University of Thi-Qar Journal of Science (UTsci)
The 4th Scientific Conference of Science College/ University of Thi_Qar
Volume (7), No.2

Linear and Nonlinear Optical Properties of Natural Dyes Freestanding Films and Application in Optical Limiting

Maha A Rahma* Emad A. Mohammed Haithem L Saadon
Laser Applications Research Group (LARG), Department of Physics, College of Science, University of Basrah, Basrah, Iraq.
* E-mail: mahabct@yahoo.com

***Abstract*-Natural dyes were followed and prepared from a pomegranate, purple carrot, and eggplant peel. The absorbance spectra was measured in the wavelength range 300-800 nm. The linear properties measurements of the prepared natural dye freestanding films were determined include absorption coefficient (α_0), extinction coefficient (κ), and linear refraction index (n). The nonlinear refractive index n_2 and nonlinear absorption coefficient β_2 of the natural dyes in the water solution were measured by the optical z-scan technique under a pumped solid state laser at a laser wavelength of 532 nm. The results indicated that the pomegranate dye can be promising candidates for optical limiting applications with significantly low optical limiting of 3.5 mW.**

Keywords: Optical limiting, Natural dyes, z-scan measurements.

I. Introduction

Organic dyes are investigated to have large nonlinear optical (NLO) properties in different applications (Jazbinsek *et al.*, 2008; Marder *et al.*, 2006). This type of dyes is extended to natural dyes which is demonstrated a great interesting in the field of nonlinear optical effect. Such of these materials are used in photonic applications including optical communications, optical limiting, optical-switching, and photonic devices (Unnikrishnan *et al.*, 2001; Zongo *et al.*, 2015). Natural dyes are derived from natural sources such as plants, animals, and minerals (Chengaiah *et al.*, 2010). Most of synthesized materials/dyes require difficult preparation method and expensive materials. Therefore, the suggestion of natural dyes due to its friendly environment, low cost, simple extracts method. Number of natural dyes which exhibit good nonlinear optical properties such as curcuma, henna, and beet root have been investigated (Henari *et al.*, 2013; Thankappan *et al.*, 2012). Anthocyanin dye is responsible for the red/purple color of many fruits and vegetables for example cherry, strawberry, purple carrot, and eggplant peel (Todaro *et al.*, 2009).

In this work, we investigate the linear and NLO properties as well as the optical limiting behavior of pomegranate, purple carrot, and eggplant peel. The technique which is used in this investigation is called the z-scan technique (Sheik-Bahae *et al.*, 1990). The nonlinear absorption coefficient β and nonlinear refractive index n_2 were measured at a laser wavelength of 532 nm.

II. Materials and Methods

Polyvinyl alcohol (PVA) (Central Drug House (P) Ltd. CDH, M.W=125000), pomegranate, purple carrot, and eggplant peel were used to prepare the natural dye freestanding films. In freestanding films, polyvinyl alcohol is used as a matrix owing to its good mechanical, thermal, and adhesive properties and water solubility, which it a suitable choice for the fabrication of optical devices (Pandey *et al.*, 2015).
However, the method which used to extract natural dye from three fresh fruits is called the simple aqueous extraction method (Kumar and Konar, 2011). Pomegranate, carrot, and eggplant were cleaned several times with distilled water to remove the adhering particles and dust from their surfaces, and then dried. Purple carrot and eggplant peel were cut into small pieces and soaked in distilled water one at time, then boiled for half an hour, while the pomegranate seeds was squeezed and placed in a clean container. All dyes were filtered by a 0.45 µm filter. For measurements reported here, the samples prepared by using PVA solution, and adding 2gm of PVA powder in 100 ml deionized (DI) water under vigorous stirring for 1 h at 90 °C. After the polymer solution is cool down to room temperature, 3 ml of each dye added to 3ml of polymer solution and the solution was stirred for 30 min. Finally, the prepared solutions were casted into a glass Petri dish and left to dry naturally at room temperature for 2 days. After the drying process was completed, a high quality film with uniform surface were peeled off from the Petri dish and the thickness of the samples was approximately 100±10 µm. The optical absorption was investigated by Shimadzu UV-vis 1800 spectrophotometer within wavelength range of 300-800 nm.

