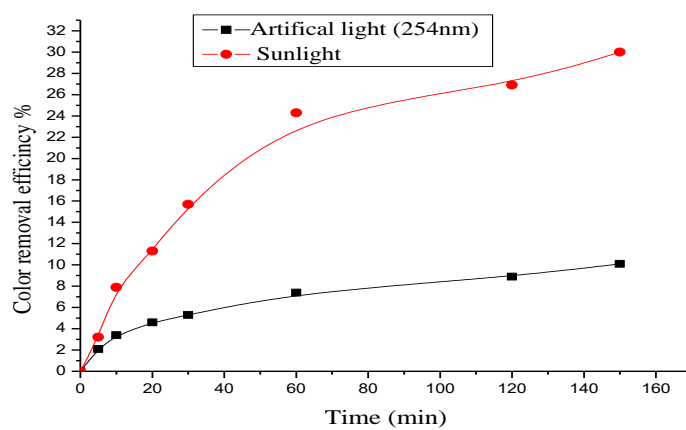


Fig.4.Effect of light on the direct photodegradation process of CV, [Dye]₀ = 10 mg/L

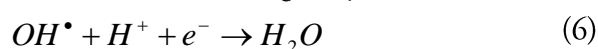
3.2. Fenton-like and photo-Fenton-like processes

3.2.1. Effect of pH

PH is an important factor that affects the degradation rate of the textile dye solution. The work is carried out at different pH values to find maximum removal efficiency. From literature, it is well known that Fenton-like reaction is effective at pH= 3.0 [13]. Taking this into account, a set of experiments were performed to obtain best color removal. In this project removal efficiency and COD removal is find out at different pH value at H₂O₂ concentration of 0.5 mM at a reaction time of 120 min.

Moreover, the effect of pH (ranging from 1 to 5) in the bleaching process of the dye, was reported in Figure.5 for Fenton-like system. Thus, by considering this figure we observed that (14):

-In very acidic medium (pH<2) the efficiency was low due to a feeble participation of radical OH[•] which are scavenged by this medium (reaction 6)



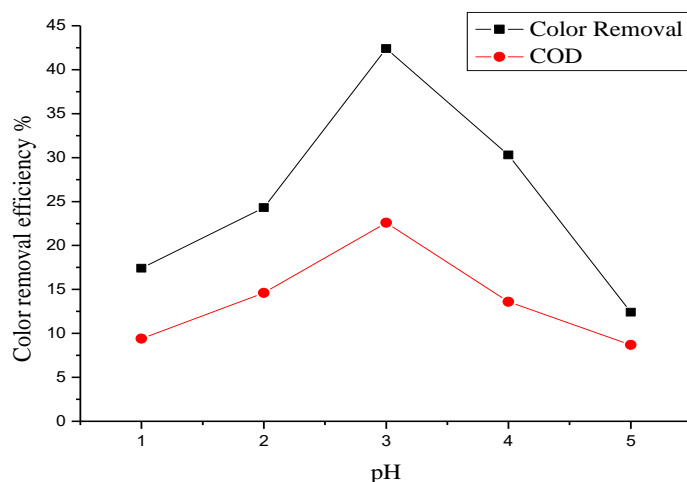


Fig.5.Effect of pH on decolorization and COD removal processes of CV in aqueous medium by Fenton-Like. Initial conditions: C_0 (dye)= 10mg L⁻¹. C_0 (Fe³⁺)= 10⁻⁴ M. C_0 (H₂O₂)=0.5 mM

3.2.2. Effect of hydrogen peroxide

Amount of H₂O₂ is one of the main parameters to influence the Fenton-like process. The main objective of this experiment was to find the best optimum concentration of H₂O₂ dosage. The experiment was carried out at a pH of 3 by varying hydrogen peroxide concentration, Figures 6 show the effect of initial H₂O₂ concentration on the decolorization and COD removal of CV dye by Fenton-like process. The results showed that with the increase in the initial H₂O₂ concentration from 0.05 mM to 0.5 mM the degradation of CV increases from 22.6% to 42.4%, respectively, We observed also under these experimental conditions, 22.6%, 19.4 %, 17.3%, and 15.4 % COD removal were achieved for [H₂O₂]= 0.5mM,0.2mM,0.1mM and 0.05mM respectively. The color removal and COD removal are obtained at a reaction time of 120 min (Fig.6).

