

UNIVERSITY OF BAHRAIN

College of Science

Department of Physics



Investigation of Nonlinear Optical Properties of Natural Dye Extracted from Fruits Using Z-scan Technique

A Thesis Submitted in Partial Fulfilment of the Requirements of the
Master Degree in Applied Physics

Submitted by

RAJA EBRAHIM AL-ASFOOR

20002250

Supervised by

Dr. Khalil Ebrahim Jasim

Assistant Professor

University of Bahrain

Kingdom of Bahrain

May, 2018

DEFENSE COMMITTEE'S APPROVAL PAGE



University of Bahrain

College of Science

Department of Physics

MSc in Applied Physics

Student **Raja Ebrahim Al-Asfoor** ID number **20002250** defended her thesis by which she fulfilled the requirement for the degree of M.Sc. in Applied Physics: Investigation of nonlinear optical properties natural dye extracted from fruits using z-scan technique on this day of (20 /6/2018).

The committee recommends awarding of M.Sc. Degree in Applied Physics with the grade of: -----

(Defense Committee)

Name		Signature
_____	Supervisor	_____
_____	External examiner	_____
_____	Internal examiner	_____

Academic department's stamp

ABSTRACT

Nonlinear materials have attracted considerable attention of many researchers; as they explore their linear and nonlinear optical properties attempting to develop photonic devices. Such materials must encompass a high nonlinearity, low absorption, fast response time, large dynamic range and broadband spectral response. To accomplish the same scientific achievement, this study focused on investigating some linear and nonlinear optical properties of specific types of natural dyes extracted from some fruits at prepared at different conditions. This project aims to develop nonlinear optical properties archive of the investigated dye extracts that are available in the Kingdom of Bahrain.

In this study, 52 samples of dye extracts from assortment of fruits were extracted such as orange, pomegranate, blueberry, cranberry, cherry, black raisin, tropical almond, avocado, prune, strawberry, mangosteen and apricot. These samples were arranged in five groups. Most of the samples were prepared at three different concentrations. pH level has been changed for some samples at specific concentration by addition of specific volume of HCl in order to realize the effect of such factor. Samples absorbance was measured in order to quantify the spectral linear absorption coefficient ($\alpha(\lambda)$) and to gain insight on absorption behaviour at range of wavelength from 400-1000 nm. Fluorescence spectra are recorded. Also, the linear refractive index was measured using the Refractometer. Under different excitation power level and three different wavelength (i.e., 488 nm, 514 nm and 633 nm) nonlinear refractive index (n_2) sign and value, nonlinear absorption coefficient, third-order nonlinear optical susceptibility $\chi^{(3)}$ were quantified after fitting raw data obtained using single beam Z-scan technique. The investigated samples show

potential capability of them to be used as optical limiters as well as all optical switching devices.

DEDICATION

To

My father and mother

To

My Husband Mohamed

To

My friends

Raja

2018

ACKNOWLEDGEMENT

I would like to express my sincere gratitude and appreciations to my supervisor Dr. Khalil Ebrahim Jasim who gave me the opportunity to join his research activities in nonlinear optics. His supported, guidance and continuous encouragements during this project is highly recognized. Working under his supervision was really a prolific and enjoyable experience.

My appreciations are extended to Department of Physics faculty at the University of Bahrain for giving me the opportunity to achieve my MSc. studies and facilitating lab work.

The continuous encouragements and support I have received from my family were valuable in and helped me a lot in overcome many frustrating situations during my graduate study, hence they deserve from me endless appreciations and thank you so much.

LIST OF CONTENTS

DEFENSE COMMITTEE’S APPROVAL PAGE	A
DEDICATION	D
ACKNOWLEDGEMENT	E
ABBREVIATIONS	N
CHAPTER 1: INTRODUCTION	2
1.1 INTRODUCTION	2
1.2 RESEARCH PROBLEM.....	3
1.3 RESEARCH QUESTIONS	3
1.4 RESEARCH OBJECTIVES.....	4
1.5 RESEARCH SIGNIFICANCE	4
1.6 RESEARCH SETTING	6
1.7 DEFINITIONS	6
CHAPTER 2 :BACKGROUND AND HISTORY	9
2.1 DESCRIPTION OF DYES	9
2.1.1 <i>Introduction to dyes</i>	9
2.1.2 <i>Natural distribution and chemical structure</i>	10
2.1.3 <i>Extraction of natural dyes</i>	16
2.2 NONLINEAR OPTICAL MATERIALS (NLO).....	17
2.3 OPTICAL LIMITING	19
2.4 BASIC CONCEPTS OF NONLINEAR OPTICS.....	22
2.4.1 <i>Kerr effect</i>	22
2.4.2 <i>Two photon absorptions</i>	23
2.4.3 <i>Intensity dependent refractive index</i>	23
2.5 Z-SCAN TECHNIQUE PRINCIPLE	26
2.5.1 <i>Close aperture z-scan technique</i>	27
2.5.2 <i>Open aperture Z-scan</i>	29
2.5.3 <i>Advantages and disadvantages of Z-scan technique</i>	31
2.5.4 <i>Theoretical analysis</i>	32
2.6 THIRD ORDER NONLINEAR PROCESSES	37
2.6.1 <i>Self-phase modulation</i>	37
2.6.2 <i>Self-focusing and self-defocusing effects</i>	38
2.7 APPLICATION OF NONLINEAR OPTICS.....	39
2.8 NONLINEAR OPTICS RESEARCH THE UNIVERSITY OF BAHRAIN	40
CHAPTER 3: METHODOLOGY	42
3.1 MATERIALS AND EQUIPMENT	42
3.2 NATURAL DYES EXTRACTION	45
3.2.1 <i>Peels</i>	45

3.2.2	<i>Pomegranate grains</i>	47
3.2.3	<i>Dry fruits</i>	48
3.3	LINEAR OPTICAL PROPERTIES	50
3.3.1	<i>Absorbance and absorption coefficient of dye extracts</i>	50
3.3.2	<i>Fluorescence of dye extracts</i>	52
3.3.3	<i>Linear index of refraction measurement</i>	52
3.4	CONSTRUCTING Z-SCAN EXPERIMENTAL SETUP.....	53
3.5	CALCULATING NONLINEAR OPTICAL PARAMETERS	54
CHAPTER 4:	RESULTS, DISSCUTION AND RECOMMENDATIONS.....	58
4.1	GROUP 1: BERRY	58
4.1.1	<i>Linear Absorption Spectroscopy</i>	58
4.1.2	<i>Fluorescence Spectroscopy</i>	64
4.1.3	<i>Nonlinear Index of Refraction</i>	69
4.1.4	<i>Nonlinear Absorption Coefficient</i>	79
4.2	GROUP 2: CITRUS	91
4.2.1	<i>Linear Absorption Spectroscopy</i>	91
4.2.2	<i>Fluorescence Spectroscopy</i>	92
4.2.3	<i>Nonlinear Index of Refraction</i>	94
4.2.4	<i>Nonlinear Absorption Coefficient</i>	97
4.3	GROUP 3: POMEGRANATE.....	99
4.3.1	<i>Linear Absorption Spectroscopy</i>	99
4.3.2	<i>Fluorescence Spectroscopy</i>	103
4.3.3	<i>Nonlinear Absorption Coefficient</i>	112
4.4	GROUP 4: PRUNES	116
4.4.1	<i>Linear Absorption Spectroscopy</i>	116
4.4.2	<i>Fluorescence Spectroscopy</i>	120
4.4.3	<i>Nonlinear Index of Refraction</i>	123
4.4.4	<i>Nonlinear Absorption Coefficient</i>	127
4.5	GROUP 5: TROPICAL	131
4.5.1	<i>Linear Absorption Spectroscopy</i>	131
4.5.2	<i>Fluorescence Spectroscopy</i>	134
4.5.3	<i>Nonlinear Index of Refraction</i>	138
4.1.2	<i>Nonlinear Absorption Coefficient</i>	142
4.3	SUMMARY OF RESULTS ANALYSIS	148
4.4	STUDY RECOMMENDATIONS.....	156
REFERENCES.....		158

LIST OF FIGURES

Figure (1): Structure of β -carotene (Phar macognosy, 2012).	11
Figure (2): Structure of Xanthophyll (Phar macognosy,2012).	12
Figure (3): Structure of Lutein (Schaffer,2008).	12
Figure (4): Structure of the two most common chlorophylls (Wageningen University, 2017).	13
Figure (5): The flavylum ion, the basic structure of anthocyanins (Wageningen University, 2017) ..	14
Figure (6): Cyanidin3-Glycoside (Delgado-Vargas, Jiménez & Paredes-López, 2000).....	15
Figure (7): General structures of the main betalain (a) betaxanthin (b) betacyanin (Isah et al., 2014).	16
Figure (8): Nonlinear refractive index of curcumin in acetonitrile as a function of incident intensity (Henari, et al., 2013).	20
Figure (9): Optical response of an optical limiter to incident power.	21
Figure (10): Schematic illustration of two-photon absorption process.	23
Figure (11): Schematics of experimental setup used for the close aperture Z-scan.	27
Figure (12): Close aperture z-scan normalized transmittance curve (From Bahae, M. S. et al., 2007).	28
Figure (13): Close aperture Z-scan for DMPM4NBCHM in DMF at 488 nm for 10 mW incident power (from Henari et al 2013).	29
Figure (14): Open aperture Z-scan normalized transmittance curve (form Bahae, M. S. et al., 2007).	30
Figure (15): Immersion method used to extract dyes.	45
Figure (16): Almond sample (a) immersing, (b) filtration, (c) almond extracted	46
Figure (17): Mandarin peel in methanol (a) dry peel, (b) grated peel, (c) immersing, (d) filtration. ...	46
Figure (18): Pomegranate grains fresh and dried.	47
Figure (19): Pomegranate grains (a) immersing, (b) filtration, (c) pomegranate grains extracted dye in methanol.	47
Figure (20): Dry cranberry dye extract in methanol.....	48
Figure (21): Prune extract in methanol (a) immersing, (b) filtrate sample.	48
Figure (22): Image of (Shimadzu, model UV-3101), and schematic representation of the spectrophotometer.	51
Figure (23): Schematic of the setup used in florescence measurements.	52
Figure (24): Digital Refractometer.	53
Figure (25): Z-scan transmittance versus time graph.	53
Figure (26): Normalized and fitted z-scan transmittance curve.	55
Figure (27): Linear absorption of blueberry extracted in ethanol at different concentrations.	59
Figure28 a) Linear absorption spectra of raisin and b) Linear absorption spectra of cranberry extracted in methanol at two different concentrations.	60
Figure (29): Linear absorption spectra of strawberry extracted in methanol at two different concentrations.	61
Figure (30): Linear absorption spectra of blueberry extracted in ethanol with 1% HCl acid, ethanol methanol and acetone at specific concentration of 0.1 g/ml.	62
Figure (31): Linear absorption spectra of berry extracted in methanol at a) 0.1 g/ml concentration, and b) 0.6 g/ml concentration.	63
Figure (32): Fluorescence spectra of blueberry extracted in ethanol at three different concentrations.	64
Figure (33): Fluorescence and absorption spectra of extract of concentration 0.3 g/ml from blueberry extracted in ethanol.	65
Figure (34): Fluorescence spectra of strawberry extracted in methanol at two different concentration.	66
Figure (35): Fluorescence spectra of raisin extracted in methanol at two different concentrations.	66