III.Experimental results and Discussion

1. Experimental Technique

The nonlinear optical properties of the samples were investigated by z-scan technique (Sheik-Bahae *et al.*, 1990) that is shown in Figure 1.

The nonlinear absorption coefficient β and nonlinear refractive index n_2 are obtained by monitoring the transmitted intensity variation via a focusing of a laser beam passing through an aperture in the far field on a NLO sample. Initially, a CW 532 nm Nd:YAG Gaussian laser beam is passed through a beam-splitter, and divided the beam into two beams. The first beam is passed through a detector1, while the other one is focused by 5 cm focal length of convex lens which leads to Rayleigh length of Z_0=2.8 mm and a radius of the beam waist of ω_0=17.7 μm, to a NLO sample. The sample is placed on the translation stage and moved by a computerize stepper-motor. The laser beam passing through the sample to an aperture and then transmitted to a detector2. Both detectors are connected to a data acquisition controller which is used to record the signal of the laser beam. For optical limiting effects, the z-scan technique is a simple and effective technique to characterize the performance of optical limiting effect, where the sample was placed at the position where the transmitted intensity shows a valley and the transmitted power through the samples was recorded for various input powers.

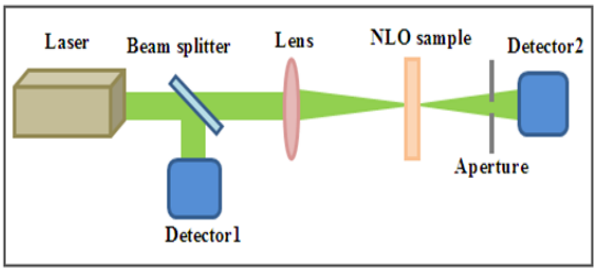

Figure 1 : Typical z-scan technique [M. Sheik-Bahae et al..(1990)].

To measure the magnitude of the nonlinear absorption coefficient β , open aperture z-scan was performed by removing the aperture in front of the detector. the nonlinear absorption coefficient β is given by the equation (Sheik-Bahae *et al.*, 1990).

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \qquad (1)$$

Where ΔT is the normalize transmittance, $L_{eff} = [1-\exp(-\alpha l)]/\alpha$ is the effective thickness of the sample where L is the thickness of the sample and I_0 is the intensity of the laser beam at focus, and α is the linear absorption coefficient. Under open aperture z-scan condition , the normalized transmission is given by (Rahma, 2018)

$$T(z,s=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}} \qquad (2)$$

Where q_0 is the free factor defined as

$$q_0(z,t) = \frac{\beta I_0 L_{eff}}{z^2 + |z_0^2} z_0^2 \qquad (3)$$

To determine the sign and magnitude of nonlinear refractive index n_2 , a closed aperture z-scan was performed by placing aperture in front of the detector. The nonlinear refractive index n_2 is given by (Sheik-Bahae *et al.*, 1990)

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\phi_0| \qquad (4)$$

$$\Delta\phi_0 = \kappa L_{eff} n_2 I_0 \qquad (5)$$

Where ΔT_{p-v} is the peak-valley transmittance difference from the closed aperture z-scan curve, $\Delta\phi_0$ is the on axes nonlinear phase shift, S is the linear transmittance of the aperture given by S= 1-exp($-2r_a^2/\omega_a^2$) where r_a is the radius of the aperture , κ is the wave vector. The normalized transmission for the nonlinear refraction is given by (Sheik-Bahae *et al.*, 1990)

$$T(z) = 1 - \frac{4x}{(x^2+9)(x^2+1)}\Delta\varphi_0 \qquad (6)$$

Where $x=z/z_0$

2. Linear optical properties

The linear optical properties were computed as the absorbance A, reflectance R, optical band gap E_g, refractive index n, and extinction coefficient k. Figures 2 and 3 show the absorption and reflection spectra as a function of wavelength and the peak absorption at (600 > λ > 400) nm for three samples.

