Study the Optical Properties of \((C_{52}H_{54}N_{4}O_{12})\) Dye

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Abstract:
This paper includes investigation of linear optical properties for malachite green oxalate (M.G.O) dye melted in ethanol solvent at several concentrates \((2\times10^{-5}, 1\times10^{-5}, 5\times10^{-6})\) Ml and for (M.G.O) dye films and optical properties of (M.G.O) dye films prepared by casting method for concentrate solution \(10^{-3}\) Ml. Measurement result using (UV-Vis) spectrophotometer to measure (absorbance, transmittance, absorption coefficient \((\alpha_0)\), refractive index \((n_0)\) and energy gap) were found two transitions wavelengths \(428, 622\) nm when dye is dissolved in ethanol and \(435, 646\) nm when preparing films. Linear optical properties were studied for the three concentrations and it was found increased absorption coefficients and refractive index by rising concentration.

Key words. Malachite green oxalate dye \((C_{52}H_{54}N_{4}O_{12})\), Liner optical properties, Laser dyes.

Introduction
Malachite green oxalate (M.G.O) dye has the chemical formula \((C_{52}H_{54}N_{4}O_{12})\) as shown in Fig.1 and there molar mass \((927.03\text{gm/mol})\). Production and use of malachite green oxalate dye for direct dyeing of wool, silk, jute, cotton and leather, biological contamination, clinical reagent, test reagent to detect sulfuric and cerium acid, reagent for acids and bases\cite{1}, and as a dye for paper \cite{2} may release it into the environment through different waste streams. It also has veterinary applications as a fungicide and parasite in aquarium water fish \cite{1}.

There are many investigation of linear optical properties of several dyes such as in (2019) the researcher study the of electronic molecular energy levels, linear optical properties and fluorescence spectra for (M.G) dye in several solvents like as water and chloroform in several concentrates \((1\times10^{-3}, 0.5\times10^{-3}, 0.2\times10^{-3}, 1\times10^{-5}, 0.5\times10^{-5})\) ML, it was found increased linear absorption coefficients and refractive index by rising concentration \cite{3}.In (2019) paper, study the optical properties of M.G dye films prepared by laser pulse deposition method to measuring absorbance, transmittance, absorption coefficient, refractive index and energy gap), the intensity of absorption is increases by rising the number of pulses laser \cite{4}. In(2005) paper, the researcher study the optical properties of dye laser (rhodamine 6G, fluorinsin, and rhodamine B) \cite{5}. In (2011) paper, study absorption and fluorescence spectra of some organic dyes(Rhodamine B , Rhodamine 6G, Fluoresin) in several solvents.
like Ethanol, Methanol, Acetone and Water in several concentrations (10^{-5} - 10^{-2}) Ml, it was found absorption spectra and fluorescence were increased with rising concentration [6].

![Molecular structure of (M.G.O) dye](image)

**Fig. (1): Molecular structure of (M.G.O) dye [7].**

**Liner Optical Properties:**

1- Absorbtion (A):
   
   It is the log. ratio between the intensity of incident light (I_0) to the intensity of light transmitted (I), and gives as follows [8, 9]:
   
   \[ A = \frac{I}{I_0} \] ..........................(1)

2- Reflection (R):
   
   It’s the reflection of light incident on a surface that separates two different mediums in optical density as follows [10]:
   
   \[ R = \left( \frac{n-1}{n+1} \right)^2 \] ..........................(2)

   The reflectance value (R) can be measured by use the following equation:
   
   \[ R = 1 - (A + T) \] ..........................(3)

   Where A is the absorbance.

3- Transmittance (T):
   
   It’s the ratio of transmitted intensity light (I) to intensity of the incident light(I_0). It is given as follows [11, 12]:
   
   \[ T = \left( \frac{l}{l_0} \right)^2 \] ..........................(4)

   Per to the Beer-Lambert’s law, transmittance reduce as the concentration molar increases (c_m) and length of the optical path (L) passes through the light [13].