Figure (36): Fluorescence spectra of cranberry extracted in methanol at two different concentrations.	67
Figure (37): Fluorescence and absorbance of blueberry in Methanol and Acid.	68
Figure (38): Fluorescence spectra of blueberry at concentration of 0.1 g/ml in three different solvent.	68
Figure (39): Fluorescence spectra of different extracts in methanol with concentration of 0.1 g/ml.	69
Figure (40): Variation of n_2 as function of excitation power ($\lambda = 514$ nm)	70
Figure (41): Normalized transmittance curve, dots are the data while solid line is the fit.	71
Figure (42): Plot of n_2 versus concentration for barriers extracts.	73
Figure 43: Variation of n_2 with concentration extracted in ethanol excited at 514 nm ($P = 6$ mW). ...	76
Figure (44): Fitted z-scan transmittance curves for strawberry sample (0.3 g/ml) when z-scanned with beam of wavelengths 488 nm, 514 nm, and 633 nm and excitation power of 6 mW.	78
Figure (45): Images of laser spot size as the sample scanned with beam of wavelength 514 nm and power 6 mW.	79
Figure (46): Variation of β as function of excitation power ($\lambda = 514$ nm) with sample extracted in methanol at concentration of 0.3g/ml.	80
Figure (47) : Fitted z-scan transmission curves to determine both the sign and magnitude of β	81
Figure (48): variation of $\chi(3)$ with excitation power for blueberry extracted in ethanol at concentration 0.1 g/ml.	84
Figure (49): Variation of n_2 and β as function of power with and without addition of HCl acid to extraction solvent.	90
Figure (50): Absorption spectrum of mandarin at 0.3 g/ml concentration extracted in methanol and 1% HCl acid.	91
Figure (51): Linear absorption spectra of citrus samples extracted in methanol.	92
Figure (52): Fluorescence spectra of mandarin extracted in methanol at concentration of 0.3 g/ml.	93
Figure (53): Fluorescence spectra of citrus extracted in methanol.	94
Figure (54): Variation of n_2 values as function of excitation power level ($\lambda = 514$ nm) for citrus.	95
Figure (55): Variation of β as function of excitation power level ($\lambda = 514$ nm) at fixed concentration.	97
Figure (56): Linear absorption spectra of Indian pomegranate extracted in methanol at different concentrations for a) peels, and b) grains.	100
Figure (57): Linear absorption spectra in different solvent of a) Indian pomegranate grains at 0.6 g/ml b) Egyptian pomegranate peels at 0.1 g/ml c) Yamani pomegranate peels at 0.1 g/ml d) Spanish pomegranate peels at 0.1 g/ml.	101
Figure (58): Linear absorption spectra at concentration of 0.1 g/ml for a) pomegranate peels in ethanol b) pomegranate peels and grains in methanol.	102
Figure (59): Fluorescence spectra of a) Indian pomegranate grains b) Indian pomegranate peels in methanol at different concentrations.	103
Figure (60): Fluorescence spectra of a) Indian pomegranate grains extracted in methanol at specific concentrations 0.6 g/ml. b) Spanish pomegranate peels c) Egyptian pomegranate peels d) Yemeni pomegranate peels extracted in methanol at specific concentrations 0.1 g/ml.	104
Figure (61): Fluorescence spectra at specific concentration of 0.1 g/ml of a) pomegranate peels extracts in ethanol, b) pomegranate peels extracts and grains in methanol.	105
Figure (62): Variation of n_2 as function of excitation power level ($\lambda = 514$ nm) for Indian pomegranate a) grains extracted in methanol with acid b) grains and peels extracted in methanol only.	106
Figure (63): Variation of n_2 as function of concentration ($\lambda = 514$ nm, 6 mW) for Indian pomegranate extracts.	110
Figure (64): Variation of β as function of excitation power ($\lambda = 514$ nm) for Indian pomegranate grains extract at concentration of 0.6 g/ml.	113

Figure (65): Variation of β as function of concentration ($\lambda = 514$ nm) for Indian pomegranate grains and peels extracts.	115
Figure (66): Linear absorption spectra of prune extracted in methanol at two different concentrations.	117
Figure (67): Linear absorption spectra of almond extracted in methanol with 1% HCl acid, ethanol, methanol, and acetone.	118
Figure (68): Linear absorption spectra of prunes extracted a) in methanol at concentration of 0.1 g/ml b) in methanol with acid at concentration of 0.6 g/ml of concentration c) in methanol at concentration of 0.6 g/ml.	119
Figure (69): Fluorescence spectra of prune extracted using methanol at two different concentrations.	120
Figure (70): Fluorescence spectra of almond at concentration of 0.1 g/ml extracted with different solvents.	121
Figure (71): Fluorescence spectra of different prunes extracts a) at 0.1 g/ml concentration using methanol as solvent, b) at 0.6 g/ml concentration using methanol with acid as extracting solvent, and c) at 0.6 g/ml concentration using only methanol as extracting solvent.	122
Figure (72): Variation of n_2 as function of excitation power ($\lambda = 514$ nm) for prunes a) at 0.6 g/ml concentration extracted in methanol, b) almond and cheery, and c) Almond with concentration of 0.1 g/ml.	123
Figure (73): Variation of β as function of concentration ($\lambda = 514$ nm, $P = 6$ mW) for prune extract.	124
Figure (74): Variation of n_2 as function of excitation power ($\lambda = 514$ nm) for: a) Prune at different concentrations b) Apricot, cherry and almond and c) Almond at 0.1 g/ml concentration using different solvents.	127
Figure (75): Variation of β as function of concentration ($\lambda = 514$ nm, $P = 6$ mW) for prune.	128
Figure (76): Linear absorption spectra for a) avocado peels extracted in methanol at different concentrations b) mangosteen peels extracted in methanol. at different concentrations c) Avocado seeds d) Kiwi extracted in methanol at different concentrations.	132
Figure (77): Linear absorption spectra for a) kiwi b) mangosteen with concentration of 0.6 g/ml extracted in different solvent.	133
Figure (78): Linear absorption spectra for different materials at a) 0.1 g/ml concentrations extracted in methanol b) 0.6 g/ml concentration extracted in methanol with 1% HCl at different concentrations.	134
Figure (79): Fluorescence spectra at excitation wavelength 514 nm of a) Avocado seeds extract b) Avocado peels extract c) Mangosteen extract d) Kiwi extract at different concentrations in methanol.	135
Figure (80): Fluorescence spectra of a) kiwi b) mangosteen at 0.6 g/ml concentration c) Fluorescence and absorbance of avocado peels extracted in methanol with 1% HCl at 0.6 g/ml concentration.	136
Figure (81): Fluorescence spectra of tropical group extracted with a) Methanol b) Methanol with 1% HCl.	137
Figure (82): Variation of n_2 as function of excitation power level ($\lambda = 514$ nm) at 0.1 g/ml concentration for a) mangosteen b) avocado seeds c) avocado peels d) kiwi extracts.	138
Figure (83): Variation of n_2 as function of concentration ($\lambda = 514$ nm) for tropical group.	139
Figure (84): Variation of β as function of excitation power level ($\lambda = 514$ nm).	143
Figure (85): Variation of β as function of concentrations ($\lambda = 514$ nm) for tropical.	144

LIST OF Tables

Table (1): Natural extracted dye materials.	42
Table (2): List the solvents used in the extraction of dye samples.	44
Table (3): List the instruments and systems used in the study	44
Table (4): Extracted dyes from berry group.	49
Table (5): Extracted dyes from tropical group.	49
Table (6): Extracted dyes from prunus group.	49
Table (7): Extracted dyes from pomegranate group.	50
Table (8): Extracted dyes from citrus group.....	50
Table (9): Nonlinear parameters for berries with concentration of 0.1g/ml extracted in methanol and scanned using Ar ion laser at 514 nm for closed aperture configuration.....	71
Table (10): Nonlinear parameters for berries with concentration of 0.6 g/ml extracted in methanol and scanned using Ar ion laser at 514 nm for closed aperture configuration.....	72
Table (11): Calculated nonlinear parameters for berries at concentration of 0.1 g/ml extracted in methanol and scanned by Ar ion laser ($\lambda = 488$ nm and 514 nm) and HeNe laser ($\lambda = 633$ nm). P = 6 mW for closed aperture configuration.	74
Table (12): Nonlinear parameters for blueberry at 0.1 concentration in ethanol with acid scanned using Ar laser at (514 – 488) nm and HeNe laser.....	74
Table (13): Nonlinear parameters for berry extract at 0.6 g/ml concentration in methanol scanned using Ar laser at (514 – 488) nm and HeNe laser.....	75
Table (14): Nonlinear parameters blueberry in ethanol at different concentration by using Ar laser at (514 – 488) nm and HeNe laser.....	76
Table (15): Nonlinear parameters strawberry extracted in methanol at concentration 0.3 g/ml (P = 6mW) for closed aperture configuration.	77
Table (16): Nonlinear parameters for berries extracted in methanol at concentration of 0.1 g/ml and scanned by Ar ion laser at 514 nm at different power for closed aperture configuration.	82
Table (17): Nonlinear parameters for berries extracted in methanol at concentration of 0.6 g/ml and excited by Ar laser at 514 nm at different power for closed aperture.....	83
Table (18): Nonlinear parameters for berries at 0.1 g/ml concentration and scanned using Ar ion laser at 514 nm for closed aperture configuration.	85
Table (19): Nonlinear parameters for blueberry in ethanol at different Concentrations of dye scanned using Ar laser at 514 nm for closed aperture configurations.	86
Table (20): Nonlinear parameters for berries at 0.6 g/ml concentrations extracted in methanol and scanned using Ar laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.....	87
Table (21): Nonlinear parameters for berries at 0.1 g/ml concentration extraced in methanol and scanned using Ar laser at (514 – 488) nm for closed aperture configuration.....	88
Table (22): Nonlinear parameters for blueberry at different concentrations of dye in ethanol by using Ar laser at (514 – 488) nm for closed aperture configuration.	88
Table (23): Nonlinear parameters for blueberry at 0.1 g/ml concentrations extracted in methanol with acid and scanned using Ar ion laser at (514 – 488) nm for closed aperture configuration.	89
Table (24): Nonlinear parameters for Strawberry at 0.3 g/ml Concentrations of dye in methanol by using Ar laser at (514 – 488) nm for closed aperture.	89
Table (25): Nonlinear parameters for mandarin	96
Table (26): Nonlinear parameters for citrus at different concentrations and scanned using Ar ion laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.....	96
Table (27): Nonlinear parameters for mandarin peels.....	98
Table (28): Nonlinear parameters for citrus extracted in methanol.....	99

Table (29): Nonlinear parameters for pomegranate extracted in methanol with concentration of 0.1 g/ml for peel and 0.6 g/ml for grains scanned using Ar ion laser at 514 nm for closed aperture configuration.....	107
Table (30): Nonlinear parameters for pomegranate extracted in acetone with concentration of 0.1g/ml and scanned using Ar ion laser at 514 nm for closed aperture configuration.....	108
Table (31): Nonlinear parameters for pomegranate extracted in ethanol with concentration of 0.1g/ml and scanned using Ar ion laser at 514 nm for closed aperture.....	109
Table (32): Nonlinear parameters for Indian pomegranate at different concentrations in methanol and scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) at for closed aperture configuration.	111
Table (33): Nonlinear parameters for pomegranate at 0.1 g/ml concentration and scanned using Ar ion laser at (514 – 488 nm, P = 6mW) for closed aperture configuration.	111
Table (34): Nonlinear parameters for pomegranate extracted in acetone with concentration of 0.1 g/ml for scanned using Ar ion laser at 514 nm for closed aperture configuration.	113
Table (35): Nonlinear parameters for pomegranate extracted in ethanol with concentration of 0.1 g/ml and scanned using Ar ion laser at 514 nm for closed aperture configuration.	114
Table (36): Nonlinear parameters for Indian pomegranate at different concentration extracted in methanol and scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.	115
Table (37): Nonlinear parameters for pomegranate at 0.1 g/ml concentration extracted in methanol and scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6 mW) at for closed aperture configuration.	116
Table (38): Nonlinear parameters for Almond at 0.1 g/ml concentration scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.	125
Table (39): Nonlinear parameters for apricot at 0.6 g/ml concentration scanned using Ar ion laser at (514 – 488) nm (P = 6mW) for closed aperture configuration.	125
Table (40): Nonlinear parameters for brown apricot at 0.6 g/ml concentration extracted in methanol scanned using Ar ion laser at (514 and 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.....	126
Table (41): Nonlinear parameters for prune at different concentration scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.	126
Table (42): n ₂ for cherry extracts at 0.6 g/ml concentration in methanol scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.	127
Table (43): Nonlinear parameters for almond at different solvent scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) at for closed aperture configuration.	129
Table (44): Nonlinear parameters for apricot at 0.6 g/ml concentration extracted using different solvent and scanned using Ar ion laser at (514 – 488) nm (P = 6mW) for closed aperture configuration.....	129
Table (45): Nonlinear parameters for brown apricot at 0.6 g/ml concentration extracted in methanol and scanned using Ar laser at (514 – 488) nm and HeNe laser (P = 6mW) at for closed aperture configuration.	130
Table (46): Nonlinear parameters for prune extracted with different solvents and concentrations scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) at for closed aperture configuration.....	130
Table (47): Nonlinear parameters for cherry at 0.6 g/ml extracted in methanol scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) at for closed aperture configuration.	131
Table (48): Nonlinear parameters for avocado peels extract at different concentrations and scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) at for closed aperture configuration.....	140
Table (49): Nonlinear parameters for avocado seeds extracts at different concentrations scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.....	141

Table (50): Nonlinear parameters for avocado seeds peels at 0.1 g/ml concentrations scanned using Ar ion laser at (514 – 488) nm (P = 6mW) for closed aperture configuration.....	141
Table (51): Nonlinear parameters for kiwi extracted at different concentrations scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.	141
Table (52): Nonlinear parameters for mangosteen at different concentrations scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.	142
Table (53): Nonlinear parameters for avocado peels at different concentrations and scanned using Ar ion laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.	145
Table (54): Nonlinear parameters for avocado seed at different concentrations in methanol scanned using Ar ion laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.....	146
Table (55): Nonlinear parameters for kiwi at different concentrations and solvent scanned using Ar ion laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.....	146
Table (56): Nonlinear parameters for avocado seed peel at different concentrations in methanol scanned using Ar ion laser at (514 – 488) nm for closed aperture configuration.....	147
Table (57): Nonlinear parameters for mangosteen peels extracted at different concentrations and solvent scanned using Ar ion laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.	147