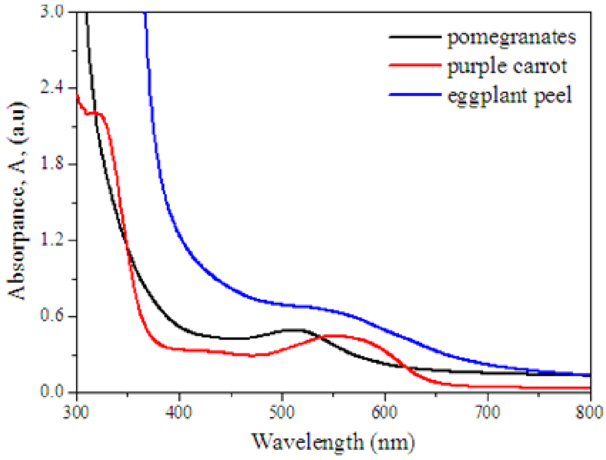

Figure 2: Optical absorption spectrum of natural dye freestanding films.

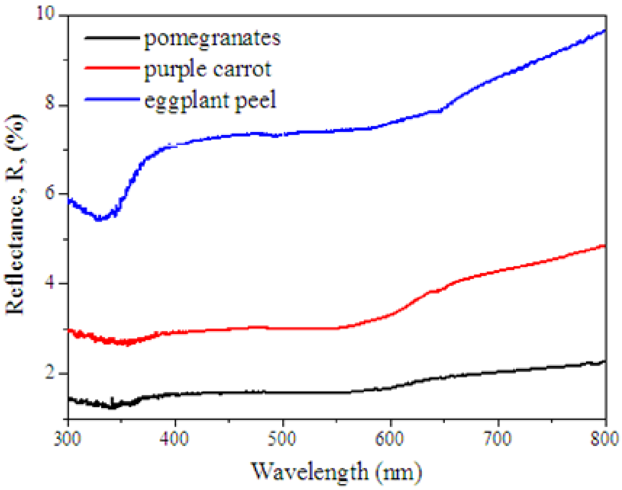

Figure 3: Reflectance spectrum of natural dye freestanding films.

The optical band gap was determined using the Tauc's formula (Kondyurin and Bilek, 2008) and the value of pomegranate, purple carrot, and eggplant peel film were 2.1, 1.98, and 1.96 eV, respectively. Figure 4 shows the linear part of $(\alpha h\nu)^2$ versus hν for freestanding films.

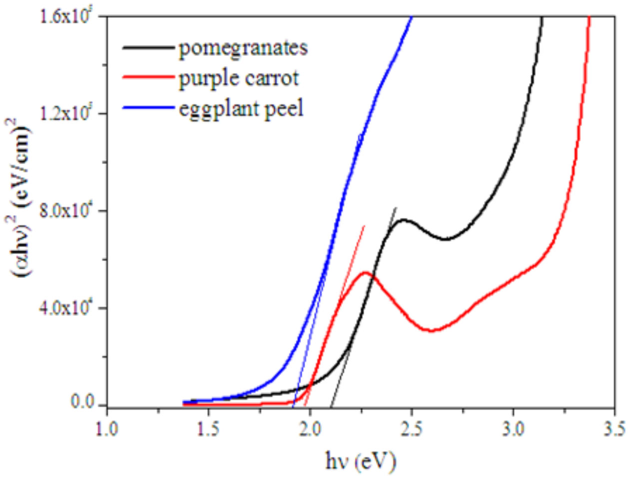

Figure 4: $(\alpha h\nu)^2$ as a function of hν

In addition refractive index n the, and extinction coefficient k can be calculated by using the equations (Pandey *et al.*, 2015; Kumar and Konar, 2011)

$$n = \left(\frac{1+R}{1+R}\right) + \sqrt{\left(\frac{4R}{(1-R)^2} - \kappa^2\right)} \quad (7)$$

$$n \cong \left(\frac{1+R}{1+R}\right) \quad (8)$$

and

$$\kappa = \frac{\alpha\lambda}{4\pi} \quad (3)$$

where α is the absorption coefficient, and λ is the wavelength of the incident light. Figures 5 and 6 explain the changing in the refractive index and extinction coefficient with the wavelength for the nature dye freestanding films.

