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RESEARCH ARTICLE

# Comparative Study on the Optical Properties and Quantum Efficiency of Congo Red Dye Doped with $SiO_2$, MgO, and $TiO_2$ Nanoparticle

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## ABSTRACT

This study focused on improving the optical properties of the Congo Red pigment using different nanoparticles (SiO2, MgO, and TiO2) at different weight concentrations (0.002, 0.004, and 0.006 g). The results showed that the addition of nanoparticles led to a significant improvement in absorbance (A), refractive index (n), and dielectric constant, while the transmittance (T) decreased. Regarding absorbance at the highest concentration (0.006 g): the pure dye recorded an absorbance of 0.204, while it increased to 0.325 with the addition of $SiO_2$, to 0.361 with MgO, and reached its maximum value of 0.626 with $TiO_2$. Conversely, the transmittance (T) decreased at the same concentration: from 0.623 for the pure dye, to 0.473 with $SiO_2$, 0.435 with MgO, and recorded its lowest value of 0.236 with $TiO_2$, indicating the high light-blocking efficiency of titanium dioxide. Fluorescence results also showed that the quantum efficiency (QE) decreased with Increasing the concentration for all samples, the highest quantitative efficiency was recorded at the lowest concentration (0.002 g) and the values were as follows: 0.0459 with SiO2, 0.04 with MgO, and the highest 0.0475 with TiO2.

***Keywords:*** Congo red dye, nanoparticles, optical properties, fluorescence, dielectric constants.

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## 1. Introduction

A solid or liquid chemical that dissolves in the medium it is added to, creating a homogenous mixture and altering its color, is called a dye (or colorant). For instance, inks and foods (such as food additives, plastics, etc.) include it [1]. The organic dyes possess a good absorption of the electromagnetic spectrum in the visible range. This property is peculiar to organic compounds with a vast network of conjugated bonds which are alternated by single and double bonds. The long-wavelength absorption band of dyes is responsible for the transition from the electronic to the absorption bond ground state S0 to the first excited singlet state S1. This mechanism, which results in the ground state S0 of the absorption bond, is frequently very important. The transition moment occurs when the strength of oscillation is of order of unity. Spontaneous emission in dye lasers is brought about by the reversal process of S1 to S0. [2]. The Beer-Lambert law, which is regarded as an empirical relationship connecting the light absorption characteristics of the material through which the light passes, states that the probability of photon absorption is directly proportional to the concentration of absorbing molecules in the sample and the thickness of the medium (path length of light). This rule states that the amount of radiation absorbed as it travels through a substance is directly correlated with the number of absorbed particles in that medium. The

amount of light absorbed or transmitted depends exponentially on the solvent content in a particular solution [3]. The development of materials with distinctive size, structure, and substance is made possible by nanotechnology, a significant scientific advancement. The physical and chemical characteristics of the material alter as the fraction of surface atoms rises with decreasing particle size [4]. Adding certain qualities to the substrate material or characteristics unrelated to its intended application is the aim of creating composite materials. When nanoparticles are added during the production process, these materials show notable improvements in their characteristics. For instance, adding carbon nanotubes and nanoparticles alters the material's electrical and thermal conductivity. Additional nanoparticles that improve optical qualities, electrical insulation, and mechanical qualities like strength and stiffness may be produced by combining different kinds of nanoparticles. The additional nanoparticles are quite small, and the ideal volume proportion of nanomaterials is between 0.5% and 5%. Another consideration is the ratio of surface area to volume [5].

## 2. Optical properties

The Optical properties are an integrated system that shows us how matter interacts with light through some basic concepts such as absorbance, transmittance, refractive index, absorption, and extinction, which are essential indicators for understanding the spectral and structural behavior of materials.

### 2.1. Absorbance

When photons hit molecules, the electrons can absorb photon energy (hf), which enables them to move from their ground state to higher (excited) electronic states. This is possible because the energy difference between the excited state and the ground state, E, and the photons' energy, E, are equal. The total energy of a molecule is commonly expressed as the product of its rotational energy (Er), vibrational energy (EV), and electronic energy (Ee), as indicated by the formula [6,7]:

$$E_{total} = E_e + E_v + E \quad (1)$$

The bands of the absorption spectra are expanded because electronic transitions might result in numerous transitions with different energies (vibrational and rotational).

