

The Study On Photo Degradation Of Crystal Violet By Polarographic Technique

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Abstract-- This work include the photocatalytic degradation of an aqueous crystal violet [Tris((dimethylamino)phenyl)methyl chloride] dyes by using ZnO catalyst photo catalyst in aqueous medium, Photocatalytic degradation of dyes was carried out by using UV radiation as light source. The result of this study expressed by current diffusion against time to using polarographic technique. The effect of some parameters, such as mass of catalyst, Initial dye concentration, initial pH of aqueous dye solution and temperature were studied.

The results indicate that the photocatalytic reactions are a pseudo first order reactions according to the Langmuir-Hinshelwood relationship. It was observed that the photocatalytic degradation efficiency increase with increase of catalyst mass up to 0.1g. For above this masses, photocatalytic degradation efficiency was decreases with increasing of catalyst mass. The results also showed an increase in the photocatalytic degradation efficiency with increasing of initial pH up to maximum value. The results also showed that degradation efficiency was inversely directed with the initial dye concentration. The degradation of crystal violet dye increases slightly with increasing temperature. The activation energy is equal to (27.55) kJ.mol^{-1} . The thermodynamic parameters of the degradation of crystal violet have been reported. The positive ΔH^\ddagger refer to endothermic reaction, the positive ΔG^\ddagger obtained indicate that the reaction is non-spontaneous, the positive ΔS^\ddagger obtained indicate the reactants is more regularly than produce. The result indicate that the dye was degraded and the suggest mechanism show that the final product of degradation of crystal violet dye was CO_2 and H_2O . De colorization and degradation of crystal violet dye in the absence of light and/or catalyst were performed to demonstrate that the presence of light and catalyst was essential for the degradation of this dye.

Index Term-- degradation; crystal violet; photo catalysis, polarography.

1. INTRODUCTION

Environmental pollution due to industrial effluents is the major anxiety because of their toxicity and threat for human life and the environment. The emptying of industrial effluent to the water bodies has stirred much concern because of potential health hazards associated with the entry of toxic components into the food chains of humans and animals⁽¹⁾. Dyes are the major pollution environmental, and the detection of dyes is a difficult process because of the large different of functional groups in different dyes, their diverse properties, are habit very complex, and intensive colors therefore be the toxic to environmental system⁽²⁾. and cause skin irritation, carcinogenic, and mutagenic for aquatic organisms⁽³⁾. Therefore in recent decades, very acute regulations have forced researchers to develop novel technologies to lower amount of pollution. Different physical,

biological, and chemical treatment processes have been employed to treat industrial wastewaters such as chemical, biological, food, pharmaceutical, paper, dye processing, and textile^(4,5). Physical methods include precipitation rain, adsorption, and reverse osmosis.

Biological methods including anaerobic and aerobic treatment. Chemical methods via oxidation and reduction, Advanced oxidation process (AOP) is the best method for treatment compared to other treatment methods because this technology needs to work in all weather conditions of mild pressure and temperature and even at very low concentrations of contaminants, in addition to be easy to maintain and replace spare parts in order to achieve the targets of environmentally friendly treatment and prevent sludge formation during the treatment process⁽⁶⁾.

In this technique it uses UV light with an oxidizing agent to generate hydroxyl radicals (OH^\bullet) that non-selectively attack organic compounds. And have an electro chemical oxidation potential of 2.80 eV relative to the normal hydrogen electrode. Other techniques include electrochemical, activated carbon adsorption, reverse osmosis or coagulation/flocculation but this technologies are cost prohibitive and therefore are not viable options for treating large waste⁽⁷⁻¹¹⁾. Methyl violet it used in vast quantities for textile and paper dyeing, and released to environment in wastewater. numerous methods have been developed to treat methyl violet pollution. The three most prominent are chemical bleaching, biodegradation, and photo degradation.

Polarography is the branch of voltammetry different from where the electrode working is dropping mercury electrode is used as the indicator electrode while in the voltammetry electrode working is solid such as carbon glass^(12,13). Was Heyrovsky from Charles University in Barak (1922), is the first device invented polarography dependent on polarograph direct current⁽¹⁴⁾. Then Heyrovsky and Shikata designed first device Polarography automatic in (1925), Which has achieved Progress because enter the selectivity factor⁽¹⁵⁾. This technique depends on the oxidation or reduction of small quantities of the active substance electrically on the surface of the mercury drop the current measured by change voltage. the curved drawing between current and voltage is called polarogram.⁽¹³⁾ the current is measured by change the voltage damocles. the voltage damocles is measurement through the working electrode against the reference electrode and who is close to him to cancel the effect of resistance solution. While the current product is measured by through the electrode factor and auxiliary electrode by measuring the current circuit⁽¹⁶⁾. Polarographic analysis can be used directly for the

determination inorganic and organic compounds containing conjugated double or triple bonds including polynuclear aromatic ring systems, as well as compounds like imines, ketones, aldehydes nitro diazo compounds and halo substituted compounds. Characterized this technique as easy as high precision as they reach to 10^{-12} Molar and analysis time is too short⁽¹⁷⁾ and is that two or even more substances can be determined by a single current potential curve. Arises equilibrium between the electrode material and ions or molecules material in the solution when the electrode it reaches to voltage the reverse and be rapid spread of ions or molecules from the electrode to the solution is equal to the speed of the spread of ions or molecules from the solution toward the electrode and under these circumstances not passes electric current in the electrode, but starts passage the electric current. When the electrode become anode or cathode. The amount of current flowing depends on the voltage difference which arises between the electrode and the electrolytic solution. Continuous equalize at the electrode includes the following phases.