4- Absorption coefficient (\( \alpha \)):
   
   The absorption coefficient (\( \alpha \)) depend on the energy of the photon depends on the energy of the photon (h\( \nu \)) and on the properties of the material per to Bear-Lambert's law, \( \alpha \) its measured as the fallowing equation at any wavelength [14]:
   
   \[ \alpha = 2.303\left( \frac{A}{d} \right) \] ..........................(5)

   Where \( d \) is the thickness and its value (1cm).

5- Refractive index (\( n_0 \))
It’s very important parameter for optical materials and applications. The \( n_e \) of the dye can be easily measured from the reflectance values (\( R \)) and extinction coefficient (\( K \)) [15]:

\[
\frac{n}{n_{air}} = \left[ \frac{4R - K^2}{(R-1)^2} \right]^{0.5} - \frac{R + 1}{R - 1}
\]

### Materials:
Physical properties of (M.G.O) dye shown as in table (1) and physical properties of the ethanol solvent shown in table (2).

#### Table (1): Physical properties of (M.G.O) dye [1, 16, 17].

| Dye (M.G.O) | Chemical formula | Molecular weight (gm/mol) | Uses                        | Color                  | Solubility                                                                 | Vapor pressure | UV Spectra                  |
|------------|-----------------|---------------------------|-----------------------------|------------------------|----------------------------------------------------------------------------|----------------|-----------------------------|
| C22H34N4O12 | 927.03          | Active laser medium, dyeing wool and cotton etc. | Green crystal by luster metallic | In Alcohol, Methanol, Amyl Alcohol, very soluble in Ethanol. | In water \((4*10^4)\) mg/L at \((25^\circ\text{C})\). | \(2.4*10^{11}\) mm Hg at \((25^\circ\text{C})\). | Max absorption: 616.9 nm. |

#### Table (2): Physical properties of ethanol solvent [18].

| Physical properties | Ethanol |
|---------------------|---------|
| Chemical formula    | C2H5OH  |
| Molecular weight    | 46.07   |
| Density             | 1.48    |
| Melting point       | -114.3(\text{C}) |
| Boiling point       | 78.4(\text{C}) |

### Experimental part:
1-Preparation of liquid dye samples dissolved in ethanol

Prepare solution concentration for (M.G.O) dye by dissolving \((3*10^{-3})\) gm of dye with \((10\text{ ml})\) of ethanol per to the concentration equation.

The concentration of the dye is as equation[19]:

\[
w_m = \frac{C \times V \times M.W}{1000}
\]

\(w_m\): Weight of (M.G.O) dye is required to get the required concentration.

\(C\): Prepared concentration.

\(V\): Size of the solvent added to the dye.

\(M.W\): Molecular weight of (M.G.O) dye.

The next step diluted solution per to the concentration dilution equation for dye as following eq.:

\[
C_1V_1 = C_2V_2 ............. ............. ....... ....... \quad (9)
\]

\(C_1\): Higher concentration.

\(C_2\): Lightest concentration.

\(V_1\): The needed volume of the higher concentration.

\(V_2\): The size needed to be added to the higher concentration for the lightest concentration.
2-Preparation of dye films

Preparing (M.G.O) dye films by dissolving the dye according to Equation 8 with a concentration of $10^{-3}$ in the ethanol solvent, then placing the solution on the slides with a lollipop pad and leaving it to dry for 24 hours. Then the absorption spectrum was measured for each slide and the thickness was calculated by means of a thin films screening device. There are several ways to measure the thickness of thin films measuring as shows in Fig. 2. The thickness of thin films was determined by the geometrical path difference resulting from the optical path difference between the beam reflected from the film and from the base.

The thickness of the film produced used in the equation of absorption coefficient. Calculate the absorption coefficient and the energy gap for it. If the film is transparent and there is optical interference, the thickness can be calculated for any sample as well if the multilayer film can calculate the thickness of each layer.

![Fig. (2): Measuring device for thin-film thickness.](image)

The results of thickness measurement for (M.G.O) dye films by casting method at several thickness shown in Table 3.

| Films | Thickness films T (nm) |
|-------|------------------------|
| 1     | 37                     |
| 2     | 41                     |
| 3     | 51                     |

Table(3): Results of thickness measurement for (M.G.O) dye films by casting method.