ABBREVIATIONS

EM	Electromagnetic waves
UV-VIS	ultraviolet and visible range of EM
CA	Close aperture
OA	Open aperture
NLO	None linear optics
OP	Optical limiting
E	Peak electric field
c	Speed of light in vacuum
I	Irradiance (intensity)
n₀	Linear refractive index
n₂	Nonlinear index of refraction
β	Nonlinear absorption coefficient
χ⁽³⁾	Third order susceptibility
SA	Saturable absorption
TPA	Two photon absorptions
RSA	Reverse saturable absorption
ESA	Excited state absorption
w(z)	Radius of beam at distance z
w₀	Radius of beam at distance z = 0
R(z)	Wave front radius of curvature
z₀	diffraction length of the beam (Rayleigh length)
Δφ(r)	Radial phase variations
SVEA	Slowly varying envelope approximation
φ_o(t)	On-axis phase shift at the focus
GD	Gaussian Decomposition method
L_{eff}	Effective length of the sample
α₀	Linear absorption coefficient
T(z)	Normalized Z-scan transmittance
Δφ_o	On-axis phase shift due to nonlinear refraction
ΔΨ_o	On-axis phase shift due to nonlinear absorption
SPM	Self-phase modulation

CHAPTER 1: INTRODUCTION

- 1.1 Introduction**
- 1.2 Research Problem**
- 1.3 Research Questions**
- 1.4 Research Objectives**
- 1.5 Research Significance**
- 1.6 Research Setting**
- 1.7 Definitions**

CHAPTER 1: INTRODUCTION

1.1 Introduction

Nonlinear optics is the science concerned on the behavior of light in the nonlinear media, and the light-matter interaction when the matter have nonlinear properties. The origin of the field of nonlinear optics is often traced back to J. Kerr observation of the change in the refractive index of organic liquids and glass in the presence of an electric field. He observed that the transmitted intensity is quadratic function of the applied voltage. This phenomenon is known as the Kerr effect phenomena. With the appearance of laser in 1960, the applied voltage was replaced with the laser because it is coherent, monochromatic and high intensity Gaussian light beam. This latter phenomenon was then called the optical Kerr effect or sometimes the intensity dependent refractive index as the intensity is proportional to the square of the electric field.

In 1931, Maria Goeppert Meyer predicted the Two Photon Absorption (TPA) which occurs when two photons are absorbed in the same time. It is a nonlinear process where the main case of the nonlinear absorption and the intensity is proportional with absorption coefficient. The first nonlinear-optical phenomena whose discovery relied on the invention of the laser was Second Harmonic Generation (SHG) in 1961 by P. A. Franken and co-workers where they focused a pulsed ruby laser into a quartz crystal and showed that light at twice the laser frequency was generated.

There is a set of scientific methods and techniques that scientists have devised to determine nonlinear optical response, each of which has its advantages and disadvantages. One of them which is a simple, well

established, and quite accurate technique named Z-scan technique which is widely employed and trusted (by majority of nonlinear optics scholars) in measuring both nonlinear absorption coefficient and index of refraction and hence quantifying third order susceptibility $\chi(3)$ (Rashidian, et al., 2008; Balaji et al., 2011; Dhinaa and Pallnisamy, 2010).

1.2 Research Problem

Advent of laser in 1960s has motivated lots of research activities that investigate the nonlinear optical properties (Sharan et al., 2002; Neethling, 2005), optical limiting behavior of materials (Balaji et al., 2011; Henari and Jasim, 2012; Rekha and Ramalingam, 2009), and all optical photonic switches (Balaji et al., 2011; Henari and Jasim, 2012; Rashidian et al., 2008). However, the high intensity of laser beam has a negative effect that results in irreversible damage of optical sensors such as human eye, night vision equipment, and range finders. Thus, many researchers are looking for materials possessing self-action behavior where transmitted beam intensity decreases as the incident light intensity increases. Such materials must have a high nonlinearity, low absorption, fast response time, large dynamic range and broadband spectral response (Ganeev et al., 2003; Henari and Mohamed, 2007).

1.3 Research Questions

Our study discusses the following questions:

1. Does natural dye extracts from some fruits have nonlinear optical activity?
2. What is the origin of nonlinearity in natural dye extracted from fruits?

3. Are there variations in values and signs of nonlinear refractive indices and nonlinear absorption coefficients when varying concentration, solvent, excitation wavelength, excitation power level?
4. Can natural dye extract from some fruits be used as optical limiting or optical switching devices?

1.4 Research objectives

The main aims of this study are:

1. Exploring linear optical spectroscopy of extracted dyes from some fruits.
2. Investigating the nonlinear optical properties of natural dye extracted from fruits, using Z-scan technique.
3. Determining the third-order nonlinearity, $\chi^{(3)}$ of natural dye extracted from fruits.
4. Calculating the nonlinear absorption coefficient and nonlinear refractive index of natural dye extracted from fruits.
5. Studying the effect of intensity of input laser beam on the nonlinear susceptibility.
6. Investigating the optical limiting capability of natural dye extracted from fruits.

1.5 Research significance

Due to the widespread use of laser in various applications, many researchers have studied the optical limiting behaviour of materials to protect human eyes and sensitive optical sensors from intense laser beams. Other potential applications of optical limiting may also include laser power regulation or stabilization, or restoration of signal levels in optical data transmission or logic systems (Al-Saidi & Abdulkareem,

2015; Chi, 2009). The use of continuous wave and pulsed coherent sources of light (Lasers) for imaging and probing of optical properties of solid and liquid media led to intensive research activities towards the development of safe, non-invasive, and inexpensive diagnostic tool.

Natural dye extracts from fruits have attracted considerable attention and many researchers have investigated their optical and nonlinear optical properties because they are non-hazard, abundant, low cost and easily extractable (Nesterov, Kuleshova & Antipin, 2001; Liu, Yang, Wang & Cao, 2016). Also, they are possessing unique nonlinear optical characteristics promoting their use in many applications such as enhanced Fourier transformed image processing, optical signal limiting, and nonlinear microscopy. Self-action phenomena such as self-focusing, self-defocusing, and phase modulation are effective nonlinear actions that are essential in fabrication of photonic devices that protect living tissues from radiation stress or damages. (Henari, et al., 2013).

In order to be a part of this scientific community, the project focus will be on investigating some linear and nonlinear optical properties of many kinds of extracted natural dyes from fruits at different preparation conditions. In addition, the well-known single-beam z-scan technique which can accurately measure the magnitudes of both nonlinear absorption and the nonlinear refractive index coefficients will be used.

The project aims to start development of archive of potential nonlinear optical materials available in the Kingdom of Bahrain. In fact, to develop a nonlinear optical device from a given medium; one must first test and quantify its capability to act as nonlinear medium, then comes the choice of the proper approach to design it as a device and finally as commercial product.

1.6 Research setting

This research studies the investigation of nonlinear optical properties of natural dye extracted from fruits at different concentrations and solvents using Z-scan technique. Fruits used in this project were orange, pomegranate, blueberry, cranberry, cherry, black raisin, tropical almond, avocado, prune, and apricot. Both absorbance and photoluminescence spectroscopy were carried out in order to characterize optical absorbance and fluorescence of the extracted natural dyes from fruits. In addition, linear index of refraction was measured, and linear absorption coefficient was calculated from absorbance data. All nonlinear optical results in this project were obtained using single beam Z-scan technique under different excitation wavelengths with diverse beam power level. Investigation of the value and sign for both the nonlinear index of refraction and absorption coefficient were carried out. Also, realizing the effect of input laser beam irradiance on the nonlinear susceptibility ($\chi^{(3)}$). Optical limiting capability of natural dye extracted from fruits is also studied.

1.7 Definitions

- **Nonlinear optics:** branch of optics that describes the behaviour of light in nonlinear media, that is, media in which the dielectric polarization P responds nonlinearly to the electric field E of the light.
- **Z-scan:** is a simple and effective tool for determining the nonlinear properties of various kinds of materials.
- **Gaussian laser beam:** light beams where the electric field profile in a plane perpendicular to the beam axis can be described with a Gaussian function, possibly with an added parabolic phase profile.

- **Nonlinear index of refraction:** a parameter for quantifying the Kerr nonlinearity of a medium or thermal nonlinearity.
- **Nonlinear absorption coefficient:** a parameter to describe the second order polarizability, two-photon absorption, two-photon cross-section, reverse saturable absorption (RSA) and saturable absorption (SA).
- **Third order susceptibility $\chi^{(3)}$:** is a complex number which describes the third harmonic generation and how light propagates in a nonlinear medium.
- **Two-photon Absorption:** a nonlinear absorption process where two photons are simultaneously absorbed.
- **Self-focusing and Self-defocusing:** are nonlinear optical processes induced by the change in refractive index of materials exposed to intense electromagnetic radiation.
- **Optical limiters:** are devices designed to have high transmittance for low level inputs while blocking the transmittance for high intensity laser beams.
- **Dye:** is a colouring compound that has an affinity to the substrate to which it is being applied

CHAPTER 2 :BACKGROUND AND HISTORY

2.1 Description of Dyes

2.1.1 Introduction to dyes

2.1.2 Natural distribution and chemical structure

2.1.2.1 Carotenoids

2.1.2.2 Chlorophyll

2.1.2.3 Flavonoid

2.1.2.4 Betalains

2.1.3 Extraction of natural dyes

2.2 Nonlinear Optical Materials (NLO)

2.3 Optical Limiting

2.4 Basic Concepts of Nonlinear Optics

2.4.1 Kerr effect

2.4.2 Two photon absorptions

2.4.3 Intensity dependent refractive index

2.5 Z-scan Technique Principle

2.5.1 Close aperture Z-scan

2.5.2 Open aperture Z-scan

2.5.3 Advantages and disadvantages of Z-scan technique

2.5.4 Theoretical analysis

2.6 Third Order Nonlinear Processes

2.6.1 Self-phase modulation

2.6.2 Self-focusing and self-defocusing

2.7 Application of Nonlinear Optics

2.8 Nonlinear Optics Research Activities at the University of Bahrain

CHAPTER 2 :BACKGROUND AND HISTORY

2.1 Description of Dyes

2.1.1 Introduction to dyes

Dyes are organic compounds that are capable of absorbing electromagnetic waves (EM) with wavelengths in the range of ultraviolet and visible (UV-VIS) range (Trakoli, 2012). The exact chemical structure of a dye molecule (chromophore) defines the colour of the dye sample when it absorbs visible light (Pramodini, 2015). Unlike other organic compounds, dyes have colour due to the chromogen. It is a chemical compound that consists of chromophore and colour helpers (auxochromes) (Carmen & Daniela, 2012). At least one chromophore absorbs the visible range of the EM spectrum. (Abrahart, 1982). On the other hand, the auxochromes are a group of atoms attached to a chromophore. Even though, auxochromes are not responsible for colour, they intensify colour of the dye by acting as electron donating groups (Abrahart, 1982).

Dye is a colour that owns both physical and chemical properties such as refraction, absorption and scattering of light. Dyes are either natural or industrial. It is well known that plants and many living organisms such as fungi and microorganisms generate natural dyes (Gürses, Açıkyıldız, Güneş & Gürses, 2016). William Hinry has invented the industrial pigments in 1856, which have been used in food colouring, cosmetics, and textile industries (Carmen & Daniela, 2012). The industrial dyes are essential because of their easy dyeing, overall cost effective factor, new colours with wide gradients and better characteristics. However, in the last few decades their use has gradually

decreased; mainly due to the environmental awareness of their harmful effects because of their toxicity or non-degradable nature. USA and India prohibited the use of some industrial dyes because of some other problems like serious health risks and problems in safe disposal methods, (Bhute & Prabhu, 2012).

Since natural dyes are eco-friendly and they are nonhazardous upon contacting human body and can be extracted from many biological sources, they have played a very important role in the food and textiles industries. Nevertheless, natural dyes have some limitations for example colour stability and dying procedure (Trakoli, 2012; Gürses, Açıkyıldız, Güneş & Gürses, 2016). The main disadvantage of natural dyes is the challenges faced during the extraction process which include the preservation problems, seasonality of plants that affect the availability of colour yields and its wobbly nature (Bhute & Prabhu, 2012). Recently, many studies of the optical properties of natural dyes and thier use in the advanced technologies are being carried out around the world in order to achieve new applications besides textiles and food industries (Gürses, Açıkyıldız, Güneş & Gürses, 2016; Pramodini, 2015).

2.1.2 Natural distribution and chemical structure

Natural dyes can be classified according to their chemical Structure (functional groups) into four major groups: Carotenoids, Chlorophylls, Flavonoid, and Betalains.