### 2.2. Transmittance (T)

The ratio of the transmitted radiation intensity (I) to the incoming radiation intensity (Io) is the definition of this part of the conservation law. Following absorption and reflection, the residual incident radiation [8]

$$R+T+A=1 \quad (2)$$

$$T = \frac{I}{I_0} \quad (3)$$

### 2.3. Absorption coefficient

The attenuation of light intensity as it passes through a material, also known as the absorption coefficient (αo), is the factor that can be mentioned as part of the absorbed ray per unit thickness of the material [9]. The following relation can be used to determine the absorption coefficient according to the Beer-Lambert law [10,11]:

$$2.303A=\alpha_0 \ell \quad (4)$$

$$\alpha_0(cm^{-1})=2.303 \frac{A}{l} \quad (5)$$

$$\alpha_0= \frac{1}{d} \ln \left(\frac{1}{T}\right) \quad (6)$$

where $\alpha_0$ is the absorption coefficient ($cm^{-1}$), A is the absorbance, T is the optical transmittance, and ℓ or d is the thickness of the sample in centimeters.

### 2.4. Refractive index

In a vacuum, light travels at its maximum speed across all wavelengths, which is constant; however, this speed decreases in other media due to the differences in the properties of the material and wavelengths. The average refractive index of a wave is the speed of light is the ratio of the speed of light. in a vacuum to its speed in any given medium at a specific wavelength [12].

$$n = \frac{C}{V} \tag{7}$$

The refractive index is dependent on the electromagnetic wave's length and is not constant. Additionally, certain materials have a refractive index that varies based on the direction of electromagnetic wave propagation in the material; these materials are utilized to alter the direction of polarization of those waves [13] in order to calculate the complex refractive index.

$$\bar{n} = n + i\,\kappa \tag{8}$$

where k is the absorption or damping coefficient (or the imaginary portion of a complex refractive index). The wavelength's frequency affects both (k) and n. The following equation can be used to get the damping coefficient K [14] .

### 2.5. Dielectric Constant

It is the degree to which a substance reacts to various frequencies, including optical frequencies, which are represented by light waves.

The only sort of polarization that outperforms the others is electronic polarization, and it does so in a complex way.

This refers to the ability of matter to decrease in energy as a result of its interaction with and absorption of energy. The complex dielectric constant of the material (ε) is typically used to explain this polarization:

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \tag{9}$$

Ɛ1: The dielectric constant's real portion, which denotes the polarization limit

Ɛ2: The imaginary part of the dielectric constant, which measures the rate of energy loss.

(Ɛ) is related to the compound refractive index through the relation:

$$n_o = \sqrt{\varepsilon} = n - ik \tag{10}$$

The values of ($Ɛ_1$) and ($Ɛ_2$) can be found from the following two equations [15]

$$\varepsilon_1 = n_2 - k_2 \tag{11}$$

$$\varepsilon_2 = 2nk \tag{12}$$

## 3. Fluorescence

A summary of luminescence is useful. When a molecule is exposed to light, it absorbs the photon, becomes stimulated to reach a higher level, and then releases more photons to reach a lower level. This phenomenon is known as fluorescence. The molecule changes from its excited electrical state to one of its vibrational modes when it absorbs light from an outside source. After colliding with neighboring molecules and losing some of its vibrational energy, it descends to the lowest vibrational level and is radioactively transferred from this level to one of the ground vibrational levels. The process happens really quickly [16,17]. Photon absorption is the first step in photoluminescence (A). This mechanism provides energy to the ground state electrons (So), enabling them to transition to higher energy states (S1, S2), therefore a state of vibrational excitation (v). They lose some of their energy without radiation by performing vibrational relaxation (VR) to

the lowest vibrational state of the stimulated electronic state. They also undergo internal conversion (IC), a nonradiative energy loss.

## 4. External Quantum Efficiency (EQE) and Internal Quantum Efficiency (IQE)

IQE considers photons which are absorbed but not lost to either reflection or transmission, whereas EQE calculates the fraction of input photons that are converted to electrons [18-22] .

## 5. Results and Discussion

A precisely weighed amount of 0.002 mg of Congo red dye was diluted in 300 mL of filtered water to create a stock solution with a defined concentration. Three different concentrations of this stock solution were then obtained by diluting it. The produced solutions' absorbance spectra were measured with a UV-Vis spectrophotometer. As shown in Figure (1). The Transmittance was also calculated for the three concentrations Figure (2).