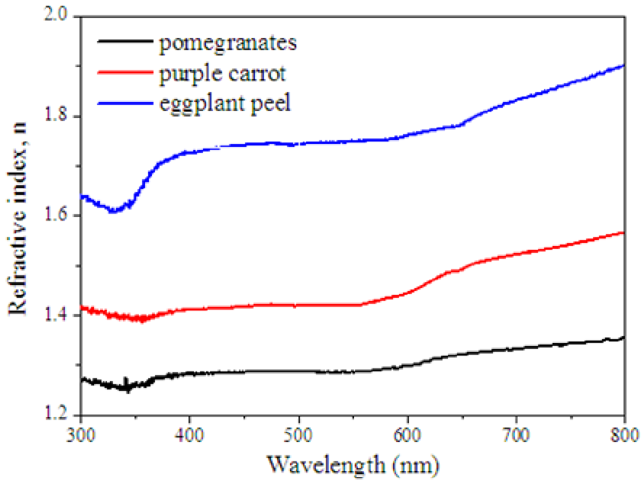

Figure 5: Refractive index of natural dye freestanding films.

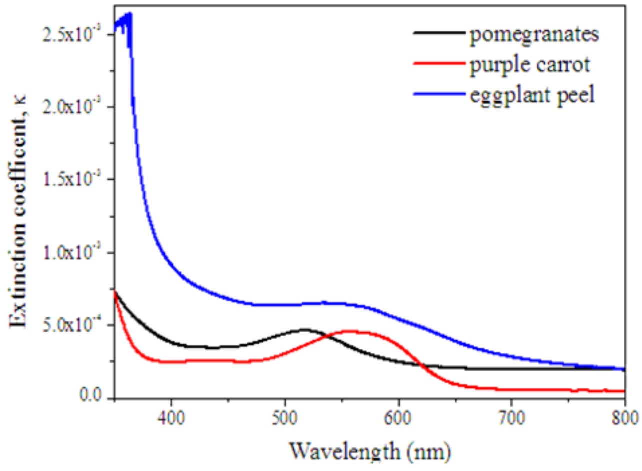

Figure 6: Extinction coefficient of natural dye freestanding films.

3.Nonlinear Optical Properties

To estimate the nonlinear refraction n_2 and nonlinear absorption coefficient β of the prepared natural dyes freestanding films, the open-aperture and close-aperture z-scan behaviors at 3 mW input pump power were used. Figure 7 (I) and (II) shows the optical nonlinearity of three samples for open and closed aperture Z-scan results, respectively. In this figure the normalized transmittance of the films as a function of sample position (z) for open-aperture and closed-aperture z-scan, was measured. The solid lines are the fitting to the experimental data. The open aperture curve exhibit the presence of saturable absorption, reverse saturable absorption, and saturable absorption for pomegranates, purple carrot, and eggplant peel dyes, respectively.

In addition, the close-aperture measurements exhibits peak-valley indicated that a negative nonlinear refraction (self-defocusing) for pomegranates dye, but the purple carrot and eggplant peel dyes display a valley-peak which indicates positive nonlinear refraction (self-focusing).

It is to be noted that the physical origin of the nonlinear refraction can be electronic, molecular or thermal in nature. In the present work, the optical nonlinearity is due to the thermal in nature as a cw laser used (Saadon *et al.*, 2014; Rahma *et al.*, 2018). Table 1 summarizes the nonlinear refraction index and nonlinear absorption coefficient. Hence it is absorbed that Pomegranate exhibited good optical nonlinearity compared with the other natural dyes

Table 1: Nonlinear optical parameters for natural dye freestanding films at input power 3 mW.