2.1.2.1 Carotenoids

Carotenoids are the main group of tetraterponoids which are responsible for the yellow, orange and red colour of many flowers,

vegetables, roots and fruits such orange (Zongo, 2012; Alkema & Seager, 1982). There are two main groups of carotenoids that are different in molecular functional group and composition, the first group is the carotenes that are constituted by carbon and hydrogen and are found in yellow and orange fruits and vegetables such as pumpkin, sweet potatoes, and apricots. One of the most familiar carotenes are beta-carotene (β -carotene) (see Figure (1)) and lycopene dye from which tomatoes, grapefruits and watermelon acquire their red and pink colour (Alkema & Seager, 1982; Vainio, 2003).

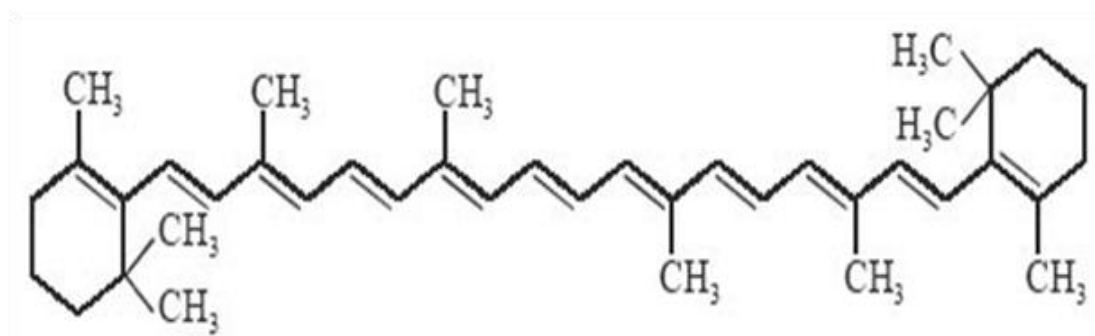


Figure (1): Structure of β -carotene (Phar macognosy, 2012).

The second group is xanthophylls (see figure (2)) that contain oxygen and are found in dark leafy greens such as spinach and kale, as well as broccoli. Lutein (see figure (3)) and zeaxanthin are two examples of xanthophylls and they are found in green leave vegetables and in some fruits like kiwi and orange (Vainio, 2003). Unlike chlorophyll, once carotenoids are produced, they do not break down rapidly in the plant but they remain in the leaves during their entire lifetime (Delgado-Vargas, Jiménez & Paredes-López, 2000).

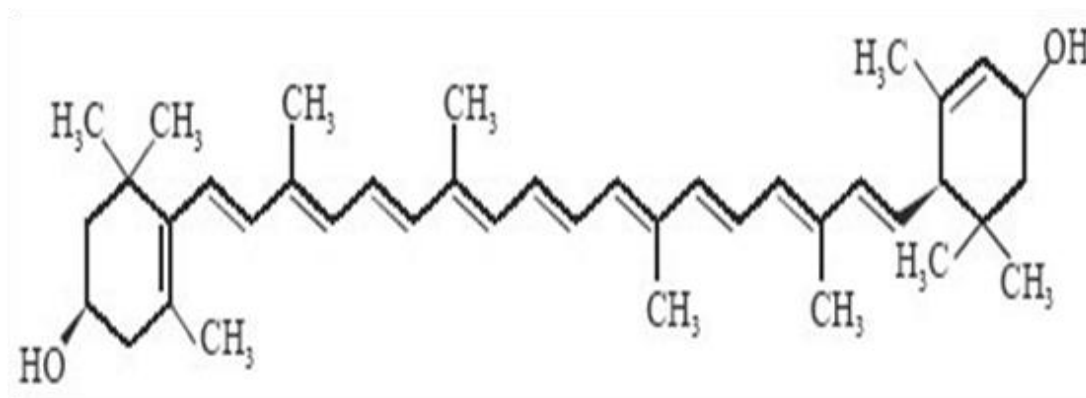


Figure (2): Structure of Xanthophyll (Phar macongny,2012).

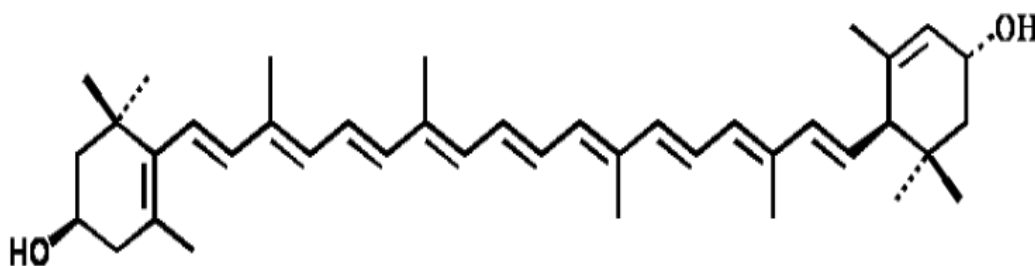


Figure (3): Structure of Lutein (Schaffer,2008).

2.1.2.2 Chlorophyll

Chlorophyll is the most important group of tetrapyrrols. It is widely spread in plant tissues, mostly leaves and fruits like kiwi, which is responsible for the green colour in the plant and is usually associated with fats or proteins. Chlorophyll allows the plant to perform photosynthesis (Zongo, 2012). Chlorophyll is composed of cyclic conjugated system of double bonds with central magnesium ion. The existence of some functional groups as substitutes results in derivatives such as Chlorophyll a, b (as shown in Figure (4)). It is very effective as photoreceptors because it contains networks of alternating single and double bonds ("Food-Info.net: Chlorophyll", 2017).

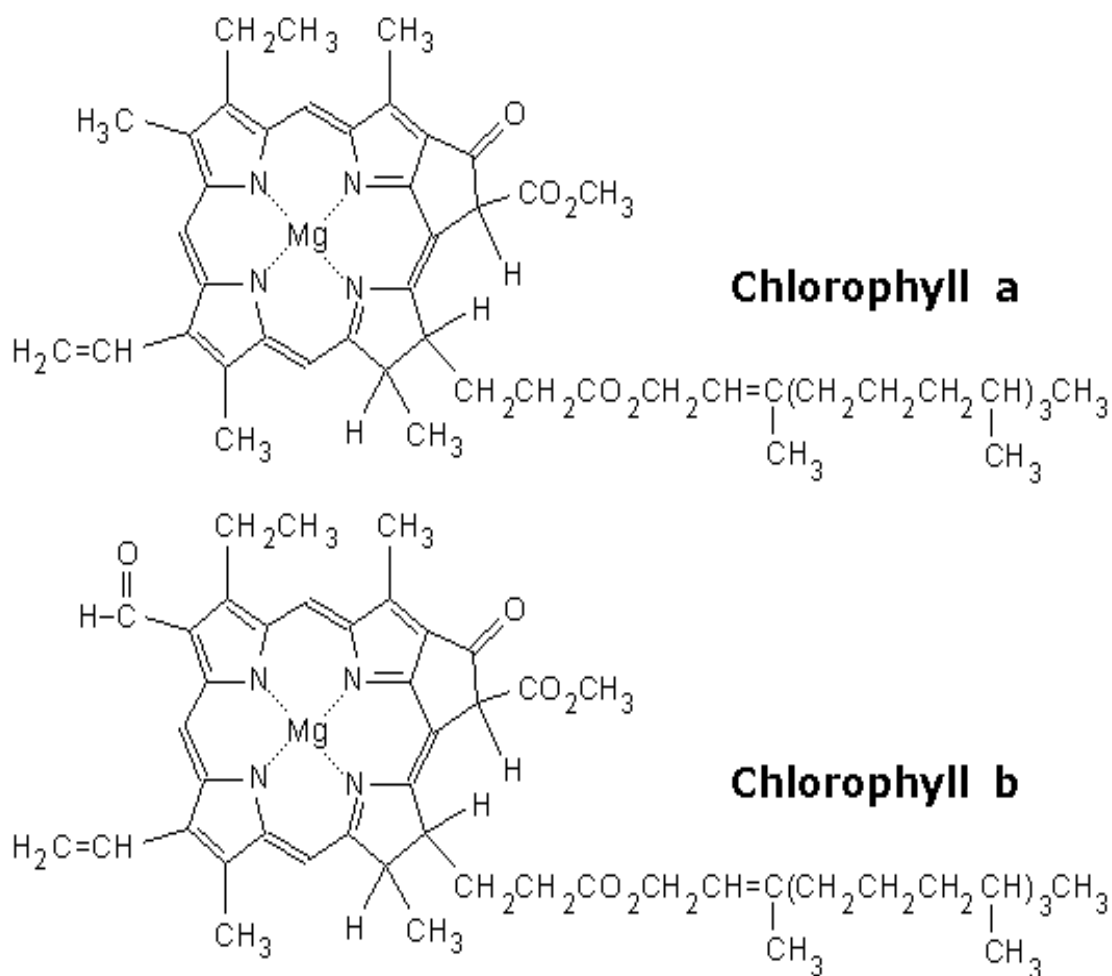


Figure (4): Structure of the two most common chlorophylls (Wageningen University, 2017).

Due to its chemical structure (where magnesium ion is central), natural chlorophyll has limited use as a colourant. However, mixing chlorophyll with another natural dye or chemical modification substance can improve its stability (Zongo, 2012).

2.1.2.3 Flavonoid

Flavonoid is an essential dye in food industries due to its multi-colour appearance feature as is the source of the white, red, purple, blue and yellow colours for several flowers, fruits and vegetables (Zongo,

2012; Alkema & Seager, 1982). Anthocyanin is the main component of the flavonoid and the most important type of dyes after chlorophyll (Delgado-Vargas, Jiménez & Paredes-López, 2000); it is soluble in water and organic solvent.

As shown in Figure (5), anthocyanin has heterocyclic structures that have the role of absorbing visible light. These structures contain an unbound electron that lower the excited energy and result in the light absorption process in the visible range (Zongo, 2012). The anthocyanin is subdivided into Anthocyanidin aglycons and anthocyanin glycosides.

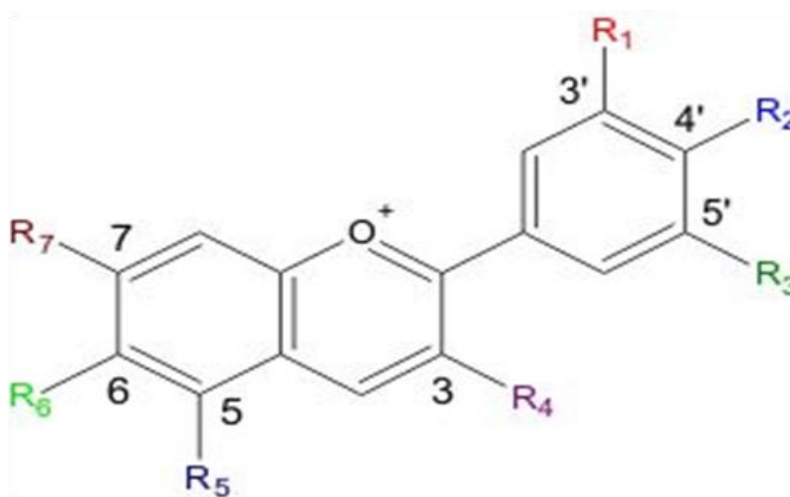


Figure (5): The flavylium ion, the basic structure of anthocyanins (Wageningen University, 2017)

A large collection of anthocyanins can be formed when attached to sugar. For instance, Cyanidin-3-glucoside (see figure 6) and Pelargonidin-3-glucoside are the most important types of anthocyanin contained in strawberries and Cyanidin, Pelargonidin and Delphinidin are the main types of anthocyanin contained in grapes. Also, the diversity can be enhanced more through chemical combination of sugars and organic acids to generate acylated anthocyanins. An example is Cyanidin-3-

(acetylglucoside) in oranges. (Wageningen University, 2017). Besides, the anthocyanin responsible for the red and orange colour is anthocyanidins pelargonidin, while cyaniding and delphinidin are the anthocyanins responsible for the pink and blue colours respectively. Also, the anthocyanin in cherry, cranberry and pomegranate give them the red colour. While the anthocyanin gives blueberry the blue colour. Another point, regarding anthocyanin is that it is greatly influenced by the pH of the medium in which they are dissolved.