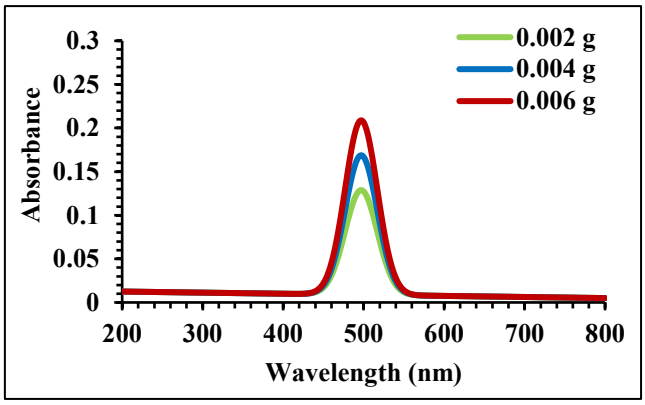



**Figure 1.** Absorption spectrum values at wavelengths within the visible spectrum for Congo red dye solution at different concentrations.

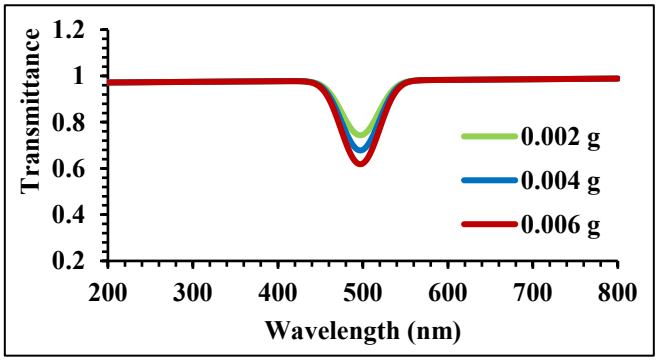



**Figure 2.** A spectrum of transmittance values at wavelengths within the visible spectrum for Congo Red dye solution at different concentrations.

The results showed an increase in the values of absorbance( A ) reflectance( R ), absorption coefficient ( -1 ), refractive index (n), and extinction( k ), with an increase in the real dielectric constant (Ɛr) and imaginary (Ɛimag ), and a clear decrease in transmittance (T ) with increasing concentration of the dye (Table 1).

**Table 1.** shows the optical characteristics of Congo Red dye at different concentrations.

| Table ( 1 ) : | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Dye** | **Dye W (g)** | **A** | **T** | **R** | **α** | **K** | **n** | **$\varepsilon_r$** | **$\varepsilon_{imag}$** |
| Red Congo | 0.002 | 0.133 | 0.736 | 0.065 | 0.306 | $1.2*10^{-6}$ | 1.67 | 2.813 | $4*10^{-6}$ |
| | 0.004 | 0.170 | 0.676 | 0.098 | 0.391 | $1.5*10^{-6}$ | 1.91 | 3.679 | $5*10^{-6}$ |
| | 0.006 | 0.204 | 0.623 | 0.152 | 0.472 | $1.8*10^{-6}$ | 2.27 | 5.158 | $8*10^{-6}$ |

UV-Vis absorbance and transmittance spectra of red congo dye solutions doped with Sio2 NPs, showing the effect of varying dye concentrations on optical performance .

Figure (3) shows an increase in absorbance with increasing concentration in the presence of the SiO2 nanomaterial. Figure (4) shows a decrease in permeability with increasing concentration in the presence of the SiO2 nanomaterial.

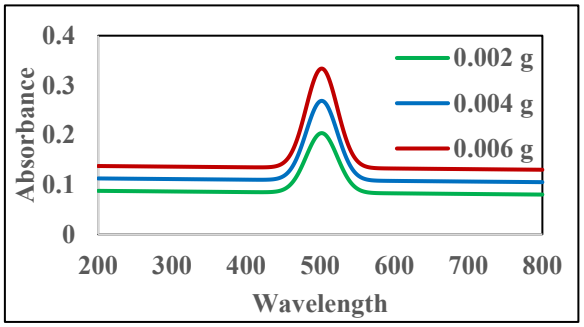



**Figure 3.** Absorption values spectrum at wavelengths within the visible spectrum of a Congo Red dye nanocomposite in the presence of SiO2 NPs.