- 1-Transition of ions or molecules from the solution to layer solution related to the electrode surface diffusion method.
- 2- The interaction of ions or molecules on the surface of the electrode to form atoms or molecular ions.
- 3-Converted ions or molecules to the form fixed to material liberated at the electrode.

Concentration polarization arises when the diffusion responsible for transmission the material to the surface of the electrode and the Polarization leads to the difference in ion concentration of the solution for the concentration of ions in the solution is directly connected to the electrode surface, (Concentration Gradient). This polarization is proportional with the current passes in the electrode. The polarization increases when the current flowing in the electrode a certain value to be equal to the concentration of ions in solution. Each ion in aqueous solution is surrounded by a number of water molecules, and this applies to the cation and anions. The process is equivalent to the cations on cathode include several stages, including diffusion the ions inside the solution toward the cathode and the removal of the water molecules from cation and equivalent on the electrode surface. After that obtain equilibrium on the electrode surface after the deposition or liberation of neutral atoms when any of these phases is slow, they lead to make the process of equivalent ions also slow⁽¹⁸⁾

Dyes are organic compounds but possess colour because⁽¹⁹⁾ It possess at least one chromophore (colour-bearing group), absorb light in the visible spectrum, also have a conjugated system, and exhibit resonance of electrons. which is a stabilizing force in organic compounds. Upon loss of one of these characteristics become discolored⁽²⁰⁾, also the dyes possess groups known as auxochromes (colour helpers), examples of which are carboxylic acid, amino, sulfonic acid, and hydroxyl groups. While these are not responsible for colour.

Crystal violet (methyl violet) is refers to mixtures from three compound tetramethyl, pentamethyl and hexamethyl. That differ in the number of methyl groups attached to the amine functional group. This dyes soluble in water, ethanol, diethylene glycol, and dipropylene glycol^(21,22) Crystal violet it is used to dye paper, as a component of dark blue, black inks for printing, and also used to coloring diverse products such as fertilizers, anti-freezes, detergents, and leather jackets. When conducting DNA gel electrophoresis, crystal violet can be used as a non-toxic DNA stain as an alternative to fluorescent⁽²³⁾, Gentian violet it used antibacterial, antifungal and anthelmintic⁽²⁴⁾; in medicine teeth can be used for dentistry, is also known as "pyocyanin" or ("pyocyanine")⁽²⁵⁾.

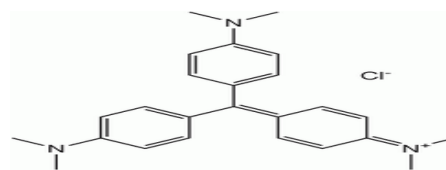


Fig. 1. Structure of crystal violet dye

The purpose of this study was to investigate the removal of crystal violet dye from aqueous solution by photodegradation, to determine the optimum removal condition by using different parameters was studied to estimate the best condition for degradation of crystal violet dye; and these parameters were the amount of catalyst, dye concentration, pH of solution and effect of temperature and this is to prevent the expansion of dye pollution in our environments.

2. EXPERIMENTAL

2-1 Polarographic analyzer

Polarography type (797VA), supplier from the company Metrohm Swiss model 2004 and is described in the fig. 2 and contain two electrode:

Rotating disk electrode Multi - Mode Electrode (MME), Which have three patterns.

1. Dropping mercury electrode (DME)
2. Static mercury drop electrode (SMDE)
3. Hanging mercury drop electrode (HMDE)

In this technique (HMDE) a drop of mercury remain hanging on the edge of the glass tube and in the process of analysis depends on three main steps are

First: include a pre-analysis, as is the concentration of the substance to be analyzed by shining a constant voltage positive or negative on the working electrode.

Second: the solution is left in order to settle

Third: include analysis reverse to remove Substance concentrate voltage to shed opposite the voltage used in the first step so called Voltammetry yanking

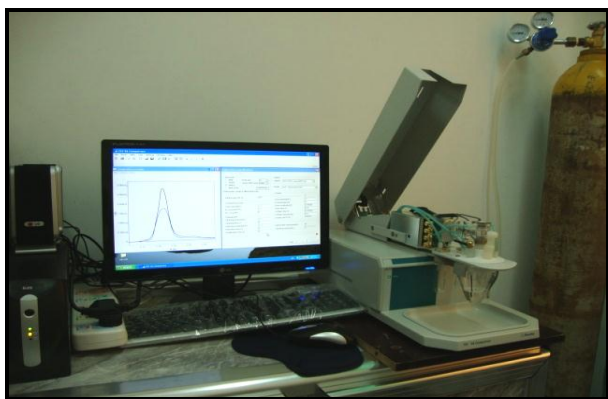


Fig. 2. Photo pictures illustrate device analysis polarography

2-2 Mercury purification:

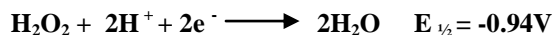
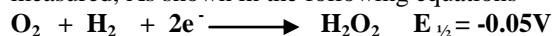
Filtering the mercury using filter paper for the purpose of getting rid of mercuric oxide and impurities present in it, then put mercury candidate in a separating funnel sticky by pregnant railing at the top of the column glass along the 100 cm and diameter of about 3cm filled with nitric acid diluted concentration 1M, Then make the mercury descends in the form of very small droplets through the faucet separating funnel through the acid in a glass column. Then wash with deionize water then nominate mercury then Placed in an electric oven at a temperature of 100C° and save in the glass bottle after filling nitrogen gas to prevent the process oxidant.

2-3 Capillary tube cleaning

Capillary tube placed in the container Baker on nitric acid 1M for a period of 24 hours after it washed with water and then with ethanol, Is dried in dryer heat, Then placed in an electric oven at 63C° for half an hour

2-4 Removal of dissolved Oxygen

The process of removing dissolved Oxygen in the solution before the start of measurement necessary due to being a highly effective electrochemical It is easy reduced on the surface of mercury, Because the oxygen gives two waves of reductase overlap with the wave of the material to be measured, As shown in the following equations



We by passing nitrogen gas within the solution in the measurement cell for a period ranging between 5-15 minutes, Then continue to pass the nitrogen during the measurement process to prevent the entry of oxygen to the solution.

2-5 Standardization of the Polarographic Analyzer

For the purpose of calibration device is placed 10 milliliters of deionize water which contains 1 milliliters Potassium Chloride solution 0.1M installed in a cell measuring the initial conditions as follows:

Initial Potential = 0.00 V

Final Potential = +3.5 V

Drop Size = 3 mm²

Deposition Time = 0.00 Sec.

Equilibration Time = 0.00 Sec.

Pulse Amplitude = 50 mV

Pulse Time = 0.04 Sec.

Voltage Step = 0.008 V

Voltage Step Time = 0.2 Sec.

And passing nitrogen for 15 minutes and measured the current, and the result does not appear any wave polarography and then added 10 ml of standard solution of Cadmium Chloride 0.001 M and 1ml of Potassium Chloride solution 0.1M as supported electrolytes to a cell measuring and pass Nitrogen gas for 5 minutes, And scored (DPP) of this solution, as shown in the fig. 2-3 was the result obtained the half-wave potential is equal to -0.625V which is identical to the values installed in the literature⁽²⁶⁾

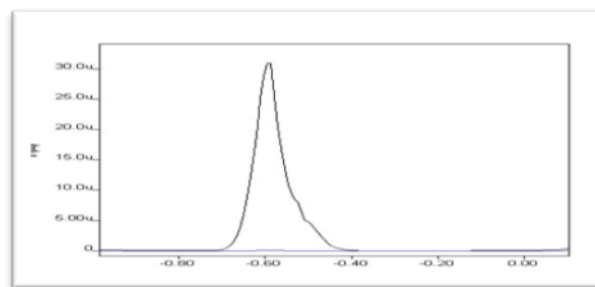


Fig. 3. differential pulse polarography of Cadmium Chloride 0.001 M. in a solution of Potassium Chloride 0.1M.

2-5 Methods measurement

2-5-1 Polarographic behavior measurements of crystal violet dye by DPP

For conducted measurements polarography put 0.1 ml with a concentration 2.43×10^{-5} M of the crystal violet, After installing measurement condition listed in the table 1 and record DPP by Hanging mercury drop electrode (HMDE), And then conducted several measurements polarography to see ideal conditions for measuring crystal violet dye.

2-5-2 Effect time on stability of crystal violet dye

1 ml of dye dissolved in the buffer phosphate solution pH = 7 in a cell measuring. The concentration of the crystal violet 2.43×10^{-5} M after installing ideal conditions for measuring for crystal violet dye to study effect time on stability of crystal violet. The results wear as in table 1.

2-5-3 Effect the acidity function on diffusion current and half-wave potential of crystal violet dye

Studied the effect of the acidic function on half-wave potential ($E_{1/2}$) and diffusion current (id) of the dye, Where he record differential pulse polarography to the solution 2.43×10^{-5} M of crystal violet dye dissolved in a solution of phosphate regulator with different values of hydrogen between 4.5 - 8.0. after installing ideal conditions for crystal violet dye that shown in table 3-9 The results wear as in table I.

2-5-4 Photocatalytic reactor

A homemade photoreactor equipped with a mercury medium pressure lamp 250W without cover glass as a source for UV radiation, was used to determine the degradation coefficient of the crystal violet dye solution. The reactor was consisted of graduated 1000 ml open Pyrex glass beaker and magnetic stirring setup. The lamp's position was perpendicularly above the beaker. The distance between the lamp and the graduated Pyrex glass was 15cm. The photocatalytic reactor was insulated in aluminum box to prevent escape of harmful radiation. In all experimental as shown in Fig. 4. The required amount of the catalyst was suspended in 200ml of aqueous solution of crystal violet and using magnetic stirrer and measured the resulting solution in different time periods by used device polarography.