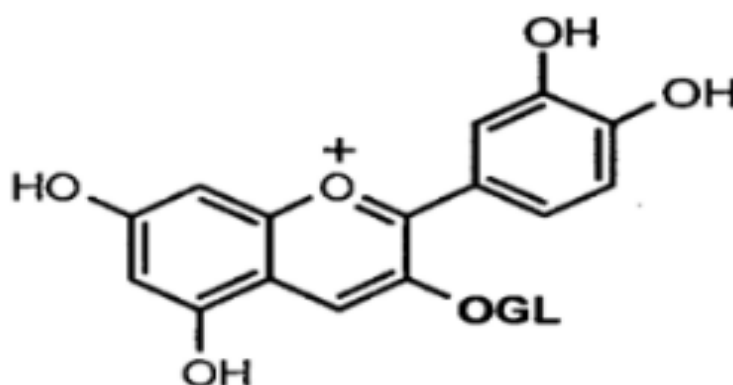


Figure (6): Cyanidin-3-Glycoside (Delgado-Vargas, Jiménez & Paredes-López, 2000)

2.1.2.4 Betalains

Betalains dye extracted from commercial sources is of vital importance to photoelectrochemical and food industries (Isah et al., 2014). It is soluble in water and strongly absorb light. Based on its acid conjugation, betalain is nitrogenous chromoalcaloid and its presence omits the anthocyanin.

Betalain is subdivided into two structural groups, the yellow betaxanthins (from Latin beta, red beet and Greek xanthos, yellow) and red-purple betacyanins (kyanos, blue color) based on R1-N-R2 moieties, these two colours are observed under basic and acidic conditions. Betalain colour is associated with resonating double bonds and is affected by pH of solvent (Isah et al., 2014). Moreover, there are over 50 types of known betalains, whose structures (see figure 7) are all basic and in which R1 and R2 could be hydrogen or an aromatic substituent.

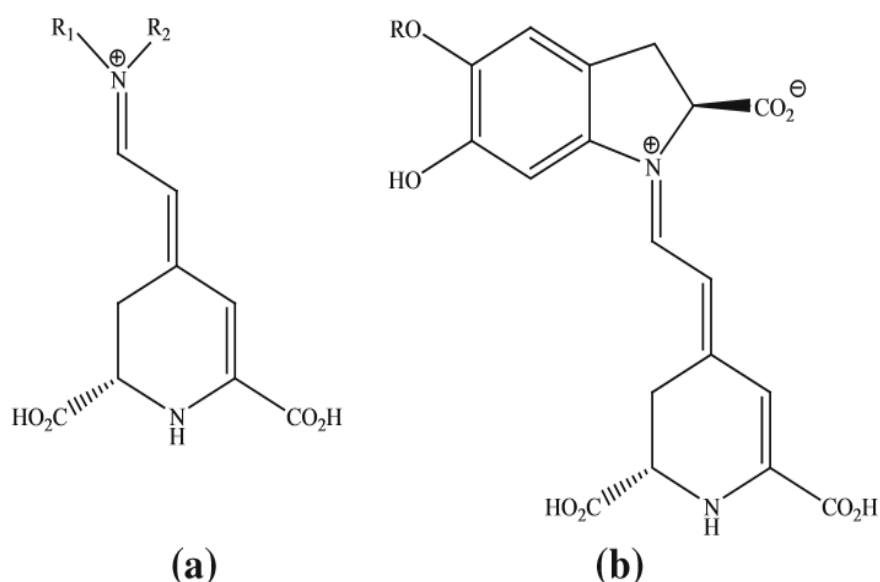


Figure (7): General structures of the main betalain (a) betaxanthin (b) betacyanin (Isah et al., 2014).

2.1.3 Extraction of natural dyes

The first step to utilize natural dyes is initiated by extracting it from its sources. The extraction process is dependent on the source nature, intended use, extraction technique and the solvent used such as aqueous, organic and acids. Another point is that by changing the pH (Hua et al., 2013), temperature, time duration and type of solvent, the colour of the

dye can change (Bhute & Prabhu, 2012). Furthermore, redness of anthocyanin increases by interacting with a larger number of methoxyl groups, while interacting with more hydroxyl changes the red colour to a more bluish colour. In addition, polar solvents like methanol, acetone and acetonitrile shows the most efficient dyes extraction when interacting with phenolic compounds. In fact, acidic solvents exhibited greater efficiency in comparison with neutral solvents while extracting non-acylated anthocyanin (Watson, 2001; Isah et al., 2014)

Organic solvents can alter the peak wavelength of the absorbance spectrum. In spite of its role in giving more efficient and precise outcomes in terms of colour discrepancy and long lifetime during the dye extraction procedure, organic solvents suffer the disadvantage of being toxic to human beings and the environment. An additional disadvantage is that a great quantity of solvent might be needed which might be expensive (Shirsath, Sonawane & Gogate, 2012)

2.2 Nonlinear Optical Materials (NLO)

Nonlinear optical materials are considered as major components to a potential photonic technology, optoelectronic. Nonlinear optical materials representing capability of two photon absorption are nominated to be employed in three-dimensional fluorescence imaging and multi-photon microscopy, eye and sensor protection, stabilizing fast fluctuations of laser power, frequency up conversion lasing, and optical signal reshaping (Yakop and Badran 2014; Ganeev, et al., 2003). Organic molecules and polymers are relatively new in the field of nonlinear optics compared to inorganic materials. The achievement of nonlinear optical effects requires a material of special specification. In addition, the

minimum standards required for non-linear third-order optical material are that the material should have a large non-linear third-degree coefficient, with good transparency, low optical loss, and fast response time (Rao, et al., 2011), as well as commercial existence and low cost (Degiorgio & Flytzanis, 1995).

Nonlinear optical materials can be classified into two categories, organic or inorganic, and each of which has its advantages and disadvantages. Pulsed and continuous laser radiations were used to investigate material in its various forms of nonlinear optical properties and number of photonic materials that have been investigated include: semiconductor thin films, inorganic and organic crystals, polymers, doped glasses, dyes, phthalocyanines, porphyrins, quantum dots and nanomaterials of both semiconductors and insulators (Pramodini, 2015).

A large number of nonlinear inorganic materials are available, but their response time is relatively slow. Large third order NLO susceptibilities have been measured in inorganic semiconductors (Fainman, Ma & Lee, 1993) in a form of quantum wire and quantum dot structures.

Recently, research activities have emphasized on the development of organic molecules and polymers, having realized the superiority of organic materials due to their flexibility and the ease of preparation and integrating their properties with properties of other materials by subjecting them to molecular engineering techniques for ultimate use. Also, organic materials manifest a lot of nonlinear advantages, especially, high damage thresholds (Al-Saidi and Abdulkareem, 2015) and high speed response time (Nesterov, Kuleshova & Antipin, 2001; Liu, Yang, Wang & Cao, 2016).

Peer reviewed studies on third-order nonlinear optical properties of a wide variety of organic liquids and solvents have reached a significant conclusion; that the third-order nonlinear parameters are affected by the number of carbon atoms, the existence of substitutions, donor acceptor functionalities and π electron system existing in nonlinear optical materials. Benzene, Stilbene, nitrobenzene, nitrocyclobexane, carbon tetrachloride, chloroform, dichloromethane etc. are some of the organic liquids possessing nonlinear optical properties (Paul, 2004; krishnamurthy & alkondan, 2010).

As stated earlier, organic materials, that are classified into solids, liquids and conjugated polymers, are considered the most capable candidates for the NLO applications (Paul, 2004).

2.3 Optical Limiting

Optical limiting (OL) researches have started in the 1960s by Geusic et al and Ralston et al. with three-photon nonlinear absorption in inorganic semiconductors. In the 1980s, organic materials have emerged as new discovery in the OL system (Chi, 2009). Moreover, many demonstrations of optimized OL were accomplished through two-photon absorption (TPA) followed by subsequent excited state absorptions. Considering the advantage of TPA, such OL systems have successfully maintained the higher linear transmittance at low input fluence than their one-photon absorption counterparts.

Nonlinear refraction might occur from molecular reorientation, the electronic Kerr effect or optically-induced heating of the material. (Paul, 2004; Rashidian & Dorranean, 2015; Hassan, et al., 2012). Nonlinear absorption is another kind of mechanisms that used in OL. At this

situation OL depends on the conclusion that transmissivity for some nonlinearly absorbing media falls as the intensity of input laser rises. RSA and TPA are nonlinear absorption mechanisms used at OL (Ganeev, et al., 2003; Rao, et al., 2011). Using TPA as the OL mechanism demonstrates the advantage of negligible linear absorption loss for weak signal, exceptionally quick temporal response, and maintaining transmitted signal high beam of good quality. Owing to that, TPA based devices are also proper for other applications such as optical power stabilization, optical pulse reshaping, optical spatial field reshaping (Rashidian & Dorranean, 2015; Zongo, 2012). Combining Nonlinear mechanisms has as well accomplished improvement in optical limiting, such as self-defocusing with TPA, TPA with excited state absorption (ESA). In organic materials combine (ESA) and (RSA) (krishnamurthy & alkondan, 2010). The nonlinear refractive index in this material decreases as the input intensity increases as shown in Figure (8) (Henari, et al., 2013).

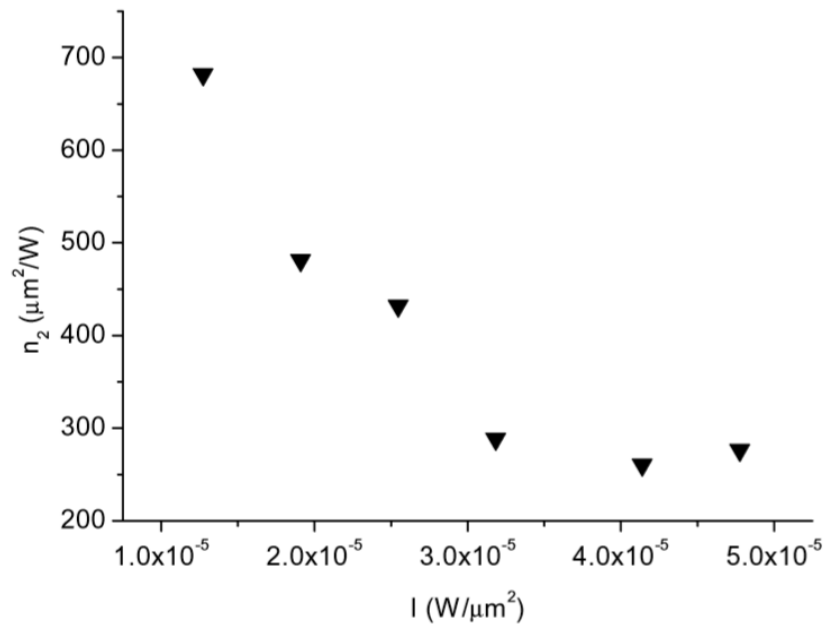


Figure (8): Nonlinear refractive index of curcumin in acetonitrile as a function of incident intensity (Henari, et al., 2013).

Optical limiter is a device that exhibits a linear transmittance to the power, irradiance, energy or fluence below a threshold and clamps the output to a constant above it as shown in Figure (9) (krishnamurthy & alkondan, 2010; Rashidian & Dorranean, 2015), thereby providing safety to sensors or eyes because nonlinear absorption coefficient increases with increase input power. the liquids have high nonlinear absorption due to their thermal expansion is large. Increasing in temperature due absorption leads to the absorption coefficient and optical limiting effect. (Rashidian, et al., 2009). A material must have high linear transmittance, low limiting threshold, fast response time, broadband response and low optical scattering to behave as an attractive optical limiter (Al-Saidi & Abdulkareem, 2015; Chi, 2009).

Large variety of organic and inorganic materials are under study in order to realize efficient OL. All-optical limiters depend on materials that demonstrate one or more of the nonlinear optical mechanisms, which are resulting from intensity dependent optical nonlinear processes.

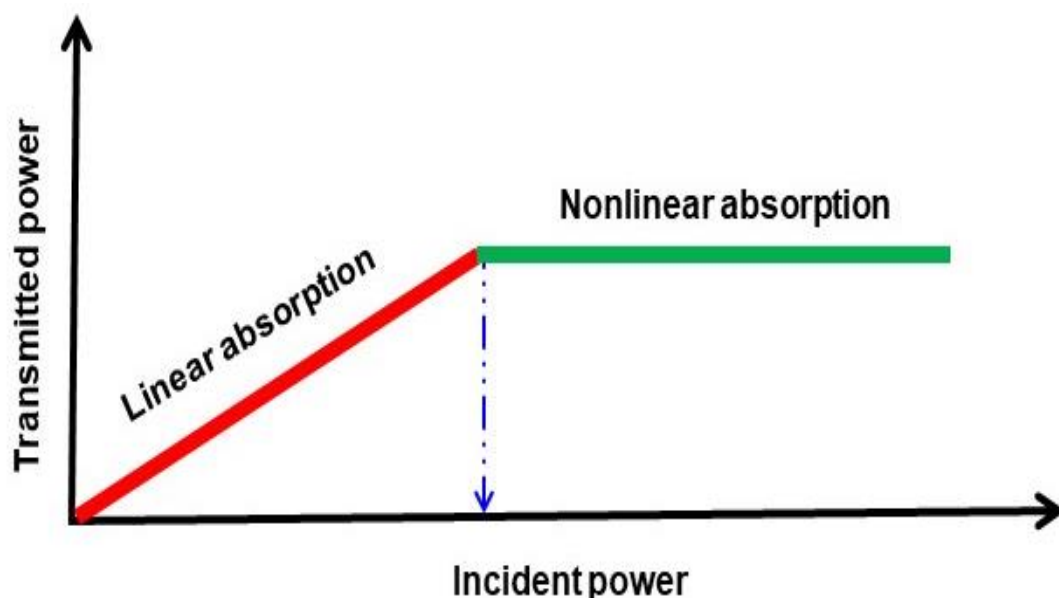


Figure (9): Optical response of an optical limiter to incident power.

