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Photo Degradation of Solochrom Violet Dye by ZnO: Experimental and Theoretical Study

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Abstract

The present project involves photodegrading the dye solochrom violet under advanced oxidation techniques at (25 oC) temperature and UV light. Zinc Oxide (ZnO) and UV radiation at a wavelength of 580 nm were used to conduct the photocatalytic reaction of the solochrom violet dye. One of the factors looked into was the impact of the starting conditions. pH, the amount of original hydrogen peroxide, and the dye concentration time radiation were used. For hours, the kinetics and percentages of degradation were examined at various intervals. In general, it has been discovered that the photodegradation rates of the dye were greater when H2O2 and ZnO were combined with UV light. The best wavelength to use was determined. Modern oxidation techniques were proven to be very effective at degrading the majority of contaminants in wastewater. Using a spectrophotometer, the dye's photocatalytic browning was investigated. The theoretical calculation concentrated on the active site using the density functional theory technique and the Gaussian 09 program.

Keywords: Density Functional Theory, Experimental, Photodegradation, Solochrom Violet Dye, Zinc Oxide.

Introduction

The main cause of water and groundwater pollution is the environmental dangers posed by the textile wastewater industry. Utilizing UV or visible light, various oxidants (O_2, H_2O_2, O_3), TiO_2 catalysts, and advanced oxidation processes, harmful and recalcitrant pollutants are successfully detoxified in industrial wastewater [1]. Added to create highly reactive radicals •OH to convert aqueous contaminants into harmless compounds [2]. Numerous studies conclusively demonstrated that the chemical makeup of the dyes [3-6] have a significant impact on the photocatalytic system's effectiveness in degrading organic and inorganic substances. A promising technology for lowering worldwide environmental pollution is heterogeneous photocatalysis by semiconductor particles. Textile wastewater contains significant amounts of heat, high acidity, and other soluble compounds. Pollutants in cloth effluent were primarily produced during dyeing and finishing processes[7-8]. Various municipal and industrial wastewaters, including chemicals, have been treated using different treatment processes, including physical, chemical, and biological [9]. Biotechnology, food[10], pharmaceuticals[11], wood and paper[12], dye production, and textiles[13]. These dyes can be easily cured, which can break the intricate structure of the dye and make it more susceptible to biodegradation

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if conventional treatment methods are mixed with contemporary oxidation processes [14]. Original hydrogen peroxide concentration's impact H_2O_2 and zinc oxide are combined in this procedure, along with UV light. In hydrogen peroxide, ultraviolet light breaks the (O-O) bond, releasing the hydroxyl radical. Below [15] are the reactions that correspond to the UV/H_2O_2 processes:

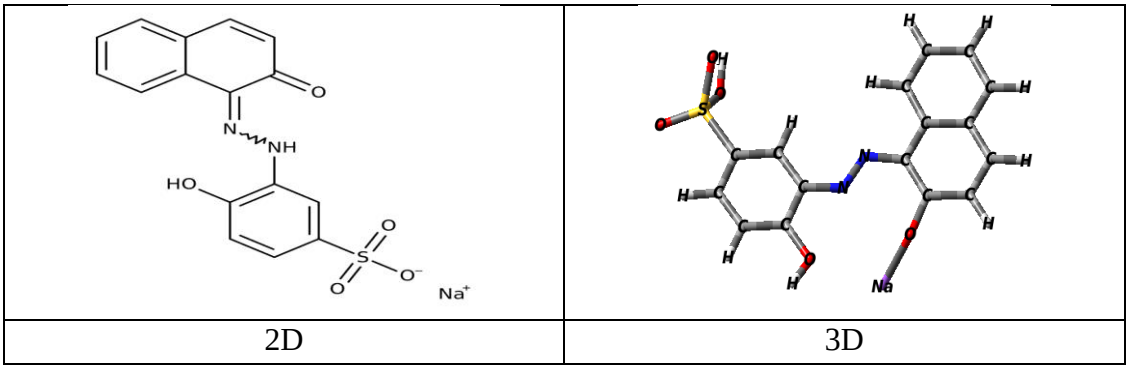
$H_2O_2 + h\nu \rightarrow 2\ HO\bullet$ 1