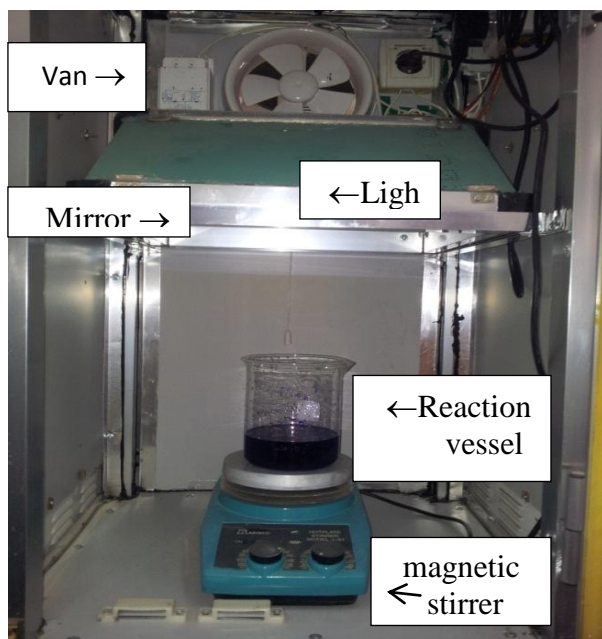


Fig. 4. The photograph of the outlook of homemade photoreactor

3- RESULTS AND DISCUSSION

Research includes the study of properties polarography of crystal violet, Which owns three groups Amine classified within aggregates electrically active as easily reducible on the surface working electrode.

3-1 Polarographic behavior measurements of crystal violet dye by DPP

Record DPP for a solution containing 2.43×10^{-5} M of the crystal violet at initial condition. At installed in the device shown in the table 1. The dye is gave wave reductase clear at +0.125 volte by Hanging mercury drop electrode against standard silver of reference electrode Ag/AgCl / 3MKCl and platinum assistant electrode and the results were as shown in Fig.5

Table I
the initial conditions installed in device polarography

Instrumental Conditions	Values
Initial purge Time	300 Sec.
Drop Size	3 mm ²
Deposition Time	0.00 Sec.
Equilibration Time	0.00 Sec.
Voltage Step	0.008 V
Voltage Step Time	0.2 Sec.
Pulse Amplitude	0.05 V
Pulse Time	0.04 Sec
Initial potential	0 V
Final potential	+3.5V

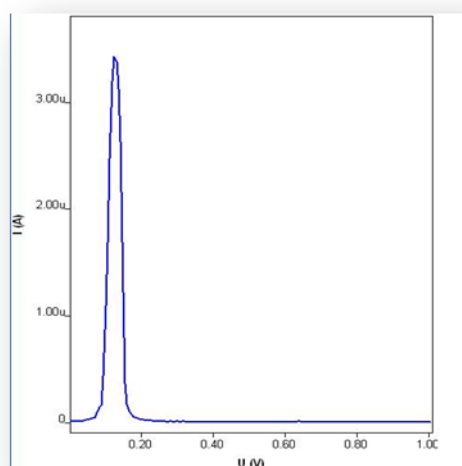


Fig. 5. Illustrates differential pulse polarography of the crystal violet dye 2.43×10^{-5} M

3-2 The determination ideal conditions for crystal violet dye

Differential Pulse polarography was measured for a solution containing 2.43×10^{-5} M of dye dissolved in deionize water, we study the effect of the mercury drop size on the current diffusion to solution 2.43×10^{-5} M from dye. Change drop size within range 3-9 mm², we found the best size for a drop of mercury is 9 mm². Which gave the best wave polarography symmetrical peak and the highest current diffusion.

By studied the effect of the deposition time on the diffusion current to solution of dye. Change deposition time within range 30-75 second and the best deposition time is 50 Sec. Which gave the best wave polarography symmetrical peak and the highest current diffusion the best equilibrium time is 30 Sec.

Studied the effect of high pulse for solution 2.43×10^{-5} M from dye. And make several measurements Polarography with change the height of the pulse within the range 0.01-0.3 V. After stability a factors measured above for the purpose of

choosing the best pulse amplitude. the best high pulse is 0.050 V . Because it has given the best wave Polarography symmetrical peak .

Conducted several measurements Polarography with change the time of the pulse within the range 0.08 - 0.001 second for the solution 2.43×10^{-5} M from dye. After stability a factors measured above for the purpose of choosing the best pulse time. the best high pulse time is 0.02 Sce.

The effect of the voltage step on current diffusion through change within the range 0.002-0.020 V was measured DPP resulting from this change of solution 2.43×10^{-5} M .After stability a factors measured above for the purpose of the of choosing the best voltage step. the best voltage step is 0.006 V. Which gave the best wave polarography symmetrical peak. The measurements polarographic other although give it a higher value of current diffusion, but it was asymmetric waves.

