Linear and Nonlinear Optical Properties of Anthocyanin Dye from Red Cabbage in Different pH Solutions

Rajaa Nader1, Slafa I. Ibrahim2 and Ali H. Al – Hamdani3*

1Department of Physics, College of Science for Women, University of Baghdad, Iraq.
2Energy and Renewable Energies Technology Center, University of Technology, Iraq.
3Laser and Optoelectronics Engineering Department, University of Technology, Iraq. Gilgamesh Ahliya University.
Dora Expressway-Iraq
*Corresponding Author.

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Abstract

This article studied some linear and nonlinear optical characteristics of different pH solutions from anthocyanin dye extract at 180 oC from red cabbage. First, the linear spectral characteristics, including absorption and transmittance in the range 400-800 nm for anthocyanin solution 5% v/v with different pHs, were achieved utilizing a UV/VIS spectrophotometer. The experimental results reveal a shift in the absorption toward the longer wavelength direction as pH values increment. Then, the nonlinear features were measured using the Z-scan technique with a CW 532 nm laser to measure the nonlinear absorption coefficient through an open aperture. A close aperture (diameter 2 mm) calculates the nonlinear refractive index. The open Z-scan shows that as the pH increases, the sample decreases transmittance, indicative a two-photon absorption process, and the samples act as a collecting lens for the laser beam. In contrast, the results with a closed Z-scan indicate that the nonlinear absorption coefficient displays a self-focusing nonlinearity. Also, the nonlinear susceptibility decreased by increasing the value of the pH solution. Due to obvious anthocyanin dye nonlinearity dependence value on dye pH, it is possible to use the natural anthocyanin dye as a photonic device.

Keywords: Anthocyanin dye, Nonlinear refractive index, Nonlinear absorption, Susceptibility, Z-scan method.

Introduction

Nonlinear optics have been rigorously studied for over fifty years to identify suitable, practical materials to realize nonlinear optical phenomena. These phenomena include the third harmonic generation, stimulated scattering, nonlinear refraction, and multi-photon absorption utilized in optical limiting optical switching all-optical devices. Further, the optimum self-focusing materials with a pH-dependent refractive index and the realization of the ability of these materials to produce optical devices have become a topic of continuous investigation. Many organic materials 1-4, including dye-doped polymer films 5-11, attract potential due to their enhanced efficiency, optimum material, and mechanical properties to fabricate reliable devices. For example, the properties of each nonlinear absorption and refraction of a material for an input light beam decide its third harmonic generation efficiency. Anthocyanin obtained from flavonol belongs to the phenolic phytochemicals class. It's in the form of a glycoside, with a basic structure of flavylum ion. The red, blue, and purple-colored plants indicate conjugated bonds in anthocyanin 12. The color and stability of anthocyanins are affected
by many parameters such as light, temperature, structure, and the solution’s pH; in acidic solution pH<7, it seems to be red (the shape of flavylumcations), but in basic solution pH>7 it’s blue (species of anionic quinoidal). In neutral pH, it’s purple (anions of resonance-stabilized quinonoid). This is due to its molecular structure having an ionic nature. Extracted photosensitizers from natural dyes to be used as dye-sensitive solar cells (DSSC) are very appealing due to their low expense, availability, sustainability, electricity conversion efficiency, and low production cost. Anthocyanin is a natural dye utilized as a sensitizer dye. Red cabbage is a source with a high anthocyanin content per unit area.

Many prior investigators have studied the optical features of organic dyes; for example, A. Diallo and co-workers 2014, studied some properties of extract solutions of Sabdarifff dye, such as nonlinear susceptibility and refractive index. S. Zongo and a co-worker 2015, studied optical performances for different concentrations of laccic acid dye solution and its thin film in PMMA. They concluded the possibility of laccic acid dye candidates for nonlinear optical applications. Christian Prinzisky and a co-worker 2017 use some anthraquinone imines and their interactions with TiO2, which can be investigated as an effective metal-binding sensitizer for wide-band-gap semiconductors optoelectronic applications. Sara S. M. Fernandes and a co-worker 2017 used two kinds of thieno dyes as sensitizers in (nano TiO2 - DSSCs) and examined the influence of the acceptor/anchoring group on it. The study proposes that Rhodanine-3-acetic acid is a lousy anchoring group due to the crack coupling between the acceptor and the anchor from the interfering methylene group. This proves the significance of the donor, the acceptor, and the anchor in the dye characteristic. Paudel P.N. and co-worker 2018 studied the optical properties of 15 natural dye extractors from different plant parts available in Nepal. The extraction operation utilized solvents with different polarity indexes (ca. 0 -10). The obtained results indicate that these extracted materials may be helpful for application in OLED devices. Najat Andam and co-worker 2021 studied the optical constants of different Azo dye concentrations doped polymethylacrylate. The outcome acquired through SPR measurements is compatible with the results obtained via UV/Vis and spectroscopic ellipsometry. Naseem Fatimah and co-workers 2021 studied the optical properties of Eu3+ activated borate glass entrenched with nano-silver utilizing nanosecond laser pulses. They concluded that the glasses, including nano-silver with high concentration, are useful in designing power optical limiters to work in the visible region in the nanosecond system.