2.4 Basic Concepts of Nonlinear Optics

2.4.1 Kerr effect

Kerr medium is the material characterized by centrosymmetric, respond to optical fields by generating third harmonics, sums and differences of triplets of frequencies. Kerr materials could be in form of gases, liquids, and certain crystals. Refractive index of an electro-optic medium is function of the applied electric field $n(E)$. It is symmetric function for the reason that it does not change if the electric field is reversed. Subsequently, third order nonlinear term is dominating while the second-order is vanishing (Saleh & Teich, 1991). Kerr effect is a nonlinear response by changing refractive index as a result of applying high intensity light beam, hence it's given according to:

$$n(I) = n_o + \Delta n = n_o + n_2 I \quad (1)$$

Where Δn is the change in the refractive index which proportional to the optical intensity and $n_2 = \frac{3\eta}{n^2 \epsilon_0} \chi^{(3)}$. The total refractive index $n(I)$ is a linear function of the optical intensity I .

The order of magnitude of the coefficient n_2 (in units of cm^2/W) as reported is 10^{-16} to 10^{-14} in glasses, 10^{-14} to 10^{-7} in doped glasses, 10^{-10} to 10^{-8} in organic materials, and 10^{-10} to 10^{-2} in semiconductors. It is sensitive to the operating wavelength and depends on polarization state of the light beam (Saleh & Teich, 1991).

2.4.2 Two photon absorptions

Two photon absorptions is a nonlinear absorption process where two photons of identical or different frequencies are simultaneously absorbed when a intense coherent beam propagates in a third-order nonlinear medium as illustrated in Figure (10) (Pramodini, 2015).

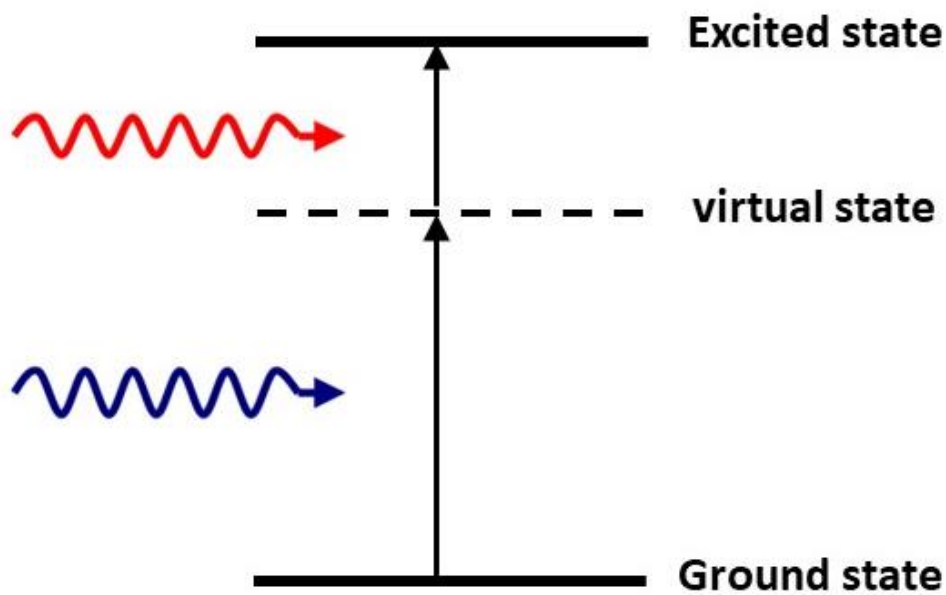


Figure (10): Schematic illustration of two-photon absorption process.

2.4.3 Intensity dependent refractive index

The result of the interaction between low intensity non-coherent light beam and high intensity coherent light beam differs as the normal (non-coherent) light interaction shows a linear response to the electromagnetic field and the optical characteristics of the material remain unchanged because they do not rely on the light intensity and the frequency remains constant. The occurrence of superposition principle

is possible, but the waves do not interact with each other. (Zongo, 2012) (Zhao, 2016) (Boyd, 2008)

On the other hand, the interaction between the laser (coherent) beam and the material shows a nonlinear response to the electromagnetic field and in which the optical characteristics of the material such as refractive index and the speed of light do change. The superposition principle is not possible because of light interaction with light (Zongo, 2012) (Zhao, 2016) (Boyd, 2008)

The refractive index of NLO materials can be described by the following relation:

$$n = n_o + \bar{n}_2 \langle \tilde{E}^2 \rangle \quad (2)$$

Where n_o is the linear refractive index, $\bar{n}_2$ is a new optical constant which is called the second-order index of refraction. $\bar{n}_2$ is the rate when the refractive index increases with increasing optical density and the angular brackets surrounding the quantity $\tilde{E}^2$ is a time average. Assume, if the optical field is expressed by

$$\tilde{E}^2(t) = E(w)e^{-i\omega t} + c.c. \quad (3)$$

$$to \quad \langle \tilde{E}^2(t) \rangle = 2E(w)E(w)^* = 2|E(w)|^2 \quad (4)$$

then, by substituting the value of $\langle \tilde{E}^2(t) \rangle$ in equation 18 we get

$$n = n_o + 2\bar{n}_2|E(w)|^2 \quad (5)$$

The change in refractive index in previous equations, which is proportional to the square of the applied electric field is called optical Kerr effect.

The total polarization of NLO materials, which changes as result of the interaction between the laser beam and NLO materials, can be described by the following relation.

$$P^{TOT}(w) = \varepsilon_o \chi^{(1)} E(w) + 3\varepsilon_o \chi^{(3)} |E(w)|^2 E(w) \equiv \varepsilon_o \chi_{eff} E(w) \quad (6)$$

Where $\chi_{eff} = \chi^{(1)} + 3\chi^{(3)} |E(w)|^2$ is the effective susceptibility. The following equation illustrates the relation between the nonlinear refractive index n_2 and the effective susceptibility (Boyd, 2008; Pramodini, 2015)

$$n^2 = 1 + \chi_{eff} \quad (7)$$

By substituting the value of n^2 and χ_{eff} in equation 21, we obtain

$$n_o^2 + 4n_o \bar{n}_2 |E(w)|^2 = (1 + \chi^{(1)}) + [3\chi^{(3)} |E(w)|^2] \quad (8)$$

The last equation illustrates that the linear and nonlinear refractive indices are related to the linear and nonlinear susceptibilities as shown on the following relations:

$$n_o = (1 + \chi^{(1)})^{1/2} \quad (9)$$

$$\bar{n}_2 = \frac{3\chi^{(3)}}{4n_o} \quad (10)$$

2.5 Z-scan Technique Principle

There is a considerable interest to develop a precise technique with which one can achieve accurate measurement of both nonlinear absorption coefficient and nonlinear index of refraction and hence determining third order susceptibility $\chi^{(3)}$. Many techniques were employed such as: nonlinear interferometry (Bahae, et al., 2007; Weber et al., 1978), degenerate four-wave mixing (DFWM) (Ganeev, et al., 2003; Friberg and Smith, 1987), nearly degenerate three-wave mixing (Sharan, et al., 2002; Yan, et al., 2009), ellipse rotation, and beam distortion measurements (Bahae, et al., 2007). However, a simple, well established, and quite very accurate technique named Z-scan technique is currently widely in use and trusted (by majority of nonlinear optics scholars) to quantify both nonlinear absorption coefficient and index of refraction, and hence quantifying third order susceptibility $\chi^{(3)}$ (Rashidian, et al., 2008; Balaji et al., 2011; Dhinaa and Pallnisamy, 2010).

The main objective of the z-scan technique is to measure the variation of incident Gaussian laser beam transmission intensity through the sample as a function of its position (Z-position) from the focus of the beam. Transmitted beam is collected in two cases: close aperture (CA) in order to tell the sign and measure the nonlinear index of refraction (n_2) as illustrated in Figure (11), and open aperture (OA) in order to measure the nonlinear absorption coefficient (β). The working principle of Z-scan technique is based on the motion of the sample along the Z axis from +Z to -Z through the focus of a tightly focussed Gaussian laser beam. The motion of the sample across the focussed beam exposes it to a varying irradiance (intensity) level reaching its maximum value at the focus point as shown in Figure (11) (Sharan, et al., 2002; Neethling, 2005).

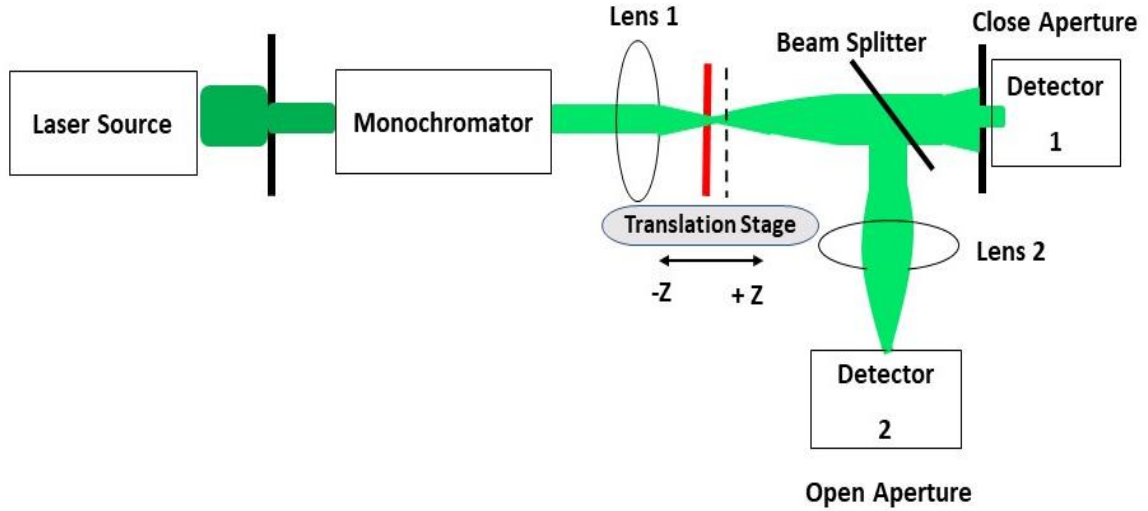


Figure (11): Schematics of experimental setup used for the close aperture Z-scan.

In this project, in order to apply theoretical models developed by Mansoor Sheik Bahae (Bahae, M. S. et al., 2007) or others (Rashidian, et al., 2008), our samples will be prepared in a form of thin samples. A thin sample is an optical medium with thickness smaller than the diffraction length of a focused Gaussian beam.

2.5.1 Close aperture z-scan technique

As shown in Figure (11), if a thin sample is scanned with close aperture setup and Gaussian laser beam, both the sign and magnitude of nonlinear refractive index are determined. Considering a sample with negative nonlinear refractive index, the scan starts far from focal length ($-Z$) and the sample exhibits negligible nonlinear refraction at low irradiance. As the sample get closer to the focus beam, irradiance increases, and the sample starts acting as a lens of variable focal length. The transmittance through the aperture changes because of variation of sample location relative to the focus. When the sample becomes very close to the focus it starts acting as a negative lens, and hence, the beam irradiance arriving

the aperture increases due to self-defocusing effect. On the other hand, as the sample moves away from the focus (+Z), the beam irradiance arriving the detector decreases due to self-focusing effect. The transmittance becomes linear again when the scan ends. The result of this scan is represented in the transmittance versus position curve as shown in Figure (12). A material possessing negative nonlinear refractive index (self-defocusing behaviour) gives a transmittance with peak followed by a valley, while that with positive nonlinear index of refraction (self-focusing behaviour) shows transmittance with valley followed by a peak. Thus, the sign of a material nonlinearity can be determined directly from the transmittance versus position curve. This feature is considered as unique for z-scan technique.