Sample	β (cm/W)	n_2 (cm²/W) x 10^{-6}
Pomegranate	**0.229**	**-7**
Purple carrot	**-0.012**	**2**
Eggplant peel	**-0.282**	**0.4**

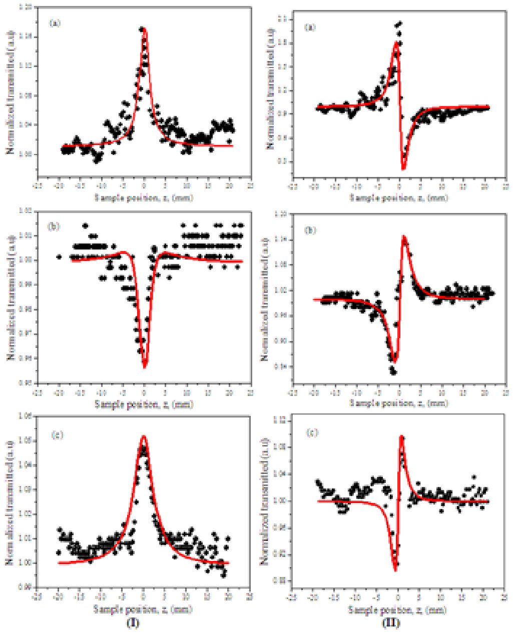

Figure 7: (I) Open-aperture and (II) closed-aperture Z-scan results of the samples: (a) pomegranates, (b) purple carrot, and (c) eggplant peel. The solid lines are theoretical fitting.

4.Optical Limiting Effect

To demonstrate the optical limiting behavior, the z-scan technique was used and performed at 532 nm wavelength by placing the sample after the focus of lens where the defocusing occurred. The sample should be fixed at the position where the normalized transmittance shows a valley in close-aperture z-scan curve. Figure 8 shows the optical limiting behavior for three natural dyes ((Pomegranate, purple carrot, and eggplant peel). The figure was plotted the output power as a function of input power. From this figure it can be determined the optical limiting threshold to be 3.5, 4, and 5.5 mW for Pomegranate, purple carrot, and eggplant peel dyes, respectively. The result should that the low limiting threshold for the Pomegranate natural dye can be used and promised as a material in optical limiting device.

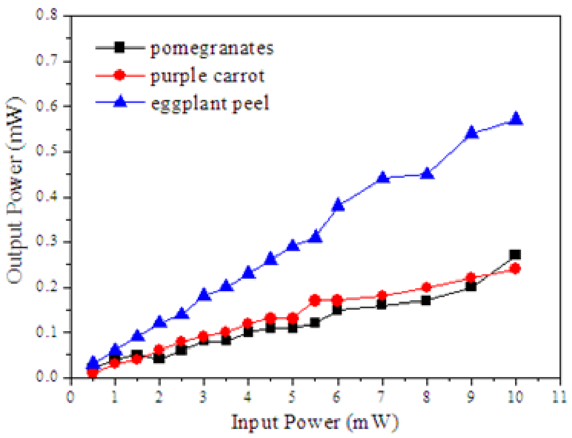

Figure 8: All-optical limiting performances for natural dye freestanding films.

IV.Conclusion

The freestanding natural dyes films were studied. Using the z-scan technique, the nonlinear refraction, nonlinear absorption, and the performances of the optical limiting of the films were investigated. The results showed that the films can be used as a nonlinear optical material by achieving nonlinear optical response and optical limiting. The maximum optical nonlinearity effect of the films is obtained with pomegranate dye with low optical limiting of 3.5 mW.

V. References

Bahae, S.; Said, A.A.; Wei, T.H.; Hagan, D.J. and Van Stryland, E.W. (1990). Sensitive Measurement of Optical Nonlinearities using a Single Beam. IEEE Journal of Quantum Electronics, 26 (4) 760-769.