The z-scan, the Eclipsing z-scan, and Diffraction Z-scan methods were utilized to evaluate the nonlinear optical properties of dyes and their polymers. This paper explains the nonlinear properties of liquid anthocyanin dye by applying the z-scan technique. The single-beam used in this technique effectively measures each of the optical nonlinear (refractive index (NLRI); and absorption coefficient (NLAC)).

**Practical part**

Natural dyes from red cabbage were utilized, and the absorption spectrum was evaluated using UV-visible Spectrophotometer T60 from PG Instruments Limited. Open and closed aperture z-scan technology, with a wavelength of CW laser Nd: YAG at the second harmonic 532 nm and hole pin diameter 2 mm, is utilized to calculate each value of nonlinear absorption coefficient (NLAC), and the nonlinear refractive index (NLRI).

**Sample preparation**

250 gm. of red cabbage leaves were treated at temperature -18°C to obtain juice and filtered by filter paper. The resulting solution was diluted with distilled water to prepare solutions with a volume ratio of 5% at different pH values 2, 4, 7, 9, and 11 by using hydrochloric acid (Assay min.35.4%) and sodium hydroxide (Assay min. 85.0%) from Laboratory Reagents & Fine Chemicals.
Results and Discussion

Absorption spectra:

The absorption of high-energy photons between ultraviolet and visible regions is a significant parameter of (DSSC). Therefore, the dye solution's wider absorption band is a fundamental fact. Depending on the absorption spectrum, all solutions give a broad absorption range. For example, anthocyanin dye absorbs the photons in visible wavelength regions between 500-620 nm as shown in Fig. 1. A red shift in the position of the peak absorption intensity as the Anthocyanin dye pH increases. It is at 502, 505, 552, and 617 nm for pH (2, 4, 7, and 11), respectively. The magnitude of the peak intensity decreases as the pH increases. It is 1.093, 1.1, 0.643, and 0.091 for pH (2, 4, 7, and 11) respectively (see Table 1). This means that the intensity of absorption increases with increasing acidity while it decreases with increasing the basicity of the solution.

![Absorption spectrum](image)

Figure 1. The absorption spectrum of (5%v/v) anthocyanin dye at different pH.

The linear absorption coefficient (LAC) ($\alpha_0$) at the wavelength (532 nm) is calculated by utilizing Eq. 1:

$$\alpha_0 = -\frac{1}{t}\ln\left(\frac{1}{T}\right) \quad ...1$$

whereas (t): sample thickness, T: transmittance.

The refractive index $n_0$ can be calculated from Eq. 2:

$$n_0 = \frac{1}{T} + \left[\left(\frac{1}{T^2} - 1\right)^{1/2}\right] \quad ...2$$

The (LAC) and (RI) for samples with different pH are shown in Table 1.

<table>
<thead>
<tr>
<th>pH</th>
<th>Position of $\lambda_{\text{max}}$ (nm)</th>
<th>Peak Intensity (T %)</th>
<th>$\alpha_0$ (μm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>502</td>
<td>1.1</td>
<td>7.9</td>
</tr>
<tr>
<td>4</td>
<td>505</td>
<td>1.093</td>
<td>8.1</td>
</tr>
<tr>
<td>7</td>
<td>552</td>
<td>0.643</td>
<td>27.7</td>
</tr>
<tr>
<td>11</td>
<td>617</td>
<td>0.091</td>
<td>68.1</td>
</tr>
</tbody>
</table>

Table 1. Linear absorption coefficient (LAC) of anthocyanin dye from Red Cabbage in different pH solutions.

Nonlinear optical properties of anthocyanin dye from red cabbage in different pH solutions.

The Z-scan proposed by Sheik Bahae et al.\textsuperscript{30} is utilized for studying the "nonlinear absorption" characteristic of the Anthocyanin dye from Red Cabbage in different pH solutions. The single beam of Gaussian laser used in the setup of the z-scan is tightly focused over the sample. Fig. 2 shows, the Z-scan test setup schematic diagram.
The beam transmission over an aperture position in the far-field is gauged utilizing a "photodetector" and "power meter" assembly. Then, a convex lens is utilized to compile the whole laser beam transmitted over the select dye sample for an open aperture Z-scan. The Z-scan test setup utilized in the open aperture Z-scan is not sensitive to (NLR). Hence, it can be utilized to determine the (NLA) cross-section of the materials. The open aperture Z-scan effect is predictable to be symmetric relative to the focus, and at the focus, the minimum transmittance or a maximum transmittance is happening.