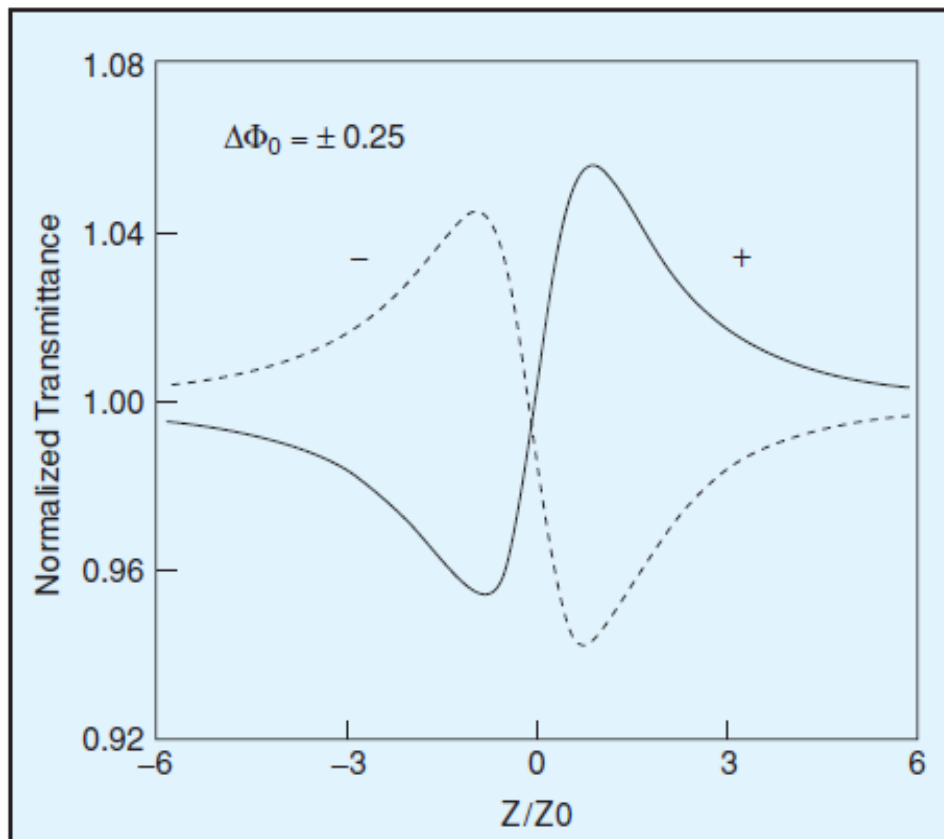


Figure (12): Close aperture z-scan normalized transmittance curve (From Bahae, M. S. et al., 2007).

Transmittance curve, in many situations, get distorted from what is shown in Figure (12). Close aperture setup is sensitive to nonlinear refractive index, but presence of nonlinear absorption effect due to saturable absorption (SA) enhances the peak and suppresses the valley as shown in Figure (13). On the other hand, two photon absorption (TPA) and reverse saturable absorption (RSA) are enhancing the valley and suppressing the peak (Bahae, M. S. et al., 2007).

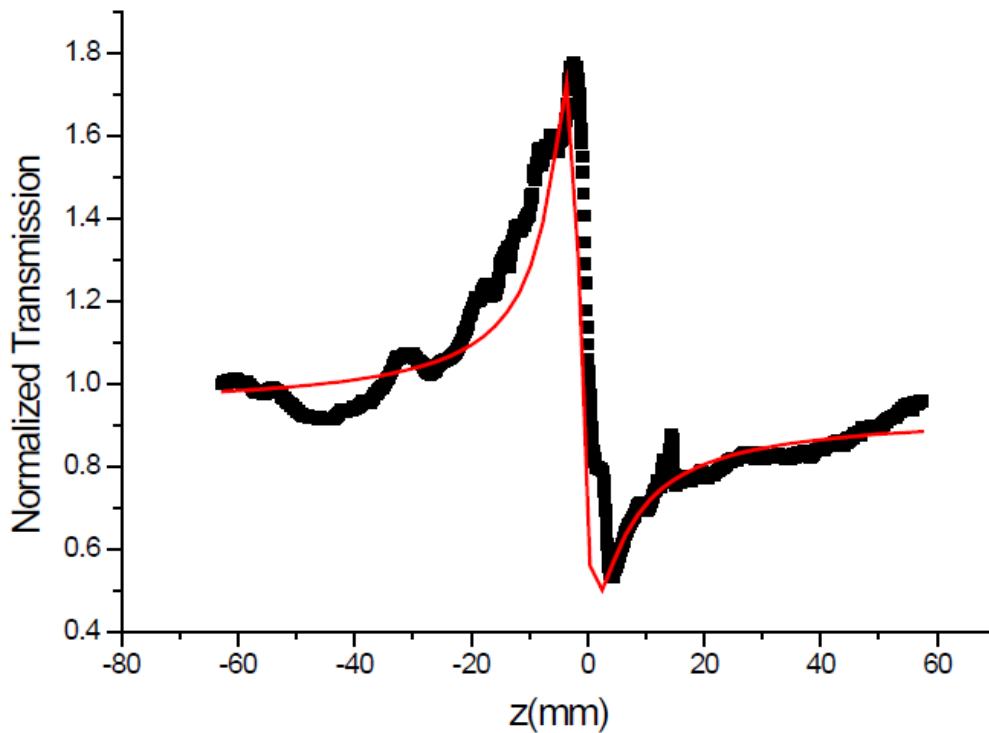


Figure (13): Close aperture Z-scan for DMPM4NBCHM in DMF at 488 nm for 10 mW incident power (from Henari et al 2013).

2.5.2 Open aperture Z-scan

When z-scan is performed with open aperture setup (i.e., removing the aperture in front of the detector D2 as shown in Figure (11) and Gaussian laser beam, the nonlinear absorption coefficient is determined from the

normalized transmittance curved. Moreover, the transmittance increases (decreases) as sample position Z gets closer to the focus point of the lens with maximum (minimum) value of the transmittance at the focal point, then it decreases (increases) as the sample moves away from the focus and attain its linear case at far $+Z$ position as illustrated in Figure (14).

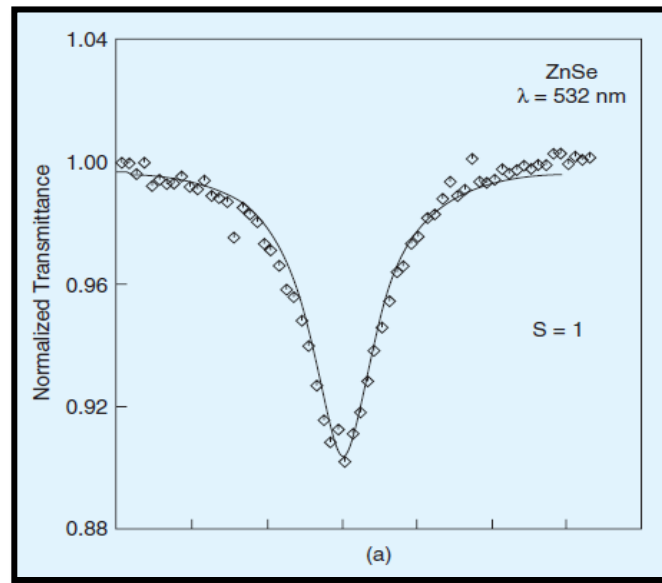


Figure (14): Open aperture Z-scan normalized transmittance curve (form Bahae, M. S. et al., 2007).

In Figure (14), the dots are the experimental data while the solid line is a fit curve based on the theoretical work developed by Sheik Bahae model. The graph of transmittance versus position has a symmetric shape around the focus, this is due to the symmetry of the distribution intensity of Gaussian beam (Neethling, 2005). If the transmittance is minimum at the focus (valley) as shown in Figure (14), this indicates the existence of two-photon absorption (TAP) or (RSA) with positive type of nonlinear absorption. However, when the transmittance is maximum at the focus (peak), this indicates the presence of saturable absorption (SA) with negative type of nonlinear absorption (Pramodini, 2015; Paul, 2004)

2.5.3 Advantages and disadvantages of Z-scan technique

In fact, Z-scan technique was developed by Mansoor Sheik-Bahae in 1980's (Zhao, 2016; Yan, et al., 2009; Dhinaa and Pallnisamy, 2010; Rekha and Ramalingam, 2009). Owing to its simplicity in application and interpretation (Rao, et al., 2011), Z-scan technique has quickly obtained the nonlinear optics community acceptance. Furthermore, it is a sensitive technique to test material aptitude as optical limiter (OL) (Yan, et al., 2009). Detects the electronic contribution, molecular orientation and redistribution (Papagiannouli, et al., 2012). Describe and determine the sign and magnitude for both nonlinear absorption coefficient and nonlinear index of refraction from which the third order susceptibility $\chi^{(3)}$ is calculated for tested sample solid or liquid media (Rashidian, et al., 2008; Neethling, 2005; Bahae, M. S. et al., 2007). Moreover, Z-scan does not only determine accurately nonlinear coefficients (to a high degree), but also determine directly the relative change in the transmission through the open [closed] aperture from the data without resorting to computer fitting (Pramodini, 2015).

On the negative sides, Z-scan requires a high-quality Gaussian beam for measurement or different analysis needed to be used alternatively (Kuzyk & Dirk, 1998). In addition, tilting of sample during the scan affects the result. Also, this technique is sensitive to all nonlinear optical mechanisms that give rise to a change of the refractive index and/or absorption coefficient. Thus, it's not possible to find out the underlying physical processes obtained from Z-scan technique.

2.5.4 Theoretical analysis

The theory of Z-scan is a specific case of nonlinear light-matter interaction theory which was developed by Mansoor Sheik-Bahae et al (Bahae, M. S. et al., 2007). Based on cubic nonlinearity assumption, the total refractive index n can be written in terms of linear and nonlinear refractive index n_2 through the relation (Gómez, Cuppo & Figueiredo Neto, 2003; Bahae, M. S. et al., 2007)

$$n = n_o + \frac{n_2}{2} |E|^2 = n_o + \gamma I \quad (11)$$

Where n_o is the linear refractive index, E is the peak electric field (cgs) and I is the irradiance of the laser beam in the sample (MKS). n_2 is the nonlinear refractive index in (esu) which is related to γ in m^2/W as illustrated by the following equation:

$$n_2(\text{esu}) = \frac{cn_o}{40\pi} \gamma \left(\frac{\text{m}^2}{\text{W}} \right) \quad (12)$$

Where c is the speed of light in vacuum (m/s). The electric field of Gaussian beam E can be expressed as:

$$E(z, r, t) = E_o(t) \frac{w_o}{w(z)} \exp \left(-\frac{r^2}{w^2(z)} - \frac{ikr^2}{2R(z)} e^{-i\phi(z,t)} \right) \quad (13)$$

Where $E_o(t)$ is the on axis electric field at the beam waist ($z = 0$, $r = 0$) which contains the temporal envelope of the laser pulse, $w^2(z) = w_o^2(1 + \frac{z^2}{z_o^2})$ is the radius of beam at z , r is the radial distance from the centre axis of the beam, w_o is the beam waist at focus, $R(z) = z(1 + \frac{z^2}{z_o^2})$ is

the radius of curvature of the wave front at z , $z_0 = \frac{kw_0^2}{2}$ is the diffraction length of the beam (Rayleigh length), and $k = \frac{2\pi}{\lambda}$ is the wave vector and λ is the laser wavelength. The $e^{-i\phi(z,t)}$ term contains all the radially uniform phase variations. The investigated sample assumed thin if the sample length is smaller than diffraction length (z_0) of focused Gaussian beam. Hence, no changes in beam profile by diffraction or nonlinear refraction which simplify the result and we can consider that the interaction position between laser and sample is not varying during scan period. In this case the self-refraction phenomena is called “external self-action”. At linear diffraction case $L \ll z_0$ where L is the sample length, and this is more restraining, so $L < z_0$ is sufficient. In practice, in nonlinear refraction case $L \ll \frac{z_0}{\Delta\phi(0)}$ this condition is met if $\Delta\phi(0)$ is small. The slowly varying envelope approximation (SVEA) is applied to calculate the radial phase variations $\Delta\phi(r)$ and amplitude I by following equations:

$$\frac{d\Delta\phi}{dz'} = \Delta n(I)k \quad (14)$$

$$\frac{dI}{dz'} = -\alpha(I)I \quad (15)$$

Where z' is the propagation depth in the sample and $\alpha(I)$ includes linear and nonlinear absorption terms. By solving these two equations which describes the propagation of Gaussian beam through the sample, the radial phase variations of incident irradiance are determined by the following equations:

$$\Delta\phi(z, r, t) = \Delta\phi_o(z, t) \exp\left(-\frac{2r^2}{w^2(z)}\right) \quad (16)$$

$$\Delta\phi_o(z, t) = \frac{\Delta\phi_o(t)}{1 + (z^2/z_o^2)} \quad (17)$$

$\phi_o(t)$ is the on-axis phase shift at the focus, is defined as:

$$\Delta\phi_o(t) = k \Delta n_o(t) L_{\text{eff}}$$

where $\Delta n_o = \gamma I_o(t)$, $I_o(t)$ is the irradiance at focus ($z = 0$) where the Fresnel refraction loss is ignored and $L_{\text{eff}} = \frac{1-e^{-\alpha L}}{\alpha}$ is the effective length of the sample, L is the length of the sample, α is the linear absorption coefficient.