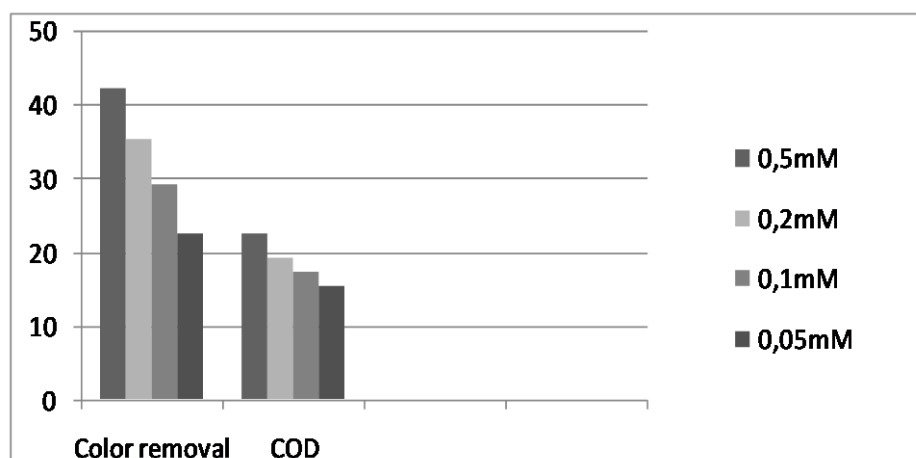


Fig.6. Effect of hydrogen peroxide on decolorization and COD removal of CV by Fenton-like process. Experimental conditions: [CV] =10 mg/l; $[\text{Fe}^{3+}] = 10^{-4}$ mol/L, pH=3 and reaction time =120 minutes.

3.2.3. Effect of light

The oxidation of the dye was greatly enhanced by light for both systems. The direct photolysis under artificial and solar light are not significant. The same results are obtained in Fenton-like process in the dark. However, when $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ is combined to UV (254nm) or solar irradiation, we observe a drastic increase in bleaching. This enhancement could be attributed to the important production of radical OH^\bullet from different sources like (13):

- The reaction between 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+} ($\text{Fe}(\text{OH})_2^+$).

The decolorization process, occurring in solar light, was achieved in typical summer day and under the same experimental conditions ($[\text{H}_2\text{O}_2]=0.5\text{mM}$, $[\text{Fe}^{3+}]=10^{-4}\text{M}$ and pH=3). In (Fig. 7.a), we observed that efficiency resulting from oxidizing process (photo-Fenton-like in artificial light) was about 98.7% in 60 min, whereas in natural light (sunlight) it was about 80.7%. Indeed, the efficiency of the decolorization faster for $\text{Fe}^{3+}/\text{UV}/\text{H}_2\text{O}_2$ comparatively to $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{Solar}$. Is observed also an increase in COD removal efficiency as we coupled light (artificial or solar) to Fenton-like system: 22.6% for $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, 67.3% for $\text{UV}_{254\text{nm}}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ and 52.8% for solar/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2$. These efficiencies have all been measured in 60 min. This is graphically represented as below (Fig7.b).

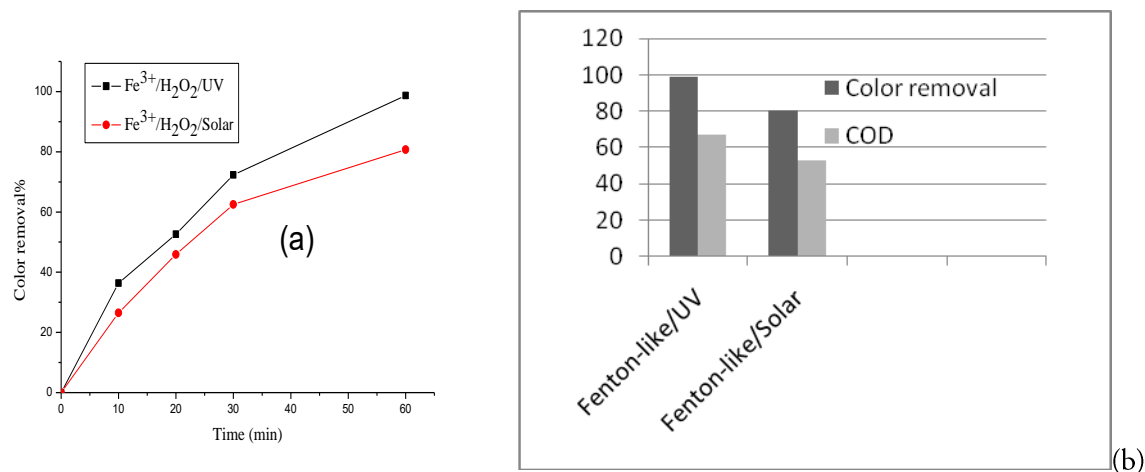


Fig.7. Comparison between Fenton-like/ $\text{UV}_{254\text{ nm}}$ and Fenton-like/solar light processes. (a): Color removal efficiency (b):COD .Experimental conditions: [CV]=10 mg/l; $[\text{H}_2\text{O}_2] = 0.5\text{m}$ mol/L; $[\text{Fe}^{3+}] = 10^{-4}\text{mol/L}$; $T = 37^\circ\text{C}$, solar light intensity = 0.92 W. cm^{-2} pH=3 and reaction time =60 minutes.

