Evaluate the Activation energy of Cresol Red by study the effect of U.V irradiation

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Abstract
This study basically designed to estimate the transition energy of cresol red by used U.V irradiation. The transition energy values were calculated according to the equation (ET = h C NA/ λ), the λmax values were measured by studied the change of λmax at different time periods including (5, 10, 15 and 20 min) of U.V irradiation. The changes of absorbance and λmax value was mainly attributed due to the electronic transitions of π → π and n- π* which are related to the original structure of dye used, the transitions of π → π* was the result of double bond and conjugate system beside the benzene rings. While the transitions of n→ π* which attributed to n electron in the original structure the indicator, this transition of (S) sulphur atom and (O) oxygen atom. The study recorded different values of ET depended up on the different period of U.V irradiations.*

Keywords — *Cresol Red, U.V irradiation, Transition Energy, λmax, electronic transitions.*

I. INTRODUCTION

The electrons in a molecule can be one of the three types namely σ (single bond), π (multiple-bond), or non-bonding (n- caused by lone pairs). These electrons when imparted with energy in the form of light radiation get excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and the resulting species is known as the excited state or anti-bonding state [1]. σ-bond electrons have the lowest energy level and are the most stable electrons. These would require a lot of energy to be displaced to higher energy levels. As a result these electrons generally absorb light in the lower wavelengths of the ultraviolet light. While π-bond electrons have much higher energy levels for the ground state. These electrons are therefore relatively unstable and can be excited more easily and would require lesser energy for excitation. These electrons would absorb energy in the ultraviolet and visible light radiations. n-electrons or non-bonding electrons are generally electrons belonging to lone pairs of atoms. These have higher energy levels than π-electrons and can be excited by ultraviolet and visible light as well [1]. Each electronic state is well defined for a particular system i.e. a double bond would have a particular energy level for the π- electrons which when absorbs a specific amount of energy would get excited to the π* energy level for the electrons. A spectrometer records the degree of absorption by a sample at different wavelengths and the resulting plot of absorbance (A) versus wavelength (λ) is known as a spectrum. The wavelength at which the sample absorbs the maximum amount of light is known as λmax. As a result of this the highest occupied molecular orbital (HOMO) is at a higher energy state and the lowest unoccupied molecular orbital (LUMO) is of at a lower energy state. In order to excite this system, the energy that would be required to excite the electrons from the HOMO to the LUMO would therefore be reduced. As a result of this reduction in energy levels, the wavelength for absorption of conjugated molecules increases. The effects of irradiation type or irradiation period studies taken place in many studies. Most of those studies concerned to the effect of this on the absorption and λ max value changes [2] & [3]. The electronic absorption and emission spectra of organic molecules are usually modified in solvation processes. Many studies were carried out to estimate of ionization constants and activation energies of every electrons transfer [4], [5], and [6], the effect of irradiation period was carried out using some dyes i.e. cresol red. Cresol red chemically known as o-Cresolsulfonphthalein, belongs to the triphenylmethane (TPM) on types of dyes which are potentially carcinogenic or mutagenic. It is used for monitoring the pH in aquaria, and extensively used in the textile industry for dyeing nylon, wool, silk, cotton, and polyacrylonitrile-modified nylon. It is also used for bio- logical stains and markers to monitor the process of agarose gel electrophoresis and polyacrylamide gel electrophoresis [7] & [8]. However, irritation, burning of skin, heart damage, anemia, liver - kidney damage and coma are the side effects of cresol red dye exposure at high concentration. Figure 1 show the chemical structure of cresol red dye.

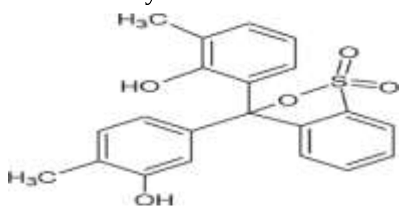


Fig 1: Structure of Cresol Red dye (source Nurafifah et al., 2015 & Ammer et al., 2015)

This study aimed to calculate the transition energy by study the effect of U.V irradiation periods on the absorbance and λ max values of the studied dyes by using the U.V lamp source at different times and different concentrations.

II. EXPERIMENTAL

A. *Materials used / Cresol red*

Molecular formula: $C_{21}H_{18}O_5S$, Molar mass 382.43(g/mol), Melting point>300 ^oC, Boiling point ~ 56.9 ^oC at 760 mmHg, Solubility 200 g/l in water at 80 ^oC and pH of the stock solution 5.5.

B. *Solutions preparation:*

100 ppm of every day was prepared by dissolved 0.01 g in 100 ml distilled water. Different volumes of (0.5, 1, 2, 3, and 4 ml) of stock solution of each dye solution were transferred into 10 ml measuring flask then the volumes were completed to the mark of the flask by distilling water to prepare standard solution of 5,10, 20, 30 and 40 ppm of studied dye.