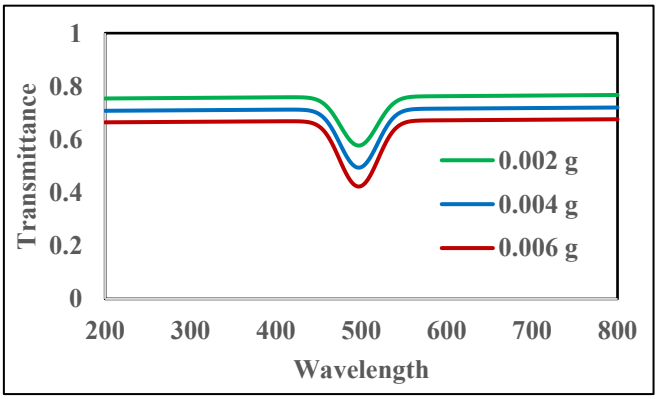



**Figure 4.** Transmittance values at wavelengths within the visible spectrum for a Congo red pigment nanocomposite at different concentrations with SiO2 NPs.

The results showed an increase in optical properties and a clear decrease in transmittance with increasing concentration of Congo red dye with the addition of 0.002g of nanomaterial -SiO2. Table (2).

**Table 2.** shows the optical characteristics of Congo Red dye doped with SiO2 NPs at different concentrations.

| Table (2) : | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Dye** | **Dye W (g)** | **A** | **T** | **R** | **α** | **K** | **n** | **$\varepsilon_r$** | **$\varepsilon_{imag}$** |
| Red Congo+ SiO2 | 0.002 | 0.193 | 0.641 | 0.065 | 0.444 | $1.7*10^{-6}$ | 1.68 | 2.837 | $5.9*10^{-6}$ |
| | 0.004 | 0.257 | 0.553 | 0.09 | 0.591 | $2.3*10^{-6}$ | 1.911 | 3.653 | $9*10^{-6}$ |
| | 0.006 | 0.325 | 0.473 | 0.152 | 0.748 | $2.9*10^{-6}$ | 2.278 | 5.189 | $13*10^{-6}$ |

UV-Vis absorbance and transmittance of the red congo dye solutions with dilution of MgO NPs, indicating the influence of different concentration of dyes on optical behavior. , Figure (5) shows an increase in absorbance with increasing concentration in the presence of the MgO nanomaterial. Figure (6) shows a decrease in permeability with increasing concentration in the presence of the MgO nanomaterial.

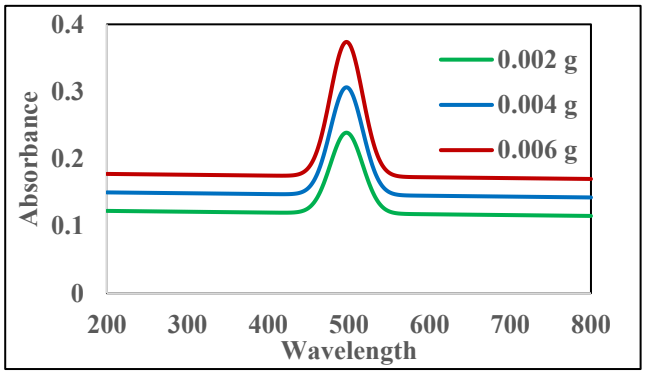



**Figure 5.** Absorption values spectrum at wavelengths within the visible spectrum of a Congo Red dye nanocomposite in the presence of MgO NPs.

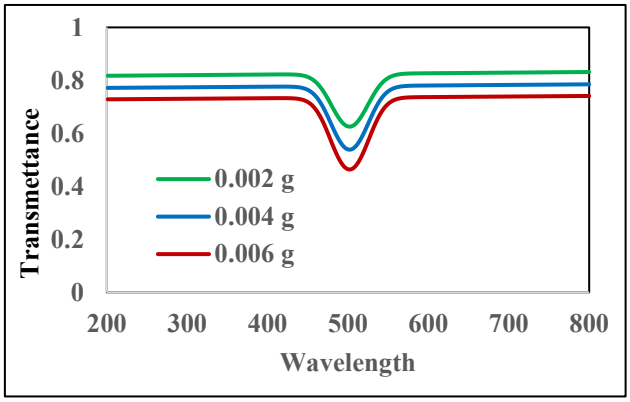



**Figure 6.** Transmittance values at wavelengths within the visible spectrum for a Congo red pigment nanocomposite at different concentrations with MgO NPs.