$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O$ 2

$HO\bullet + HO_2\bullet \rightarrow H_2O + O_2$ 3

Using various homogeneous (H_2O_2/UV-Vis and H_2O_2/Fe_2+/UV-Vis) and heterogeneous (TiO_2/UV-Vis) systems, Carla and colleagues studied the photo-oxidation of cork manufacturing effluent with the goal of evaluating the degradation performances in terms of total organic carbon (TOC) removal [16]. The structural composition of a dye is shown in **Scheme 1**

The aim of this study is to remove water pollution from solchrome violet dye by using simple and available materials, by using zinc oxide.



2D	3D

Scheme 1. Molecular structure of Dye's.

Materials and Methods

Without further purification, all compounds were used. The following substances were provided by BDH: sodium hydroxide (NaOH), hydrochloric acid HCl , and hydrogen peroxide (H_2O_2, 30% w/v). From Omega, dyes (a USA.MSDS substance) were bought. Merck provided the photocatalyst ZnO for this project (99 percent purity). Double-distilled water was used to make all of the other chemicals and solutions.

General Procedure

The dye solutions that were exposed to radiation for 120 minutes are the subject of the first section (the primary experiments indicated that most dye molecules are degraded or became colorless at a time close to this period). Samples were collected during this time in order to measure the dye absorption at max=580 nm and then calculate the dye concentration using the calibration curve shown in Figs. 1 and 2, which represent the dye's UV-Visible absorption spectrum. Using sodium hydroxide and hydrochloric acid [17] in the concentration of 0.1 N, the pH was adjusted to the desired value. ZnO in the solutions and UV irradiation with an H_2O_2 percent were used in the control tests, which were performed under UV illumination. In each trial, the lamp warmed up for 10 minutes before the reaction even starts. To create aqueous ZnO suspensions (all colors had a (0.004)% concentration), 0.004 gm of powder was added to 1L of ZnO aqueous dye solution ($1X10^{-5}$ M). Following sample collection, a pH meter was used to determine the pH. (211- Instrument, Romania). Following centrifugation (CORP Triup International, Italy instruments) and filtration to remove the ZnO particles, the absorption was measured simultaneously using a spectrophotometer (Shimadzu UV-Visible 1650 spectrophotometer). The results and absorbance at λ_{max} 580 nm were recorded after these steps.

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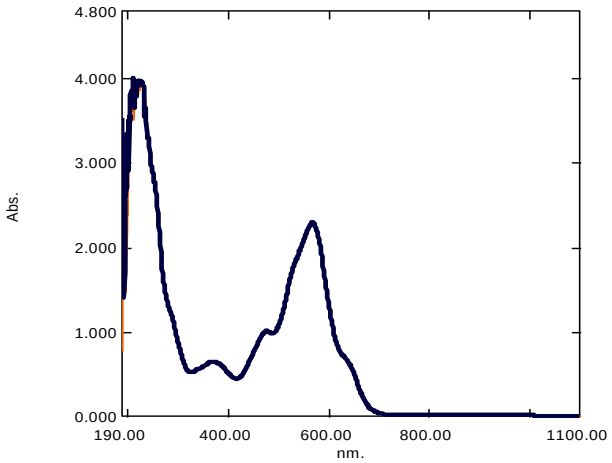