C. *The procedure*

The procedure basically is the study of the effect of time of U.V. radiation period on the absorbance and λmax. All the prepared solutions of dyes used were treatment by U.V. irradiation by using radiation of U.V lamp at different times of (5, 10, 15, and 20 minutes) by using U.V lamp instrument. Then the samples were transferred to spectrometer. The absorbance and the λmax were measured at each treated time. The effect of radiation was observing from the U.V curves and λmax value chances. The absorption spectra of unirradiated and irradiated solutions were measured in a wavelength range of 250 to 650 nm according to λmax of the original solution. The transition energy of cresol red was calculated by used U.V irradiation. The transition energy values were calculated according to the equation (ET = h C NA/ λ), where ET is the transition energy, h is Planck's constant, C is the speed of light and NA is the Avogadro's number.

III. RESULTS AND DISCUSSION

The absorbance curves of the original solution (unirradiated) Cresol red solutions were shown in Figure (2). The wavelength was scanned in the range of 250 to 600 nm. The results showed two absorbance bands λ max obtained at 266 nm and 430 nm.

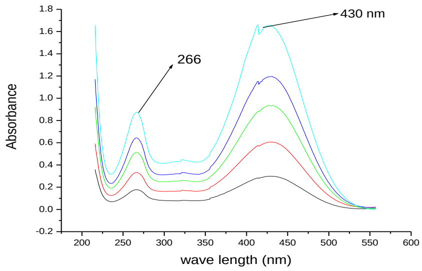


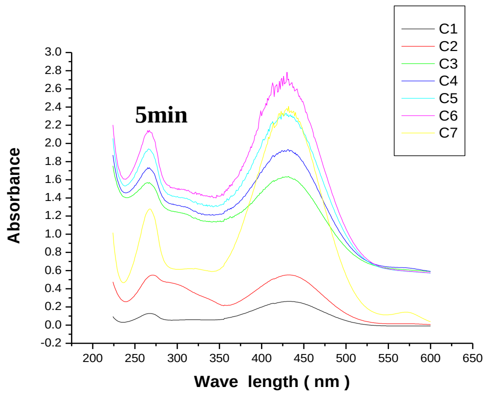
Fig 2: The spectrum curve of Cresol red before treatment by U.V irradiation.

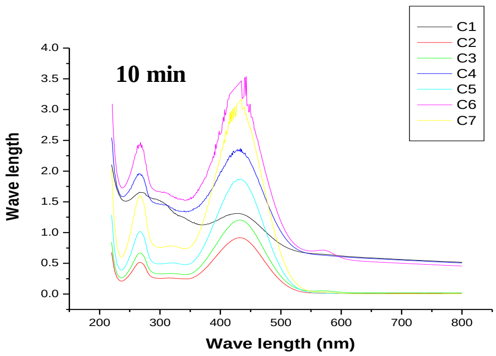
After treatment the solutions by U.V irradiation at different times of (5, 10, 15 and 20 minutes). The results showed that there are relative changes in λ max at treatment times of 5, 15, and 20 minutes (449 , 432 and 433 nm) respectively, whereas high change in λ max value was recorded after using 10 minutes of U.V radiation (449 nm) as shown in Table (1). The U.V irradiation of treatment samples are shown below in Figures 4,5,6 and 7, where C1, C2, C3, C4, C5, C6 and C7 represent the chosen concentration of cresol red 5ppm, 10ppm, 15ppm, 20ppm, 25ppm, 30ppm, and 40ppm, respectively. The absorbance values were changed compared to the original absorbance , where the absorbance values were showed slight changes of (2.7 , 3.4 and 2.3) after 5 , 10 and 15 minute treatments of U.V , respectively, compared with the original absorbance value of the original solution (1.6) as shown in the Figure (3) and Table (2) which showed increase in the absorbance with increase the time of U.V irradiation. Also the results showed affecting of irradiation on the absorbance of some the studied concentrations, where the concentration of 30 ppm gave absorbance of 2.7 after 5 minutes of U.V irradiation. This changes of absorbance values and λ max values attributed to excitation energy and the electronic transitions of π – π* and n – π*. Those electrons transition are related to the original of cresol red structure , the double bond and conjugate system beside the benzene rings give the transition of π – π* . Also the structure of cresol red involving the (n) electrons of sulphur atoms, this is gave the transition electrons transfer of n – π*[9]. According to the chemical structure of cresol red, which the type of (n) electrons are available to produce these electronic transfer as (O and S), in addition to the presence of the double bond and conjugate system beside the benzene rings give the transition of π – π*. Also the presence of the bonds of: - C = C - , C - OH, - C –S and O = S = O mainly gave those electronic transitions [9].