The results showed a clear increase in optical properties such as absorbance, reflectance, absorption coefficient, refractive index, extinction, and real and imaginary dielectric constant, with a clear decrease in transmittance with increasing dye concentration and the addition of 0.002g of MgO nanomaterials (Table 3).

**Table 3.** shows the optical characteristics of Congo Red dye doped with MgO NPs at different concentrations.

**Table (3) :**

| Dye | Dye W (g) | A | T | R | α | K | n | $\varepsilon_r$ | $\varepsilon_{imag}$ |
|---|---|---|---|---|---|---|---|---|---|
| Red Congo+ MgO | 0.002 | 0.224 | 0.597 | 0.065 | 0.515 | $2*10^{-6}$ | 1.67 | 2.837 | $6.9*10^{-6}$ |
| | 0.004 | 0.293 | 0.509 | 0.098 | 0.674 | $2.6*10^{-6}$ | 1.91 | 3.653 | $1*10^{-5}$ |
| | 0.006 | 0.361 | 0.435 | 0.152 | 0.831 | $3.3*10^{-6}$ | 2.27 | 5.489 | $1.5*10^{-5}$ |

UV-Vis absorbance and transmittance of Tio2 NP-doped red congo dye solutions., illustrating how the optical performance depends on different dye concentrations, Figure (7) shows an increase in absorbance with increasing concentration in the presence of the Tio2 nanomaterial. Figure (8) shows a decrease in permeability with increasing concentration in the presence of the Tio2 nanomaterial.

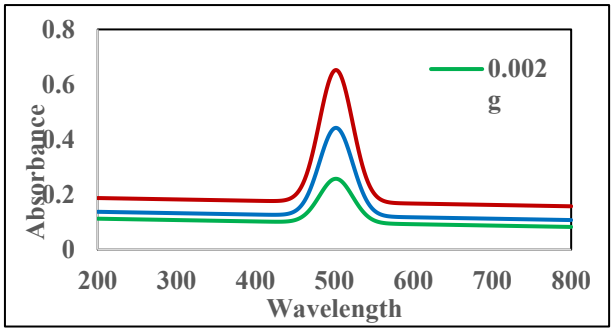



**Figure 7.** Absorption values spectrum at wavelengths within the visible spectrum of a Congo Red dye nanocomposite in the presence of TiO2 NPs .

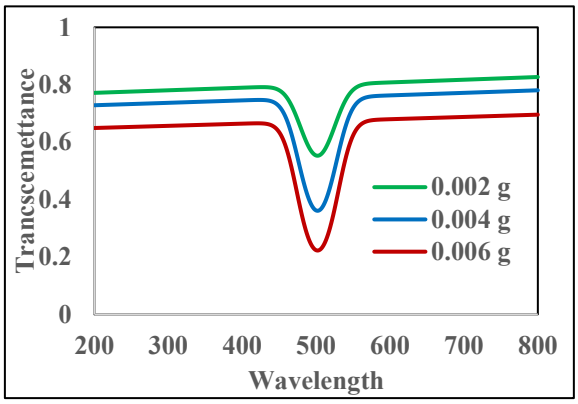



**Figure 8.** Transmittance values at wavelengths within the visible spectrum for a Congo red pigment nanocomposite at different concentrations with TiO2 NPs.

The results showed a clear increase in optical properties such as absorbance, reflectance, absorption coefficient, refractive index, extinction, and real and imaginary dielectric constant, with a clear decrease in transmittance with increasing dye concentration and the addition of 0.002g of TiO2 nanomaterials (Table 4)

**Table 4.** shows the optical characteristics of Congo Red dye doped with TiO2 NPs at different concentrations.

**Table (4):**

| Dye | Dye W (g) | A | T | R | α | K | n | $\varepsilon_r$ | $\varepsilon_{imag}$ |
|---|---|---|---|---|---|---|---|---|---|
| Red Congo+ TiO2 | 0.002 | 0.245 | 0.568 | 0.065 | 0.564 | $2.2*10^{-6}$ | 1.67 | 2.84 | $7*10^{-6}$ |
| | 0.004 | 0.419 | 0.381 | 0.098 | 0.964 | $3.8*10^{-6}$ | 1.91 | 3.65 | $1.4*10^{-5}$ |
| | 0.006 | 0.626 | 0.236 | 0.152 | 0.441 | $5.7*10^{-6}$ | 2.27 | 5.20 | $2*10^{-5}$ |