The effect of the voltage step time on current diffusion to solution 2.43×10^{-5} M from dye. Change the voltage step time within range 0.08-0.80 Sce.. After stability a factors measured above for the purpose of the of choosing the best voltage step time8 the best voltage step time is 0.40 Sce. . which gives a symmetrical peak while the measurements polarographic other although give it a higher value of current diffusion , but it was asymmetric waves.

Based on the results obtained above can clarify the optimal conditions for the dye crystals violet as in the following table II and plotted in fig.6

Table II
optimal conditions for the crystals violet

Instrumental Conditions	Values
Initial purge Time	300 Sce.
Drop Size	9 mm ²
Deposition Time	50 Sce.
Equilibration Time	30 Sce.
Voltage Step	0.050 V
Voltage Step Time	0.02 Sce.
Pulse Amplitude	0.006 V
Pulse Time	0.40 Sce.
Initial potential	0 V
Final potential	+3.5 V

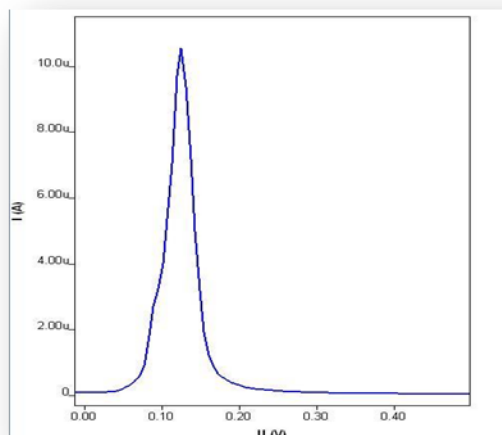


Fig. (6) the wave crystal violet dye after installed conditions

3-3 Effect time on stability of crystal violet dye

Effect of time on stability of crystal violet dye was measured by differential pulse polarography to a solution containing 2.43×10^{-5} M of dye at optimal conditions that shown in the table II. Has been measuring ten times separates the measurement ten minutes and the results were as shown in the table III

Table III
effect of time on stability of crystal violet dye

NO.	Time / min.	$E_{1/2}$ / V	$I_d / 10^{-5}$ A
1	10	0.125	1.6
2	20	0.125	1.6
3	30	0.125	1.6
4	40	0.125	1.6
5	50	0.125	1.6
6	60	0.125	1.62
7	70	0.125	1.70
8	80	0.123	1.71
9	90	0.123	1.75
10	100	0.125	1.79

Noted from the table 3 that dye remain stable for a period of 50 minute at least, and this gave indication that the dyes that is not affected during the period of measurement. After this period there was a rise current diffusion. The reason for this is due to that the dye became the form of molecular clusters.

3-4 Effect the function of acidity on current diffusion and half-wave potential of crystal violet dye

To studied the effect of the acidic function on half-wave potential ($E_{1/2}$) and diffusion current (i_d) of the dye. Where he

scored differential pulse polarography to the solution $2.43 \times 10^{-5} \text{ M}$ of dye dissolved in a solution of buffer phosphate with different values of hydrogen between 4.5 - 8.0 . Measurement has been the application of optimal conditions set forth in the table 2. And recorded the results that have been obtained in the following table IV

Table IV
effect the function of acidity on current diffusion and half-wave potential of crystal violet dye

pH	$E_{1/2} / \text{V}$	$I_d / 10^{-5} \text{ A}$
4.5	0.321	0.62
5	0.303	0.74
5.5	0.286	1.05
6	0.274	1.23
6.5	0.256	1.57
7	0.244	1.77
7.5	0.232	1.78
8	0.222	1.86

Notes from the table 4 that a half-wave potential decline with increase acidic function because in the middle basic the oxidation process is more easily , As a result the number of protons is small which leads to decrease half-wave potential , and on the contrary, the diffusion current increase with increasing acidic function because the number of protons in the middle basic is small therefore the dye ,Be in the form of molecular associations this means that the number of particles reaching the surface of the electrode are many, which leads to increased diffusion current⁽²⁷⁾

3-5 photooxidation reaction of crystal violet dye

3-5-1 Dark reaction ,Photolysis and photooxidation

Dark adsorption studies were carried out with the crystal violet solution . The addition of 0.1gm from ZnO to solution 200ml from dyes $2.43 \times 10^{-5} \text{ M}$.The results are plotted in figures 4

Noted from fig.4 in the dark reaction the efficiency of degradation showed a very little 4.7% . After some time the degradation rate became constant because of the monolayer formation on the catalyst surface. After monolayer formation, no free active sites were available for further adsorption so no further degradation was observed, Also thus results observed that decrease in concentration of crystal violet solution was due to adsorption no degradation⁽²⁸⁾
Direct photolytic degradation in the absence of any photocatalyst was first investigated, to compared with photocatalytic degradation in the presence of semiconductor. Crystal violet solution was irradiated under ultraviolet (UV) light alone in the absence of ZnO . It was observed that after 30 min of UV treatment the degradation was not significant as compared to UV\semiconductor.