Figure 1. Calibration curve for Violet Dye content 1×10^{-5} M at pH 6

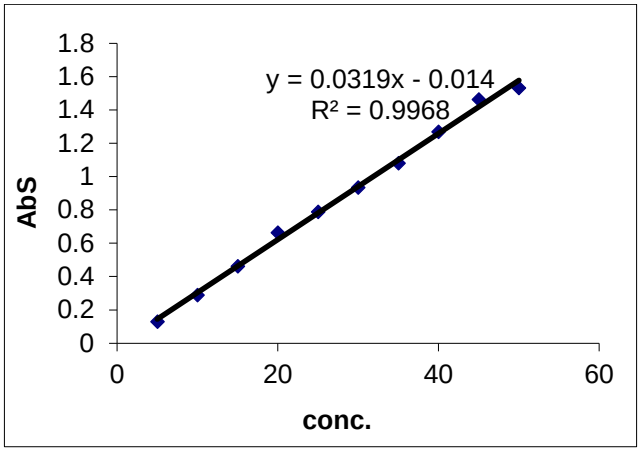

Figure 2. The UV-Visible spectrum of an aqueous solution with a dye content of (1×10^{-5}) M, pH = 6, and a temperature of 298 K.

Results and discussion

Photolysis of Zin Oxide

On the dye, the effect of ZnO on the elimination of color was examined. As a result, by adding more ZnO, the rate of color removal was considerably increased. By raising the catalyst, the ZnO surface's active sites expand, producing more OH and O_2 radicals [18]. It takes 120 minutes to completely photobleach the pigment when it is exposed to sunlight. According to Fig. 3, the degradation of the dye increases as the catalyst concentration rises. We stated that zinc oxide and titanium dioxide were preferred in our earlier research [19–21]. Due to their photocatalytic properties, which showed adequate activity in the visible irradiation range, both catalysts are appealing substrates for the photodegradation of water contamination.

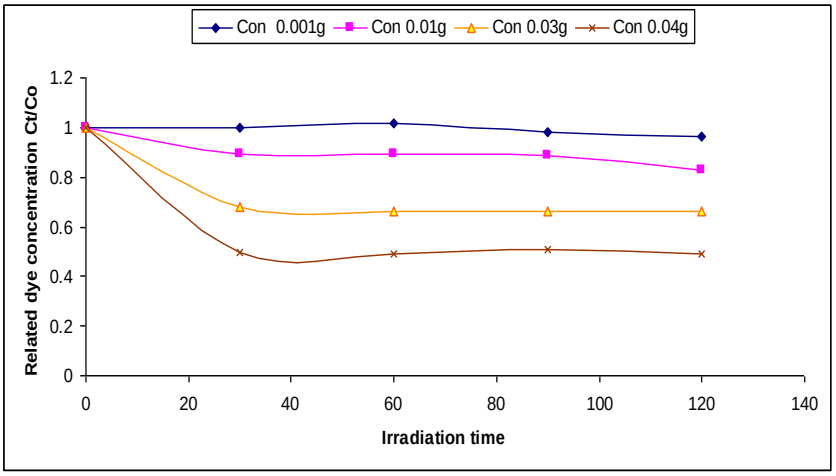

Figure 3. The photo degradation of dye content of ($1x10^{-5}$) M, pH = 6 as a function of irradiant time in the presence of different concentrations of ZnO.

Effect of pH

Photo-degradation is significantly impacted by the pH. pH substrates were used to assess the impact of pH (2, 4, 6 and 9). Experiments are carried out at a dye concentration of (1×10^{-5})M in the presence of a dosage of 6 ml H_2O_2 and 0.04gm ZnO for 120 minutes at a temperature of 298 K. The gradient of the relative dye concentration, C_t/ C_o, is shown in

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Fig. 4 for increasing irradiation duration. According to the findings, the rate of color removal increased in low pH values because more factors reached a maximum of 65% under acidic conditions at a pH of 2. Because of a free hydrogen atom, OH radical generation causes structural changes in the molecule, which exposes the dye molecule to attack by the hydroxyl radical in acidic circumstances [22]. In an alkaline medium, hydrogen peroxide experiences decomposition; because HO was produced, the removal was low. Slowed down and broke down water and oxygen instead of generating hydroxyl free radicals when exposed to UV radiation[23].