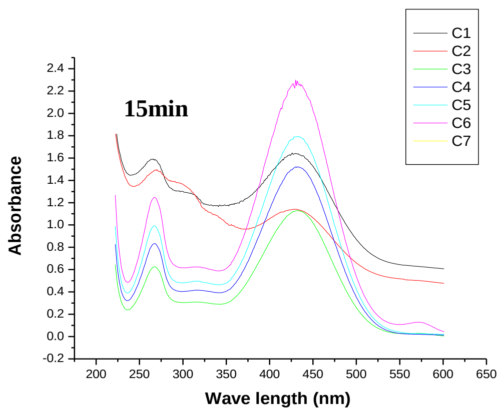
TABLE 1

The change of λ max at each period of U.V iiradiation treatment of cresol red.

U.V treatment time	λ_{max} 1	λ_{max} 2
0	266	430
5	267	449
10	268	432
15	269	432
20	267	433







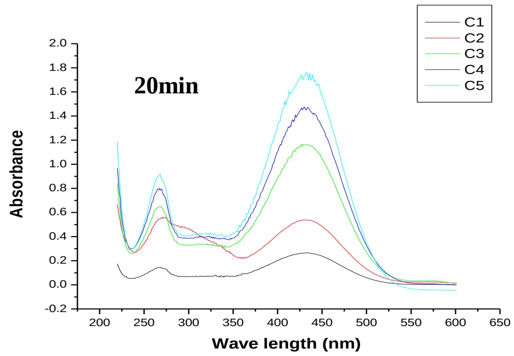


Fig 3: The effect of U.V irradiation at different times of Cresol red.

TABLE 2

The values of absorbance at each period of U.V iiradiation treatment of Cresol red.

	Absorbance				
Time (min) / Conc (ppm)	**0 min**	**5 min**	**10 min**	**15 min**	**20 min**
5	0.3	0.28	1	1	0.28
10	0.6	0.55	1.3	1.1	0.5
15	0.9	1.6	0.59	1.6	0.1
20	1.2	1.9	1.2	1.1	1.1
25	1.6	2.3	2.3	1.5	1.4
30		2.7	1.8	1.8	1.7
40		2.3	3.4	2.3	1.5

The most effect of U.V irradiation on the organic molecules are concerning to the degradation of those compounds. Also different mechanisms mainly occurred for each compounds and depend on the chemical structure, this is mainly the most factor which give different values of absorbance for each dye [10]. Also the activation energy (ET) of each electron transfer may be effect on the absorbance; the activation energy can be calculated from the following equation**:**

$$ET = (h\ C\ NA) / \lambda$$

Where ET is the transition energy, h is Planck's constant, C is the speed of light and NA is the Avogadro's number.

By applying the above equation on the values of cresol red which recorded in this study, the results are illustrated in Table (3) and Figure (4). The results showed that, the ET was decreasing after 10 min of irradiation and directly concerning to the wave length values.

Table 3
The transition energy values at the U.V irradiation periods of cresol red.

Time (min)	**λ_{max}1 (nm)**	**(ET)** (kJ/mol)	**λ_{max}2 (nm)**	**(ET)** (kJ/mol)
0	266	0.449	430	0.278
5	267	0.448	430	0.278
10	268	0.446	449	0.266
15	269	0.444	432	0.277
20	267	0.448	433	0.276

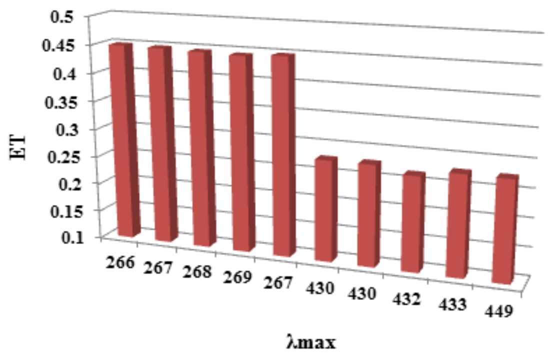


Fig 4: change of ET with U.V irradiation period of cresol red.

IV. CONCLUSIONS

The effect of the U.V. irradiation on the aqueous solution of cresol red and study the effect of the transition energy of each electron transfer on the absorbance and λ max values were the aimed of this study. The absorbance and λ max values of the selective λ max solutions were chanced in most solutions, where the U.V radiation gave different values at different irradiation time periods, most of solution showed a relative changes in λ max values and gave high absorbance values comparing with the original standard solutions of the dye. Those changes in absorbance are due to the effecting to U.V irradiations on the type of electronic transition of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ which they were attributed to the original structure of the indicator used.

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