The efficiency of degradation is 3.7%. These results show that the dye is not affected or slightly affected by the ultraviolet radiation. Photooxidation in presence both ultraviolet radiation and semiconductor to compared with photocatalytic degradation in presence only UV light or in presence only semiconductor. The results are shown in Fig.7 The efficiency of degradation is 92% This results demonstrated that both UV light and photocatalyst are needed for the effective destruction of crystal violet solution.

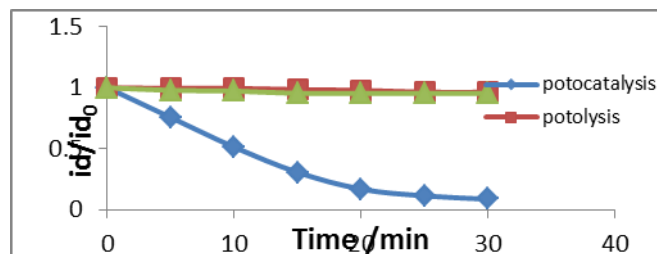


Fig. 7. dark reaction ,photolysis and photooxidation

3-5-2 Factors affecting on photocatalyst of crystal violet solution

1-Effect of Zinc oxide mass on the rate of photocatalytic degradation of crystal violet

Studied the effect of change mass zinc oxide on the rate of photocatalytic degradation of crystal violet with range 0.05-0.5 g and record DPP of solution $2.43 \times 10^{-5} \text{ M}$ from crystal violet dye dissolved in the buffer phosphate solution and the results are plotted in fig. 8.

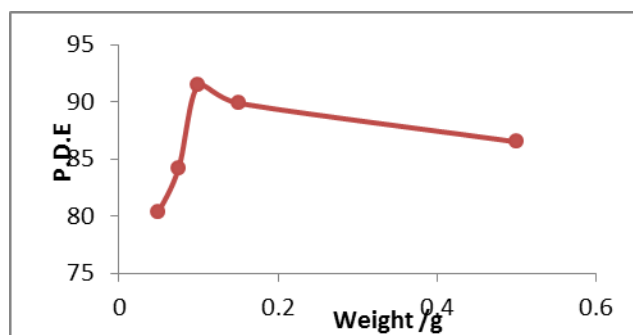


Fig. 8. The relation between P.D.E of crystal violet solution and weights of ZnO catalyst

The best mass of Zinc oxide is 0.1g because the time of irradiation the time of removing the color dye and convert to the colorless was 25 minutes, Is less irradiation time was obtained through experience, And the maximum photodegradation efficiency which is equal to 91.5% As shown in fig.8 . Because increase the mass of catalyst lead to increase the active sites on catalyst surface, As a consequence the number of dye molecules adsorbed on the surface of catalyst increase , and this lead to increase in the number of particles in the field light^(29,30)
The plateau is reached when the increase in the mass of catalyst can no longer increase the overall efficiency of utilizing incident radiation .After reaching the plateau noted the rate of photocatalytic degradation is decrease with increase

the mass of the catalyst because higher concentration of catalyst lead to light scattering and this leads to reduced radiation entering the reaction vessel^(31,32)

2-Effect of acidity function on the rate of photocatalytic degradation of crystal violet

Studied the effect of change acidity function on the rate of photocatalytic degradation of crystal violet with rang pH 2-10 and record DPP of solution $2.43 \times 10^{-5} \text{M}$ from dye dissolved in the buffer phosphate solution .And the results are shown and plotted in fig.6. After choose the best mass of zinc oxide is 0.1g . The best pH is 10 because the time of removing the color of crystal violet was 25minutes in this time the color violet to the dye convert to the colorless , Is less irradiation time was obtained through experience irradiation, And the maximum photodegradation efficiency which is equal to 93% , Because the photodegradation efficiency strongly dependent on pH solution because the reaction of heterogeneous photocatalytic takes place on the surface of semiconductor.. This behavior could be explained on the basis of zero point charge (ZPC). The zero point charge is equal to 9.00 for ZnO when increase pH the surface of catalyst be charged negatively charged by adsorbed hydroxyl ions, therefore the presence of large quantities of adsorbed OH^- ions on the surface of catalyst promote OH^\bullet radicals formation so the rate of photocatalytic degradation increase with increase the pH^(33,34)

Also studied the effect of pH =11 and pH=12 on dye but no taken into consideration because in the pH=11 turning color of crystal violet from violet to pale yellow, and this shows that the formula dye t is convert from case of saline formula to OH^- within pH=11 therefore the dyes is deposited in this pH .As in the pH=12 transformation of the color dye from violet to colorless without irradiation the reason for this is as shown in the ionic – chromophoric theory

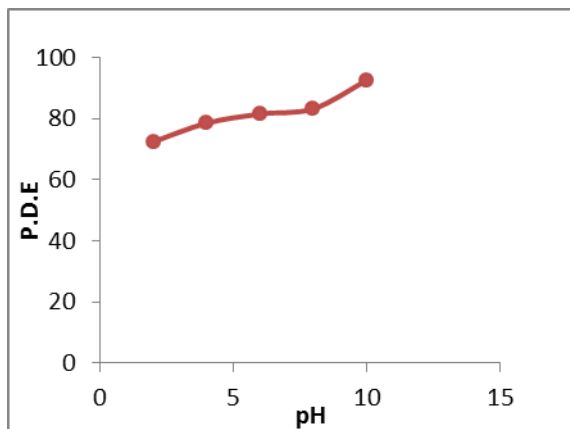


Fig. 9. The relation between P.D.E of crystal violet solution and value of pH

3- Effect of change concentration of crystal violet on rate constant of photoreaction of crystal violet solution