**Nonlinear Absorption Study (Open Aperture Z-Scan)**

Figure 3, shows laser beam transmittance after crossing through the dye sample; the transmittance decrease to form a valley at the focus for samples with pH (2, 4, 7 and 11). In addition, the nonlinear absorption coefficient displays a "two-photon" absorption attitude. This behavior is caused by the change in the laser intensity moving forward on the sample via the beam waist.

The (NLAC) (β) is calculated from the following Eq. 31:

\[
\beta = \frac{2 \sqrt{2} \Delta T}{I_0 L_{\text{eff}}} \quad \ldots \; 3
\]

Here, \(I_0\) is the focal spot intensity, and it is calculated via Eq.4:

\[
I_0 = \frac{2P_{\text{peak}}}{\pi \omega_0^2} \quad \ldots \; 4
\]

and from Eq.5, we can calculate the sample effective length:

\[
L_{\text{eff}} = \frac{(1 - e^{\alpha_0 L})}{\alpha_0} \quad \ldots \; 5
\]
where: \( I_0 \): the intensity of the laser beam when \(( z = 0)\), 
\( I \): irradiance (power per unit area), and \( L_{\text{eff}} \): the 
effective thickness of the samples.

The transmittance and excitation intensity values are inversely proportional and have a
minimum value near the focus for low input intensity. As the pH increases, the sample shows a
decrease in transmittance indicative of reverse, as Sheikh Baha's theory states.

The experimental values of nonlinear absorption coefficient \( \beta \) for liquid anthocyanin dye at
different pH are listed in Table. 2.

<table>
<thead>
<tr>
<th>pH</th>
<th>Absorption at 532nm</th>
<th>( A ) (cm(^4))</th>
<th>( L_{\text{eff}} ) (cm)</th>
<th>( T(z) )</th>
<th>( \beta ) cm/mW</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.078</td>
<td>2.482</td>
<td>0.369</td>
<td>0.0024</td>
<td>0.5386</td>
</tr>
<tr>
<td>4</td>
<td>1.074</td>
<td>2.473</td>
<td>0.370</td>
<td>0.0002</td>
<td>0.5383</td>
</tr>
<tr>
<td>7</td>
<td>0.614</td>
<td>1.414</td>
<td>0.535</td>
<td>0.0010</td>
<td>0.3720</td>
</tr>
<tr>
<td>11</td>
<td>0.074</td>
<td>0.170</td>
<td>0.919</td>
<td>0.0155</td>
<td>0.2134</td>
</tr>
</tbody>
</table>

Nonlinear Refraction Study (Closed Aperture Z-Scan)

Figure.4, shows The plot of the Z-scan for the
solutions under test display a minimum transmittance, i.e.(valley) at pre-focal, and maximum transmittance, i.e. (peak) at post-focal. This indicates that the anthocyanin dye has a positive nonlinearity because of self-focusing nonlinearity. Self-focusing is due to the difference in refractive index value with two-photon absorption and/or the inverse saturation absorption.

\[
\Delta \Phi_0 = \frac{n_2 I_0 L_{\text{eff}} K}{\text{...6}}
\]

Where: \( \Delta \Phi_0 \): Nonlinear phase shift, \( k \): Wave number.

Table. 3, contains experimental values of nonlinear phase shift and the NLRI \((n_2)\) for liquid anthocyanin dye at different pH; its value was positive for the solutions under test, indicating that it conducts as a lens collected the laser beam.

The plot of the Z-scan for the solutions under test display a minimum transmittance, i.e.(valley) at pre-focal, and maximum transmittance, i.e. peak at post-focal. This indicates that the anthocyanin dye has a positive nonlinearity because of self-focusing nonlinearity. Self-focusing is due to the difference in refractive index value with two-photon absorption and/or the inverse saturation absorption.

<table>
<thead>
<tr>
<th>pH</th>
<th>( \Delta T_p \times 10^{-4} )</th>
<th>( \Delta \Phi_0 \times 10^{-9} )</th>
<th>( n_2 ) (cm(^2)/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.64</td>
<td>8.788</td>
<td>0.14213</td>
</tr>
<tr>
<td>4</td>
<td>1.75</td>
<td>9.3225</td>
<td>0.121614</td>
</tr>
<tr>
<td>7</td>
<td>6.33</td>
<td>33.8</td>
<td>0.37754</td>
</tr>
<tr>
<td>11</td>
<td>8.2</td>
<td>439.4</td>
<td>28.5332</td>
</tr>
</tbody>
</table>