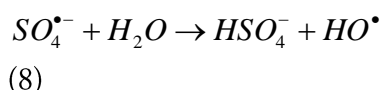
3.2.4. Effect of potassium monopersulfate (oxone) addition

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Photo-Fenton-like degradation of Crystal violet was investigated in presence of potassium monopersulfate (oxone). The result obtained is shown in (Fig. 8). The degradation rate was enhanced by the addition of oxone. The decolorization increased with increasing oxone concentration. An initial removal rate of 98.7% was attained upon Photo-Fenton-like process for a reaction time of 60 min, while in the presence of oxone, the color removal increased to 96%, 97%, 98% and 99% for oxone concentrations of 10^{-4} M, 10^{-3} M, 10^{-2} M and 10^{-1} M respectively for a reaction time of 30 min, Besides the degradation process, in presence of oxone resulted in the formation of hydroxyl radical and sulfate radical anion according to the reaction 7:



In another part, the radical anion is a powerful oxidizing. It may also remove an electron from a molecule in H_2O to give a hydroxyl radical:



The formation of hydroxyl radical and sulfate radical anion are powerful oxidant that can degrade dye molecules at faster rate. As with radicals $SO_4^{\bullet-}$ and HO^{\bullet} have the unique nature of attacking the dye molecule at same positions, hence, leading to a rapid fragmentation of dye molecules (15).

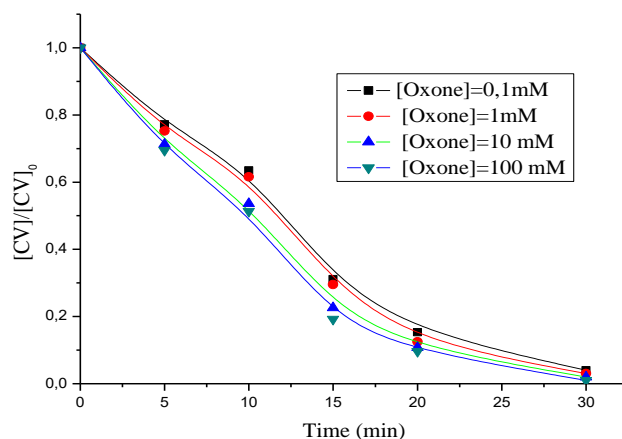


Fig. 8. Effect of oxone addition on decolorization of CV by photo-Fenton-like process
Experimental conditions: [CV]=10 mg/l; $[H_2O_2] = 0.5 \text{ mmol/L}$; $[Fe^{3+}] = 10^{-4} \text{ mol/L}$; pH=3 and reaction time =30 minutes.

Conclusion

In the present study, a treatment of a cationic dye solution using Fenton-like in one part and photolysis and photo-Fenton like under artificial and natural light in another part. Was taken into account. Based on the obtained results, the following conclusion can be drawn:

- The Fenton-like and Photo Fenton-like processes are a type of advanced oxidation process which is adopted for the treatment of different dye solutions with different concentration.

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- The optimal experimental conditions for these processes, with a CV concentration of 10 mg/L can be summarized as: pH =3, hydrogen peroxide dosage=0.5m mol/L and iron (III) dosage = 10 m mol/L.
- Under these experimental conditions, 5.3%, 15.7 %, 19.4%, 62.5% 72.3%,and 99% decolorization were achieved for direct photolysis/UV, photolysis/Sunlight, Fenton-like, Fenton-like/sunlight, Fenton-like/UV_{254nm} and Fenton-like/Oxone/UV_{254nm} respectively. These efficiencies have all been measured in 30 min.
- We observed that, dye decolorization is much higher than COD in the presence of the systems listed above.
- The decolorization and mineralization processes in the presence of solar light and on typical summer days, was found to be more efficient than that obtained in dark conditions (Fenton-like).
- The decolorization was totally reached at 30 min for H₂O₂/Fe³⁺/Oxone/UV, which representing then the best performance.
- From the above conclusion, it is proved that Fenton-like and Photo Fenton-like are an effective processes for the treatment of synthetic dye solution.
- The application of the Fenton-like process using solar energy might be interesting in the treatment method of wastewater in industrial applications.

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