Was prepared solutions of different concentrations of crystal violet according to the law of dilution . The concentrations 2.23×10^{-4} , 2.43×10^{-5} , 2.45×10^{-6} molar and after installing the

optimum conditions for the dye, And a measure differential pulse polarography. The results were as follows in the fig. 10 .The effect of different dye concentration on the rate of photocatalytic degradation is studied by keeping all other experimental conditions and changing dye concentration ZnO concentration equal to 0.1 g the pH was 10 and the temperature equal to 328 K

From the figure 10 we can deduce that the relationship between the diffusion current and concentrations is directly proportional any more the concentrations increased current diffusion .Either the relationship between half-wave voltage and concentrations are inverse relationship any more the concentrations decreased half-wave potential

The fig.10 which shows the degradation increased with the decreasing dye concentration. Because when dye concentration increases, the path length of the photon entering the solution decrease so the number of photons reaching to catalyst surface decrease and number of catalyst molecules undergoes excitation is decreased so the rate of photocatalytic degradation increased with the decreasing dye concentration^(35,36), Also in higher concentration the active sites in the system is fewer and causing little adsorption of dye molecules at active site of catalyst and remaining dye molecules in dye solution until attached molecules are degraded⁽³⁷⁾

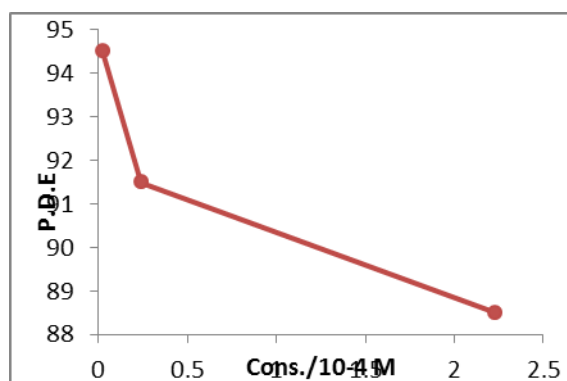


Fig. 10. The relation between P.D.E of crystal violet solution and different dye concentration

4- EFFECT OF THE TEMPERATURE ON THE RATE OF PHOTOCATALYTIC DEGRADATION OF CRYSTAL VIOLET

Studied the effect of change temperature on the rate of photocatalytic degradation of crystal violet with range 25-55°C and record DPP of solution $2.43 \times 10^{-5} \text{M}$ from dye dissolved in the buffer phosphate solution and the results are shown in fig. 11 .Also thermodynamic results are shown in table 5 and plotted in fig.12 .The activation energy E_a was calculated from the Arrhenius equation,

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln A$$

the Arrhenius plot of $\ln k$ vs. $1/T$ the slope of linear plot is equal to $-E_a/R$ The entropy of activation ΔS^\ddagger was calculated from equation⁽³⁸⁾

$$\ln A = \ln (kT/h) + \frac{\Delta S^\ddagger}{R}$$

The Enthalpy of activation (ΔH^\ddagger) was calculated from equation:

$$\Delta H^\ddagger = Ea - RT^{(30)}$$

The free energy of activation (ΔG^\ddagger) was calculated from equation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

After choose the best weight of zinc oxide is 0.1g and pH =10 ,The best temperature is 55°C because the time of removing the color of crystal violet was 25minutes, Is less irradiation time was obtained through experience, And the maximum photodegradation efficiency which is equal to 92.5% .As shown in the fig.11

The table 5and fig.11 which shows that the rate constant of reaction increases with the increase temperature because the rise of the temperature may lead to promote the production of free radicals ,but at a low temperature because the desorption of the products it is slower than the adsorption of the reactants on the surface and degradation on the surface of catalyst for that desorption of the products it limits the reaction

The figure 9 which shows the activation energy for photodegradation and decolorization of crystal violet dye by using zinc oxide catalyst in the temperature range 298-328 K was equal to 27.55 kJ.mol⁻¹. The obtained activation energy is very small, which indicates that the photocatalytic reaction is temperature independent. This behavior could be explained on the basis of photonic activation, as well known the irradiation is the primary source of electron-hole pair generation which responsible for initiation photoreaction, photocatalytic systems do not require heating and operate at near ambient temperature⁽³⁹⁾. The true activation energy for photocatalytic systems E_a is nil, whereas the apparent activation energy E_a is often very low (a few kJ/mol)in the medium temperature range (20°C-80°C) The activation energy of photocatalysis reaction is reported as 5 to 20 kJ/mol in the literature⁽⁴⁰⁾ . However at very low temperatures (-40°C - 0°C) adsorption of final products formed is favors ,desorption of which tends to be the rate-limiting step. because it is slower than the degradation on the surface and the adsorption of the reactants on the surface of catalyst. at "high" temperatures (>70-80°C) for various types of photocatalytic reactions, the limited stage is the adsorption of the dye on the surface of catalyst⁽³⁵⁾