The fluorescence spectra of Congo red dye at different concentrations were investigated to understand its optical behavior and electronic transition mechanisms. Analysis of the emission wavelengths and Stokes shift provides essential information about energy relaxation and fluorescence efficiency, enabling evaluation of the dye for optical and sensing applications, Figure (9).

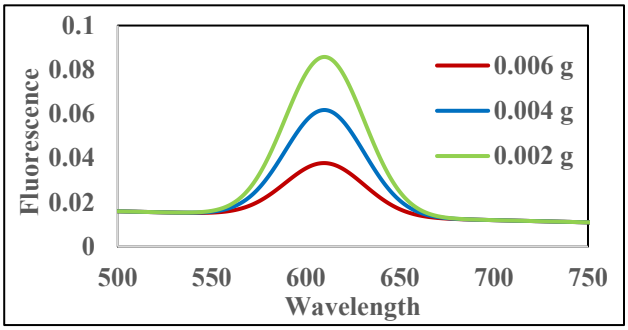



**Figure 9.** Spectrum of fluorescence emission values at wavelengths within the visible spectrum for Congo red dye solutions at different concentrations.

The fluorescence spectra of Congo Red dye doped with SiO2 nanoparticles at different concentrations were investigated to understand its optical behavior and electronic transition mechanisms. Analysis of the emission wavelengths and Stokes shift provides fundamental information on energy relaxation and fluorescence efficiency, enabling the evaluation of the dye for optical and sensing applications, Figure (10) .

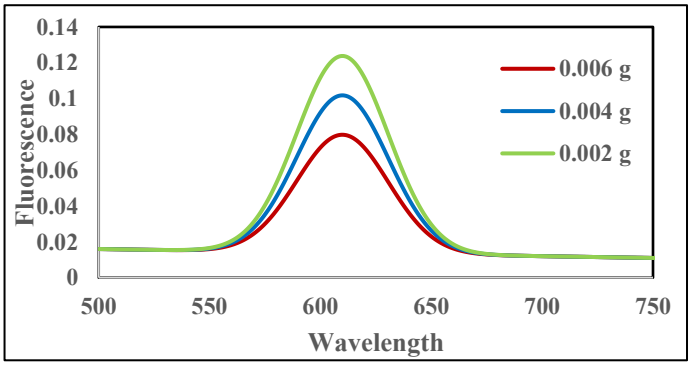



**Figure 10.** Spectrum of fluorescence emission values at wavelengths within the visible spectrum of a nanocomposite of Congo red dye at different concentrations with the addition of SiO2 NPs.

**Table 6.** Absorption maximum (λA), fluorescence maximum (λF), and Stokes shift (Δλ) of red congo dye doped with SiO2 NPs at different concentrations.

| Wieght (g) | λAmax | λFmax | Δλ=λF-λA | QE |
|---|---|---|---|---|
| 0.002 | 511 | 613 | 102 | 0.045911 |
| 0.004 | 511 | 613 | 102 | 0.034821 |
| 0.006 | 513 | 614 | 101 | 0.024429 |

The fluorescence spectra of Congo Red dye doped with MgO nanoparticles at different concentrations were investigated to understand its optical behavior and electronic transition mechanisms. Analysis of the emission wavelengths and Stokes shift provides fundamental information on energy relaxation and fluorescence efficiency, enabling the evaluation of the dye for optical and sensing applications, Figure (11).

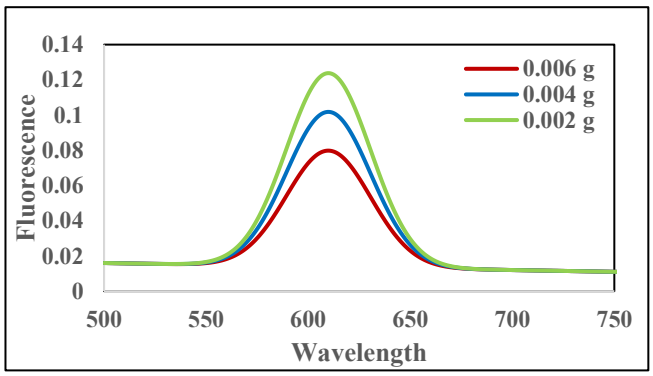



**Figure 11.** Spectrum of fluorescence emission values at wavelengths within the visible spectrum of a nanocomposite of Congo red dye at different concentrations with the addition of MgO NPs.