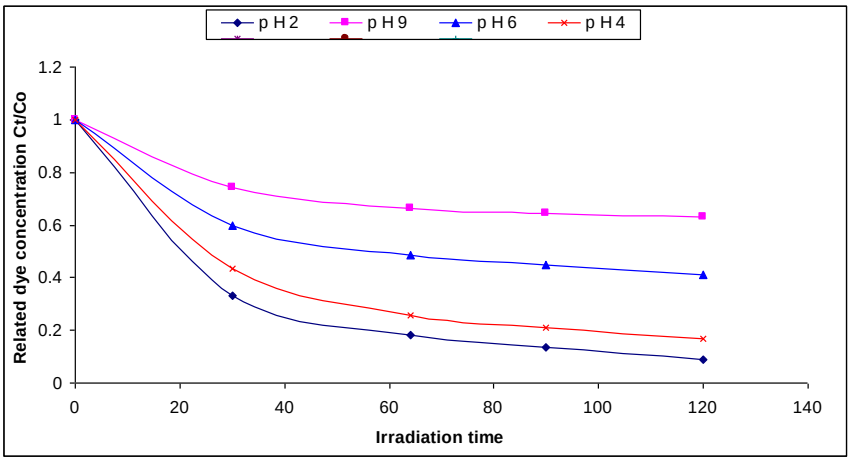

Figure 4. Appears the impact of varying pH levels on 1×10^{-5} M dye color removal as a function of irradiation time = 120 min at T=298 k.

Effect of Initial Hydrogen Peroxide Concentration

In experiments involving photo oxidation in the presence of UV light, the research investigated the effects of various H_2O_2 concentrations between (100 to 500 mg/L) on the decolorization. The formation of (•OH) is the kinetic determining process at modest hydrogen peroxide concentrations. Oxidation occurs at a logically slow pace because hydrogen peroxide cannot produce enough hydroxyl radicals. The rate of oxidation increased as hydrogen peroxide content increased because more •OH is created. The excess H_2O_2 was the favored reaction site for these free radicals as opposed to the chromophore [24] dye. According to the UV exposure duration and different initial H_2O_2 dosages, the decolorization of dye is shown in Fig. 5 as a function.

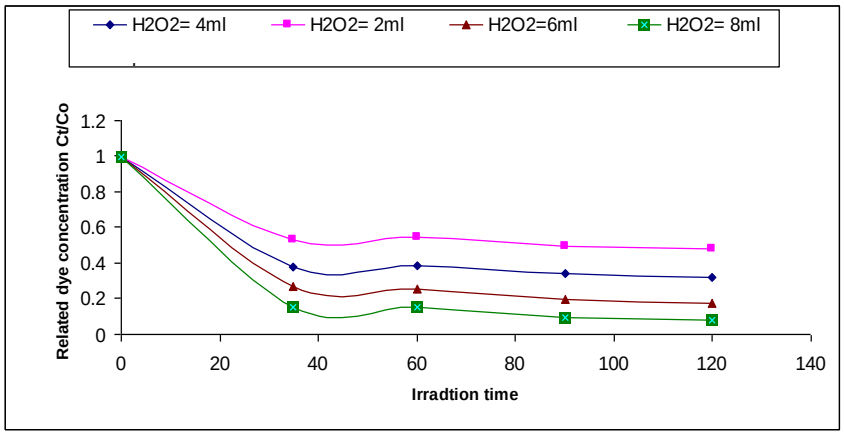

Figure 5. Shows the impact of various initial H_2O_2 concentrations on the removal 1×10^{-5} M of dye using the UV/H_2O_2 technique at 298K and 120 min irradiation time.