The positive ΔH^\ddagger refers to endothermic reaction , the positive ΔG^\ddagger refers the reaction is non-spontaneous. Positive ΔG^\ddagger this could be because the activated state is a well solvated structure formed between the dye molecules and the reaction intermediates that is hydroxyl radicals which is also supported by positive entropy of activation. In the present case the value of ΔS^\ddagger is positive as in tables 3-28 so that the reactants is more ordered than the complex formed. Initially the complex formed is stable.⁽³⁶⁾

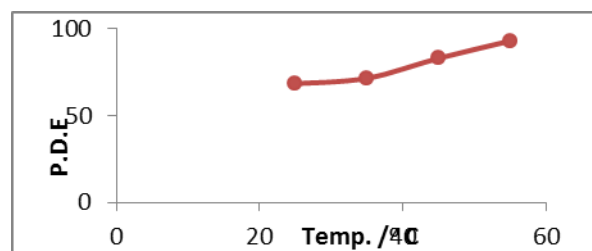


Fig. 11. The relation between P.D.E of crystal violet solution and temperature

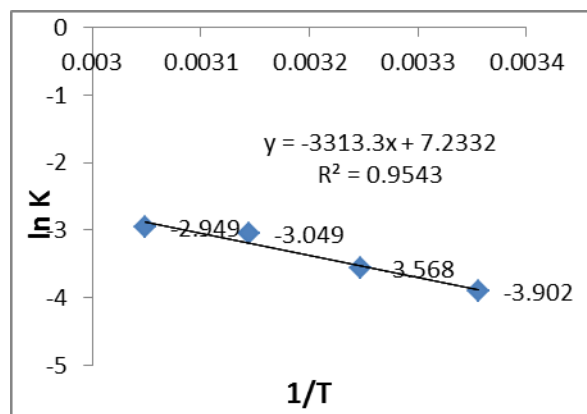


Fig. 12. Arrhenius plot by using ZnO as catalyst with crystal violet dyes.

Table V

The values of rate constant for photodegradation of crystal violet dyes. at range of temperature 298-328 K° in presence ZnO .

T/K	k/min	1/T	Ln k
298	0.0202	0.003356	-3.902
308	0.0282	0.003247	-3.568
318	0.0474	0.003145	-3.049
328	0.0524	0.003049	-2.949

Table VI

Values of kinetics and thermodynamic parameters for the photocatalytic degradation of crystal violet dye by using ZnO catalyst

T/K	k/min ⁻¹	Ea/kJ.mol ⁻¹	ΔH^\ddagger /kJ.mol ⁻¹	ΔS^\ddagger /kJ.K ⁻¹ .mol ⁻¹	ΔG^\ddagger /kJ.mol ⁻¹
298	0.0202	27.55	25.07	0.0517	9.67
308	0.0282		24.99		9.14
318	0.0474		24.91		8.06
328	0.0524		24.82		8.04

4. CONCLUSION

The study is designed to treat the waste water of dye by using UV light and ZnO as catalyst. This study explained the importance of the UV light and catalyst as a basic factors in the photocatalytic degradation for crystal violet dye. The results indicate that the photocatalytic reactions are a pseudo first order reactions according to the Langmuir-Hinshelwood relationship. It was observed that the photocatalytic degradation efficiency increase with increase of catalyst weight up to 0.1g. For above this weights,

photocatalytic degradation efficiency was decreases with increasing of catalyst mass .

The results also showed an increase in the photocatalytic degradation efficiency with increasing of initial pH up to maximum value. The results also showed that degradation efficiency was inversely directed with the initial dye concentration. The change of temperature was the factor that has less effect on photocatalytic degradation rate. The degradation of crystal violet dye increases slightly with increasing temperature. The activation energy is equal to (27.55) kJ.mol^{-1} . The temperature is the factor that has the smallest effect on the photocatalytic degradation of crystal violet solution, E_a , which was found to be smaller than 40 kJ.mol^{-1} . The results illustrate the decoloration of crystal violet dye is mainly physical interaction.

The thermodynamic parameters of the degradation of crystal violet have been reported. The positive ΔH^\ddagger refer to endothermic reaction, the positive ΔG^\ddagger obtained indicate that the reaction is non-spontaneous, the positive ΔS^\ddagger obtained indicate the reactants is more regularly than produce. Fairly positive ΔH^\ddagger and ΔG^\ddagger this could be because the activated state is a well solvated structure formed between the dye molecules and the reaction intermediates that is hydroxyl radicals which is also supported by positive entropy of activation.

The result indicate that the dye was degraded and the suggest mechanism show that the final product of degradation of crystal violet dye was CO_2 and H_2O . Decolorization and degradation of crystal violet dye in the absence of light and/or catalyst were performed to demonstrate that the presence of light and catalyst was essential for the degradation of this dye.

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