**Table 7.** Bsorption maximum (λA), fluorescence maximum (λF), and Stokes shift (Δλ) of red congo dye doped with MgO NPs at different concentrations.

| Wieght (g) | λAmax | λFmax | Δλ=λF-λA | QE |
|---|---|---|---|---|
| 0.002 | 504 | 614 | 110 | 0.046832 |
| 0.004 | 504 | 614 | 110 | 0.034941 |
| 0.006 | 508 | 614 | 106 | 0.025013 |

The fluorescence spectra of Congo Red dye doped with TiO2 NPs nanoparticles at different concentrations were investigated to understand its optical behavior and electronic transition mechanisms. Analysis of the emission wavelengths and Stokes shift provides fundamental information on energy relaxation and fluorescence efficiency, enabling the evaluation of the dye for optical and sensing applications, Figure (12).

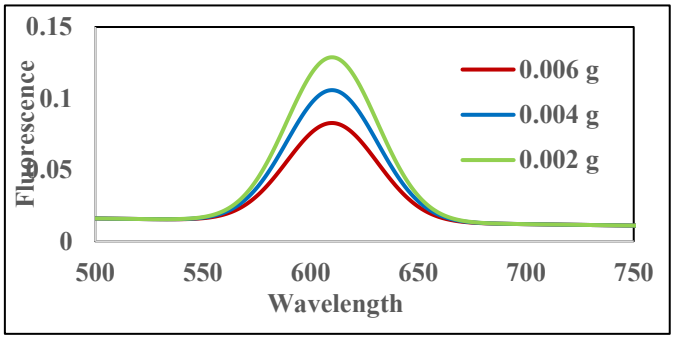



**Figure 12.** Spectrum of fluorescence emission values at wavelengths within the visible spectrum of a nanocomposite of Congo red dye at different concentrations with the addition of TiO2 NPs.

**Table 7.** Absorption maximum (λA), fluorescence maximum (λF), and Stokes shift (Δλ) of red congo dye doped with TiO2 NPs at different concentrations.

| Wieght (g) | λAmax | λFmax | Δλ=λF-λA | QE |
|---|---|---|---|---|
| 0.002 | 507 | 614 | 107 | 0.047541 |
| 0.004 | 508 | 614 | 106 | 0.037453 |
| 0.006 | 511 | 614 | 103 | 0.025213 |

## 6. Conclusions

**Concentration Effect:** The optical properties are strongly dependent on the dye and dopant concentration. An increase in concentration led to a significant increase in absorbance, absorption coefficient, refractive index, and dielectric constants (real and imaginary), while optical transmittance decreased exponentially, adhering to the Beer-Lambert law behavior.

**Role of Nanoparticles:** Doping the dye with metal oxide nanoparticles significantly enhanced its optical limiting properties compared to the pure dye. The effectiveness of the nanoparticles in enhancing absorbance and reducing transmittance followed the order: TiO2 > MgO > SiO2. This suggests that TiO2 nanoparticles interact more effectively with the dye molecules, modifying the electronic structure and transition probabilities.

**Dielectric Properties:** The increase in the real and imaginary parts of the dielectric constant with doping indicates enhanced polarization and energy dissipation capabilities of the nanocomposites, making them suitable for optoelectronic applications.

**Fluorescence Quenching:** The fluorescence analysis revealed that the Quantum Efficiency (QE) decreases as the concentration of the dopants increases. This suggests a concentration-quenching mechanism or non-radiative energy transfer processes dominating at higher concentrations. However, at lower concentrations, TiO2 doped samples exhibited the highest quantum efficiency (0.0475).

**Application Potential:** The tunable optical band gap and high absorbance of the synthesized nanocomposites, particularly those doped with TiO2, indicate promising potential for use in optical sensors, solar cell concentrators, and laser shielding applications.

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