Result and Discussion:
Optical properties for (M.G.O) dye dissolved in Ethanol solvent

The absorption spectra of the dissolved (M.G.O) dye in ethanol solvent at several concentrations ($2 \times 10^{-5}$, $1 \times 10^{-5}$, $5 \times 10^{-6}$) Ml, and measured using UV -Vis spectrophotometer as shown in figure (3) and the table (4).
Fig. (3): Absorption spectra of (M.G.O) dye in ethanol at several concentrations.

![Absorption spectra](image)

Table (4): Absorbance result of (M.G.O) dye in ethanol at several (C).

| C    | λ<sub>max</sub> | A   |
|------|----------------|-----|
| 2×10<sup>-5</sup> | 428 | 0.150 |
|      | 622 | 0.726 |
| 1×10<sup>-5</sup> | 426 | 0.066 |
|      | 621 | 0.350 |
| 5×10<sup>-6</sup> | 424 | 0.053 |
|      | 620 | 0.277 |

From the result of absorbance spectra in Fig. 3, it was two energy transfers at (428,622) nm, it was found that the intensity of (A) is reduced by reducing the (C). Fig. 4 and Table 5 are show the result of transmittance spectra.

![Transmittance spectra](image)

Fig. (4): Transmittance spectra of (M.G.O) dye in ethanol at several (C).
It was found increase the intensity of transmittance by reducing the concentration as shown in Fig.4. After finding the transmittance results, the ($\alpha_o$) and the (n_o) was calculated for the prepared samples by using Equations 5,6. It was found decrease in ($n_o$) and ($\alpha_o$) according to decrease of concentration as shown in Tables 6,7.

**Table (6): Absorption coefficient result of (M.G.O) dye in ethanol at several (C).**

| $\lambda_{\text{max}}$ nm | $\alpha$ cm$^{-1}$ | $\lambda_{\text{max}}$ nm | $\alpha$ cm$^{-1}$ | $\lambda_{\text{max}}$ nm | $\alpha$ cm$^{-1}$ |
|--------------------------|---------------------|--------------------------|---------------------|--------------------------|---------------------|
| 428                      | 0.345               | 426                      | 0.135               | 424                      | 0.122               |
| 622                      | 1.673               | 621                      | 0.806               | 620                      | 0.637               |

**Table (7): Refractive index result of (M.G.O) dye in ethanol at several (C).**

| $\lambda_{\text{max}}$ nm | $n_o$ | $\lambda_{\text{max}}$ nm | $n_o$ | $\lambda_{\text{max}}$ nm | $n_o$ |
|--------------------------|-------|--------------------------|-------|--------------------------|-------|
| 428                      | 1.717 | 426                      | 1.340 | 424                      | 1.272 |
| 622                      | 1.392 | 621                      | 1.151 | 620                      | 1.082 |

Figure (5) and table (8) shows the energy gap were measured for the samples of (M.G.O) dye in ethanol solvent at several concentrations (C).
Fig. (5): Energy gap of (M.G.O) dye in ethanol at several (C).

Table (8): Energy gap result of (M.G.O) dye in ethanol at several (C).

| C     | EG(eV) |
|-------|--------|
| $2\times10^{-5}$ | 1.83   |
| $1\times10^{-5}$ | 1.85   |
| $5\times10^{-6}$ | 1.86   |

Note that the energy gap of (M.G.O) dye solution dissolved in ethanol at several concentrations increases as the concentrations decreases and the substance thus acts as a semiconductor.

Optical properties for (M.G.O) dye films by casting method

The absorption spectra of the films at several thickness (37, 41, 51) nm, were measured using (UV-Vis) spectrophotometer as shown in Fig. 6 and Table 9. Where T thickness measurement.

Fig. (6): Absorption spectra of (M.G.O) dye films by casting method at several (T).