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Computational Details

For violet dye structure [25], the 6-311G (d, p) basis set was chosen because it provides precise electronic properties and geometries. Limitations in orbital theory with regard to the centers of these molecules being drawn to the metal surface [26] were used to predict the absorption of inhibitor molecules. The energy of the lowest unoccupied molecular orbital (E_{LUMO}= -0.0779 a.u.) is lower than that of the greatest electron occupancy in a molecular orbital (E_{HOMO}= -0.1696 a.u.). LUMO and HOMO density distributions for compounds investigated in the gas phase are shown in Fig. 6's geometry optimization. The green color depicts a low electron density, while the red color denotes a high electron density [26]. High electron density is a region of electrons that are donats the metal surface. Receiving electrons from ZnO[27] is represented by the Green region. So it is important to consider how these two regions are distributed. The double bond in (N) atoms in and out of the ring with the nonbonding electrons of all atoms is what causes the dye in the ground state to have a high electron abundance from the receptor site.

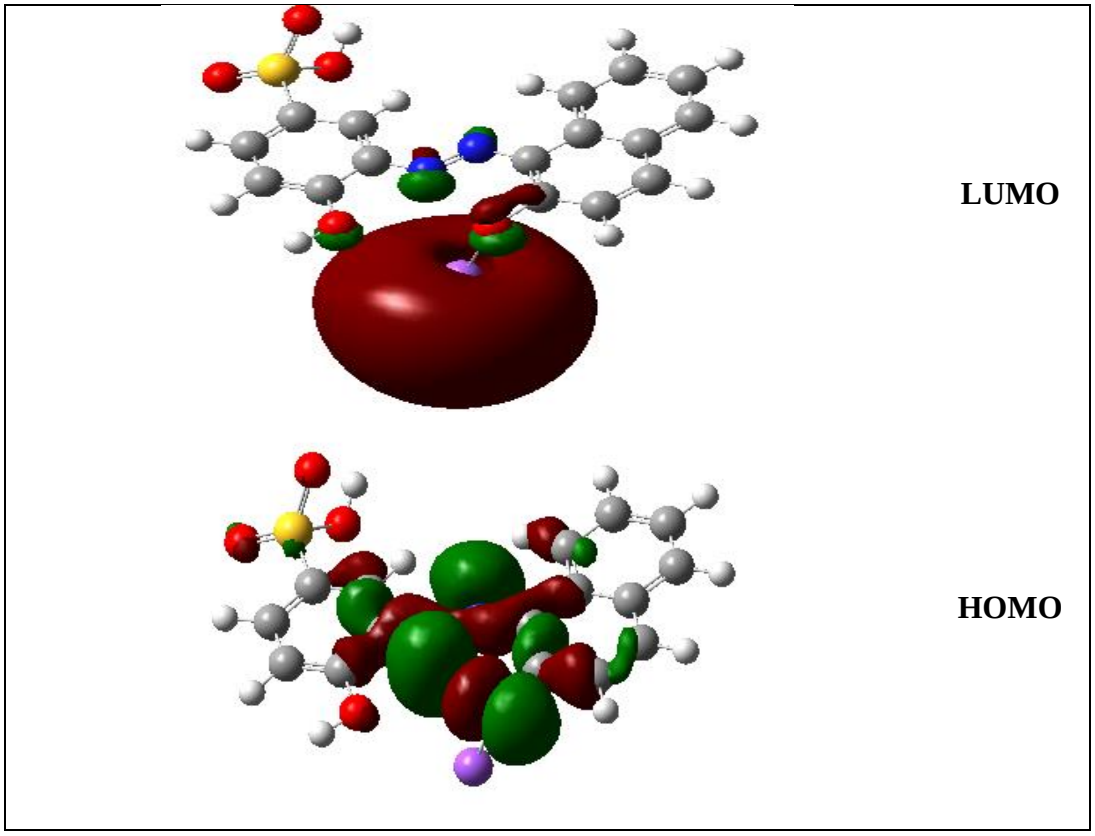

Figure 6. HOMO-LUMO orbitals of violet dye at pH=6.