The values of the (NLRI)(\(n_2\)) can be calculated using
the following Eq.:
Third-order Nonlinear Optical Susceptibility (NLOS)

Through the values of the (NLRI) \((n_2)\) and the (NLA) that were practically calculated, the value of the 3rd-order nonlinear optical susceptibility \((\chi_3)\) can be extracted by using Eq.7

\[
|\chi^{(3)}| = \left[ \left( \chi_I^{(3)} \right)^2 + \left( \chi_R^{(3)} \right)^2 \right]^{1/2} \quad \ldots \quad 7
\]

Where: \(I\chi^{(3)}\) Absolute value of 3rd-order (NLOS), \(\chi_I^{(3)}\) imaginary part and can be extracted by using Eq.8, and \(\chi_R^{(3)}\) real part from Eq.9:

\[
\chi_R^{(3)} = \frac{10^{-4} \varepsilon_0 (n_0^2) c^2 \lambda}{\pi n_2} \left( \frac{\text{cm}^2}{W} \right) \quad \ldots \quad 8
\]

**Conclusion**

The anthocyanin dye’s nonlinear absorption and nonlinear refraction properties are studied at different pH solutions using the Z-scan experimental method with a CW laser beam of 532 nm. The third-order optical susceptibility of these samples is also studied by changing the pH of the sample. It is found that the nonlinear properties depend on the sample pH. The absorption intensity of anthocyanin dye decreases with the increase in the pH value with red-shifted. The open Z-scan results show that the nonlinear absorption coefficient decreases as the pH increases (two photons absorption process).

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**Author’s Declaration**

- **Conflicts of Interest**: None.
- **We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images that are not ours have been included with the necessary permission for re-publication, which is attached to the manuscript.**
- **Ethical Clearance**: The project was approved by the local ethical committee in University of Technology.
Author’s Contribution Statement

This work was carried out in collaboration with all authors. R. N. collected the samples, S. I. I. did the measurement and calculation, and A. H. Al.

References

الخصائص البصرية الخطية واللاخطية لصبغة الأثنتوسينات من الملفوف الأحمر في محاليل الأس الهيدروجيني المختلطة

رجاء نادر، سلافة إسماعيل إبراهيم، و علي هادي الحمداني

قسم الفيزياء، كلية العلوم للبنات، جامعة بغداد، بغداد، العراق.

1- مركز تكنولوجيا الطاقة والطاقات المتعددة، الجامعة التكنولوجية، العراق.
2- قسم هندسة الليزر وال الإلكترونيات البصرية، الجامعة التكنولوجية، العراق.
3- قسم الفيزياء، كلية العلوم للبنات، جامعة بغداد، بغداد، العراق.

الخلاصة

درس هذا البحث بعض الخصائص البصرية الخطية واللاخطية لمحلول الأس الهيدروجيني المختلط من الأثنتوسينات من الملفوف الأحمر عند درجة حرارة 180 درجة مئوية. أولاً، تم تحقيق خصائص البصرية الخطية، بما في ذلك الامتصاص والانتشارية في النطاق 400-800 نانومتر لمحاليل الأس الهيدروجيني 5% حجم / حجم بدرجات محددة مختلفة، باستخدام مقياس البصرية الضوئي. كما تم دراسة الأنماط السطحية على النواحي الفيزيائية. تم استخدام LPR لمستويات بالانزلاق في النطاق 332 نانومتر. تم قياس معدل الامتصاص البصرية الخطية من خلال نسب تقليلة في المحاليل المختلطة باستخدام تقنيات UV / VIS و Z-scan. تم تكذيب النتائج السابقة باستخدام تقنيات الامتصاص البصرية الخطية، من خلال قياس معدل الامتصاص البصرية البصرية الخطية في النموذج بقليل زائد وقليل نقص على النواحي الفيزيائية. تم قياس معدل الامتصاص البصرية الخطية في المحاليل المختلطة باستخدام تقنيات UV / VIS. تم تكذيب النتائج السابقة باستخدام تقنيات الامتصاص البصرية خطية، من خلال قياس معدل الامتصاص البصرية البصرية الخطية في النموذج بقليل زائد وقليل نقص على النواحي الفيزيائية. تم قياس معدل الامتصاص البصرية خطية في المحاليل المختلطة باستخدام تقنيات UV / VIS. تم تكذيب النتائج السابقة باستخدام تقنيات الامتصاص البصرية خطية، من خلال قياس معدل الامتصاص البصرية البصرية الخطية في النموذج بقليل زائد وقليل نقص على النواحي الفيزيائية.

الكلمات المفتاحية: سبعة أثنتوسينات مختلطة، معدل الانكسار البصرية خطية، الانكسار البصرية اللاخطية، الامتصاص البصري، طريقة المحم