Table (9): Absorbance result of (M.G.O) dye films by casting method at several (T).
From the result of absorbance spectra in Fig. 6, it was found two energy transfers (433, 644) nm, also found the intensity of absorption is decrease according to decrease concentration. Fig. 7 and Table 10 shows the transmittance spectra.

| T=37nm | T=41nm | T=51nm |
|--------|--------|--------|
| \( \lambda_{\text{max}} \) nm | A | \( \lambda_{\text{max}} \) nm | A | \( \lambda_{\text{max}} \) nm | A |
| 433    | 0.152  | 434    | 0.144  | 435    | 0.128  |
| 644    | 0.286  | 645    | 0.271  | 646    | 0.217  |

It was found increased in the intensity of transmittance according to decreases in the thickness as shown in Fig. 7. After finding the transmittance results, the \((\alpha_o)\) and the \((n_o)\) was calculated for the prepared samples using Equations 5,6. It is found decrease in \((n_o)\) and \((\alpha_o)\) according to increase of thickness as shown in tables 11,12.

| T=37nm | T=41nm | T=51nm |
|--------|--------|--------|
| \( \lambda_{\text{max}} \) nm | T | \( \lambda_{\text{max}} \) nm | T | \( \lambda_{\text{max}} \) nm | T |
| 433    | 0.704  | 434    | 0.717  | 435    | 0.744  |
| 644    | 0.516  | 645    | 0.534  | 646    | 0.606  |

*Figure (7): Transmittance spectra of (M.G.O) dye films by casting method at several (T).*

*Table (10): Transmittance result of (M.G.O) dye films by casting method at several (T).*

*Table( 11): Absorption coefficient result of (M.G.O) dye films by casting method at several (T).*
Energy gap were measured for the prepared samples of (M.G.O) dye films by casting method at several thickness. Fig. 8 and Table 13 shows the results.

**Table (12): Refractive index result of (M.G.O) dye films by casting method at several (T)s.**

|          | T=37nm |          |          |          |          |
|----------|--------|----------|----------|----------|----------|
| \( \lambda_{\text{max}} \) nm | 433    | 434      | 435      |
| \( n_\text{r} \) | 1.971  | 1.738    | 1.645    |
|          | 644    | 645      | 646      |
| \( n_\text{r} \) | 1.564  | 1.351    | 1.161    |

**Table (13): Energy gap result of (M.G.O) dye films by casting method at several (T).**

| Thickness films | EG(eV) |
|-----------------|--------|
| 37              | 1.73   |
| 41              | 1.72   |
| 51              | 1.71   |

It was observed in Fig.8 that the energy of (M.G.O) dye films by casting method at several thickness decreases as the thickness increases, and the substance thus acts as a semiconductor.

It was found that the absorption spectra of (M.G.O) dye films prepared by casting method at several thickness has a higher wavelength and intensity. While the absorption spectra of (M.G.O) dye in ethanol solvent has lower wavelength and intensity. The reason for this change is due to the differing way of prepared samples for the same dye.

**Conclusion:**
1-In the absorption spectra appears two transitions energy at the wavelengths (428,622) nm for ethanol solution and wavelength (435,650) nm for dye films by casting method.
2-The values of \( \alpha_0 \) and \( n_\text{r} \) of (M.G.O) dye dissolving in ethanol solvent reducing per to concentration of the solution decreases to low wavelength (blue shift type).
3-There were noticeable change in the intensity and values of wavelength of absorption spectra for solutions dye and films dye.
4. Two absorption peaks in the dye films (two energy transitions) at the wavelengths (≈428 nm) and (≈622 nm), and two absorption peak in the dye films (two energy transition) at the wavelengths (≈435 nm) and (≈650 nm).

5. The values of (α˳) and (n˳) of (M.G.O) dye films decrease as the thickness films increase.

6. The broadening of absorption peaks results from the presence of many vibration and rotational energy levels of electronic energy levels.

7. Energy gap of (M.G.O) dye in ethanol solvent range from (1.83-1.86) eV, while energy gap of (M.G.O) dye films range from (1.71-1.73) eV.

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