Chengaiah, K.; Rao, M.; Kuma, K.M.; Alagusunddaram, M. and Chetty, C.M. (2010). Medical Importance of natural dyes- a review. International journal of pharm Tech research CODEN (USA), 2 (1) 144-154.

Diallo , A.; Zongo, S.; Mthunzi, P.; Rehman, S.; Alqaradawi, S.Y.; Soboyejo, W. and Maaza, M. (2014). Z-scan and Optical Limiting Properties of Hibiscus Sabdariffa Dye. applied Physics B, 117 (3) 861-867.

Henari, F. Z. (2012). Optical Nonlinear Properties and Optical Switching of Henna (Lawson) Films. International Journal of Thin Films Science and Technology, 1 (2) 55-60.

Henari, F.Z.; Cassidy, S.; Khaulil Jasim E. and Dakhel, A.A. (2013). Nonlinear Refractive Index Measurements of Curcumin with CW Laser. Journal of Nonlinear Optical Physics & Materials, 22 (2) 1350017/1-8.

Jazbinsek, M.; Mutter, L. and Gunter, P. (2008). Photonic applications with the organic nonlinear optical crystal DAST. IEEE *Journal* of Selected Topics in *Quantum Electronics*, 14 (5) 1298-1311.

Kondyurin, A. and Bilek, M. (2008). Ion Beam Treatment of Polymers: Application Aspects from Medicine to Space. (Netherlands: Elsevier).

Kumar, A. and Konar, A. (2011). Dyeing of Textiles with natural dyes. In Tech book,. Marder, S. R. (2006). Organic nonlinear optical materials: where we have been and where we are going. Chemical Communication, 37 (2) 131-134.

Marder, S.R. (2006). Organic nonlinear optical materials: where we have been and where we are going. Chemical Communication, 37 (2) 131-134.

Pandey, J.K.; Takagi, H.; Nakagaito, A.N. and Kim, H.J. (2015). Handbook of Polymer Nanocomposites.

Processing, Performance and Application (Springer-Verlag: Berlin Heidelberg) .

Rahma, M. A.; Saadon, H.L. and Mahdi, M.A. (2018). High-performance all-optical limiting based on nonlinear refraction of metal-doped PbS/PVA freestanding nanocomposite Films. Optic, 174 (4) 580–590.

Saadon, H.L.; Basil, A. and Adil Al-Fregi, A. (2014). Nonlinear optical properties of new organotellurium compounds containing azomethine and azo groups under CW laser illumination. Optics & Laser Technology, 58 (58) 33-38.

Thankappan, A.; Thomas, S. and Nampoori, V.P. N. (2012). Effect of Betanin Natural Dye Extracted From Red Beet Root on the Nonlinear Optical Properties ZnO Nanoplates Embedded in Polymeric Matrices. Journal of Applied Physics, 112 (1) 123104/1-5.

Todaro, A.; Cimino, F.; Rapisarda, P.; Catalano, A. E.; Barbagallo, R. N. and Spagna, G. (2009). Recovery of Anthocyanins from Eggplant Peel. Food Chemistry, 114 (2) 434–439.

Unnikrishnan, K.P.; Thomas, J.; Nampoori,V.P.N. and Vallabhan, C.P.G. (2002). Third order Nonlinear Optical Studies in Europium Naphthalocyanine using Degenerate Four Wave Mixing and *Z*-scan. Optics Communications, 204 (1) 385-390.

Unnikrishnan, K.P.; Thomas, J.; Paul, B.; Kurian, A.; Gopinath, P.; Nampoori, V.P.N. and Vallabhan, C.P.G. (2001). Nonlinear Absorption and Optical Limiting in Solutions of some Rare Earth Substituted Phthalocyanines. Journal of Nonlinear Optical Physics and Material, 10 (1) 113.

Zongo, S.; Sanusi, K.; Britton, J.; Mthunzi, P.; Nyokong, T.; Maaza, M. and Sahraou, B. (2015). Nonlinear Optical Properties of Natural Laccaic Acid Dye Studied Using Z-scan Technique. Optical Materials, Elsevier, 46 (1) 270-275.