TED Maps

The donor atom's electron density affects how strong the adsorption link is. The molecule's electron density was displayed by total electron density (TED). The O atom and some regions of the (O-Na) in the molecules under study are examples of sites with strong electron negativity, as shown in Fig. 7, and these sites can aid in an electrophilic attack. Furthermore, the yellow hue denotes atoms with a modest electronegativity. The best positive area to receive electrons from donor compound [27] is shown in blue. Due to the positive charge, the protonated state has a blue color and refers to the capacity of accepted electrons.

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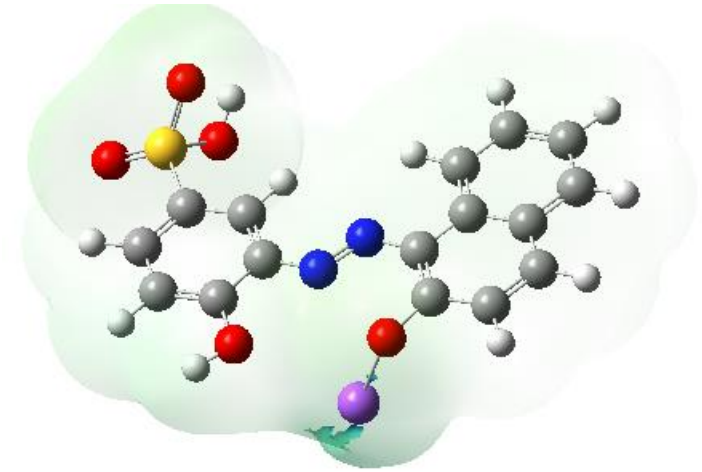

Figure 7. TED map of the studded structure

Conclusion

Solochrom violet dye photo oxidation using UV/H_2O_2 is more effective in an acidic medium, with an initial dose of H_2O_2 ranging from 4 to 8 ml. A variety of variables had a big impact on the decline. In particular, the amount, pH, dye concentration, original H_2O_2 dose, and semiconductor type. In the case of bleaching solochrom violet dye, it has been demonstrated that a particular number of semiconductor oxides can be used as a photo catalyst in UV light. UV light assists to remove dye more effectively. Theoretical part discusses the more active site.

Acknowledgment

We extend our thanks to everyone who contributed to the completion of this research, especially College of Science for Women ,Department of Chemistry.

Author's Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

Authors' Contributions

All authors contributed to the design and implementation of the research, to the analysis of the results and to the writing of the manuscript.

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التحلل الضوئي لصبغة سولوكروم البنفسجية بواسطة اوكسيد الزنك:دراسة تجريبية ونظرية

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الخلاصة

يشمل العمل الحالي التحلل الضوئي للصبغة البنفسجية سولوكروم باستخدام عمليات اكسدة متقدمة عند درجة حرارة 25°C باستخدام الاشعة فوق البنفسجية H_2O_2 . تم اجراء التحفيز الضوئي لصبغة سولوكروم البنفسجية عند الطول الموجي 570 نانومتر مع ZnO. تم دراسة تاثير عوامل مختلفة وهي تركيز الصبغة ,درجة الحموضة ,والتركيز الاولي لمادة بيروكسيد الهيدروجين ,وقت التشعيع . ودراسة الحركية على فترات مختلفة كما تم دراسة نسب التحلل بشكل عام.وجد ان معدلات التحلل الضوئي للصبغة كانت اعلى في وجودH_2O_2 و ZnO مع الاشعة فوق البنفسجية .تم تحديد الطول الموجي الافضل . اثبتت عمليات الاكسدة المتقدمة فعاليتها العالية في تحلل معظم الملوثات في مياه الصرف الصحي . تم استخدام مقياس الطيف الضوئي لمراقبة التحلل الضوئي للصبغة .ركزت الحسابات النظرية على المواقع النشطة باستخدام طريقة the density functional theory في برنامج Gaussian.

الكلمات المفتاحية: دراسة النظرية، تجريبي، تحلل ضوئي، صبغة سولوكروم البنفسجية، أكسيد الزنك.