The complex electric field emerging from the sample E_e that contains the nonlinear phase distortion, is defined as

$$E_e(z, r, t) = E(z, r, t) e^{-\alpha L/2} e^{i\Delta\phi(z, r, t)} \quad (18)$$

The Huygens principle was used to get the electric field at the aperture $E_a(r, t)$ through a zeroth-order Hankel transformation of E_e . Then, the Gaussian Decomposition (GD) method given by Weaire et al. was implemented by Sheik-Bahae et al. This method constitutes of some complex mathematical steps used to decompose the complex electric field emerging from the sample into a summation of Gaussian beams through Taylor series expansion of the nonlinear phase term. This approach was performed because only the small phase changes are considered, thus only a few terms of Taylor expansions are used. The normalized Z-scan transmittance $T(z)$ can be calculated by using the following equation

$$T(z) = \frac{\int_{-\infty}^{+\infty} P_T(z, \Delta\phi_o(t)) dt}{S \int_{-\infty}^{+\infty} P_i(t) dt} \quad (19)$$

Where $PT(\Delta\phi_o(t)) = c\varepsilon_o n_o \pi \int_0^{r_a} |E_a(r, t)|^2 r dr$ is the transmitted power through the aperture, ε_o is the permittivity of vacuum, $P_i(t) = \frac{\pi w_o^2 I_o(t)}{2}$ is the instantaneous input power (within the sample) and $S = 1 - \exp(-\frac{2r_a^2}{w_a^2})$ is linear transmittance through the aperture. $T(z)$ does not depend on the geometry or the wavelength while the size of aperture is an effective parameter. The large aperture ($S = 1$) the effect will disappear in $T(z)$ in all z and $\Delta\phi_o$.

The normalized transmittance is expressed as (Ganeev, et al., 2003).

$$T(z) = 1 + \frac{4x \Delta\phi_o}{(x^2+9)(x^2+1)} - \frac{2(x^2+3) \Delta\Psi_o}{(x^2+9)(x^2+1)} \quad (20)$$

Where $x = \frac{z}{z_o}$, $\Delta\phi_o$ and $\Delta\Psi_o$ are the on-axis phase shift due to nonlinear refraction and nonlinear absorption, respectively.

$$\Delta\phi_o = k n_2 I_o L_{\text{eff}} \quad (21)$$

$$\text{and} \quad \Delta\Psi_o = \frac{\beta I_o L_{\text{eff}}}{2}. \quad (22)$$

The nonlinear refractive index and nonlinear absorption coefficient are calculated from equations (11) and (12).

The nonlinear refractive index and nonlinear absorption coefficient is attributed to real and imaginary part respectively of third-order

nonlinear susceptibility $\chi^{(3)}$. This means it is a complex quantity as given by:

$$\chi^{(3)} = \chi_R^{(3)} + i\chi_I^{(3)} \quad (23)$$

$$\left| \chi_I^{(3)} \right| = \frac{n_o^2 \varepsilon_o c \lambda \beta}{2 \pi} \quad (24)$$

Where $\chi_I^{(3)}$ is the imaginary part of third-order nonlinear susceptibility which attributed to nonlinear absorption coefficient β .

$$\chi_R^{(3)} = 2n_o^2 \varepsilon_o c \gamma \quad (25)$$

and $\chi_R^{(3)} = 2n_o^2 \varepsilon_o c \gamma$ is the real part of third-order nonlinear susceptibility which could be attributed to nonlinear refractive index.

The total absorption coefficient α (I) can be written in terms of linear and nonlinear absorption coefficient β through the following relation (Gómez, Cuppo & Figueiredo Neto, 2003; Bahae, M. S. et al.,2007).

$$\alpha(I) = \alpha_o + \beta I \quad (26)$$

where α_o linear absorption coefficient and β intensity dependent coefficient (m/W).

2.6 Third Order Nonlinear Processes

2.6.1 Self-phase modulation

Self-phase modulation (SPM) is a nonlinear optical phenomenon of light-matter interaction which was discovered in the early days of nonlinear optics (Alfano, 2006). The strong field of a laser beam, when propagating in a third-order nonlinear medium, interacts with the medium and induce a varying refractive index of the medium due to the optical Kerr effect. This interaction imposes a phase shift in the pulse, leading to a change of the pulse's frequency spectrum (Saleh & Teich, 1991; Boyd, 2008). In brief, the self-phase modulation is the intensity-dependent nonlinear refractive index modulates the optical phase of the beam electric field which is given by the following relation.

$$\Delta\phi = 2\pi n_2 L \frac{P}{A\lambda_0} \quad (27)$$

Where P is an optical beam of power, L is a traveling distance in the medium and A is cross-sectional area.

The laser beam has a finite cross section. However, due to SPM, laser beam will appear to have self-diffraction, which is responsible for the known phenomena of nonlinear optical of self-focusing and self-defocusing. Moreover, the temporal variation of the laser intensity leads to SPM in time. As the time derivative of the phase of a wave is simply the angular frequency of the wave, SPM also appears as a frequency modulation. Thus, the output beam appears with a self-induced spectral broadening (Alfano, 2006).

2.6.2 Self-focusing and self-defocusing effects

Another attention-grabbing phenomenon of light-matter interaction associated with SPM is self-focusing. It occurs whenever the strong field of a laser beam propagates in a third-order nonlinear medium whose refractive index depends on the beam intensity. The real part of the third order susceptibility result in a change in the index of refraction of the material (Paul, 2004).

If the nonlinear refractive is positive and the incident beam is of higher intensity in the centre than the edge, then the self-focusing will occur. In that case, the refractive index and the optical path length for rays at the centre are greater than that at their edges. The same condition will occur for propagation via focusing lens and because of that the light beam will create its own positive lens in the nonlinear medium. Furthermore, when the beam focusing the strength of the nonlinear lens increases resulting in stronger focusing and strength of the lens, this will result in catastrophic focusing where the beam is breaking down into a very intense small spot, unlike the relatively gentle focusing which occurs for small lenses. This phenomenon may occur in materials that have transparency at high intensity such as crystals, glasses, gases, liquids and plasmas. (Paul, 2004; Saleh & Teich, 1991)

In contrast, If the nonlinear refractive is negative (n_2) and the incident beam is of higher intensity in the centre than the edge, then the self-defocusing will occur. In that case, the refractive index and the short optical path length for rays at the centre are smaller than that at their edges. The same condition will occur for propagation via negative focal length lens and beam defocuses (Paul, 2004).

2.7 Application of Nonlinear Optics

Nonlinear optical materials are expected to hold a prominent place in the future revolution of nonlinear optics in general and its effect in technology, medical (Perry, et al., 20012) and industrial applications in specific (Garmire, 2013). The development in nonlinear optics has been massive since the emergence of an all-optical nonlinear effect in the early sixties, however, the most substantial noticeable progress, until these days, was on the physical aspects of the nonlinear radiation matter interaction. But in the last decade this achievement has also borne its fruits in applied aspects of nonlinear optics. This can be basically seen in the improved performances of the nonlinear optical materials. Our understanding of the nonlinear polarization mechanisms and their relation to the structural features of the materials has been drastically improved. Furthermore, the new advancement of techniques for the fabrication and growth of artificial materials has greatly contributed to this evolution. The target is to search for and build up materials demonstrating large nonlinearities and fulfilling at the same time all the technological requirements for applications such as wide transparency range, fast response, high damage threshold but also processability, compliance and interfacing with other materials. Improvements, besides rendering possible the application of nonlinear effects in devices, would pave the way of investigating new nonlinear optical effects and the establishment of new concepts. (Degiorgio & Flytzanis, 1995).

2.8 Nonlinear Optics Research the University of Bahrain

Many published research activities and studies were carried out at the University of Bahrain. Studying nonlinear optical properties of materials have been seen to demonstrate laser induced refractive index changes like fullerenes, liquid crystals, natural substances such as Henna, Chinese tea and Curcumin and organic materials such as Porphyrin, Phthalocyanine and their derivatives.

(Henari, Cassidy, Jasim & Dakhel, 2013), measured the nonlinear refractive index coefficient for curcumin at three different wavelengths using CW argon-ion laser ($\lambda = 488 \text{ nm}$, 514 nm and 633 nm and excitation power of 20 mW) and a Z-scan technique. Curcumin shows a negative and large nonlinear refractive index equal $2.61 \times 10^{-6} \text{ cm}^2/\text{W}$ by fitting the data with the thermal model. The nonlinear refractive index decreases as intensity increases when using excitation laser at 488 nm , this behaviour is a clear indication of optical limiting process.

(Dakhel and Henari, 2003) measured the third order optical nonlinearities of CdO films by using z-can technique. At an excitation wavelength of 514 nm , the real and imaginary parts of $\chi^{(3)}$ were measured, real and imaginary values are $1.7 \times 10^{-3} \text{ esu}$ and $3.0 \times 10^{-3} \text{ esu}$, respectively. The sample shows reserve saturation absorption $\beta = 6.6 \times 10^{-3} \text{ m/W}$, the normalized transmission for closed aperture fitting using equation 10.

(Almadhoob, Yousif, Henari & Patil, 2014) measured the nonlinear refractive index and the nonlinear absorption ethy l2-{(2E)-2-[4(dimethylamino)benzylidene]hydrazinyl}-5nitrobenzoate (DMBH5NB) in solution by using the z scan technique. By using CW argon ion laser at wavelength 488 nm and 514 nm with excitation power 10 mW , nonlinear

refractive index value of $n_2 = 1.01 \times 10^{-11} \text{ m}^2/\text{W}$ at 514 nm and $n_2 = 1.49 \times 10^{-11} \text{ m}^2/\text{W}$ at 488 nm were measured. Nonlinear absorption value of $\beta = 1.95 \times 10^{-4} \text{ m/W}$ at 488 nm and $\beta = 6.42 \times 10^{-5} \text{ m/W}$ for 514 nm were also measured.

(Henari & Patil, 2014) measured the nonlinear refractive index and the nonlinear absorption of coefficient for {(1Z)-[4-(Dimethylamino) phenyl]methylene}4-nitrobenzocarboxy hydrazone mono-hydrate (DMPM4NBCHM) solution using the z scan technique with continuous wave (cw) argon ion laser at 488 nm and 514 nm (power 10 mW). Nonlinear refractive index $n_2 = 3.39 \times 10^{-11} \text{ m}^2/\text{W}$ at 514 nm and $n_2 = 7.82 \times 10^{-12} \text{ m}^2/\text{W}$ at 488 nm. Nonlinear absorption $\beta = 1.95 \times 10^{-4} \text{ m/W}$ at 488 nm and $\beta = 6.42 \times 10^{-5} \text{ m/W}$ for 514 nm.

This project aims to contribute further to the above mentioned activities.

CHAPTER 3: METHODOLOGY

3.1 Materials and Equipment

3.2 Natural Dyes Extraction

3.2.1.1 Peels

3.2.1.2 Pomegranate grains

3.2.1.3 Dry fruit

3.3 Linear Optical Characterization

3.3.1 Absorbance and absorption coefficient of dye extracts

3.3.2 Fluorescence of dye extracts

3.3.3 Linear index of refraction measurement

3.4 Constructing Z-scan Experimental Setup

3.5 Calculating Nonlinear Optical Parameters

CHAPTER 3: METHODOLOGY

This chapter includes the method used to extract natural dyes from fruits and classifying these dyes into five groups which are berry, citrus, pomegranate, prunes and tropical. Details of the spectroscopic method used to characterize extracted dyes such as measuring the absorbance, fluorescence spectra and linear refractive index are presented. Then eventually construction the Z-scan setup and obtained transmission spectra are detailed. All extracted dye samples are prepared, tested, and stored at room temperature.

3.1 Materials and equipment

Our research relies on natural dyes extracted from fruits. These dyes are divided into five groups based on their association with food component concentrations. Table (1) presents the group, fruit name and origin of the fruit.

Table (1): Natural extracted dye materials.

Group	Arabic name	English name	Origin
Berry	الفراولة	Dry strawberry	Turkey
	التوت الطازج	Fresh blueberry	Bahrain
	التوت المجفف	Dry blueberry	America
	الزبيب	Raisin	Pakistan
	التوت البري المجفف	Dry cranberry	America

Citrus	قشور الكريب فروت	Grapefruit peels	
	قشور اليوسفي	Mandarin peels	
	قشور البرتقال	Orange peels	
Pomegranate	قشور الرمان	peels	Egypt
			Spain
			Yemen
			India
	حبات الرمان	grains	India
Prune	لوز	Almond	Bahrain
	المشمش المجفف	Apricot	Turkey
	المشمش المجفف	Dry brown Apricot	Turkey
	الكرز المجفف	Dry cherry	America
	برقوق مجفف	Dry prune	America
Tropical	قشور نواة الأفوكادو	Avocado seed peels	Australia
	نواة الأفوكادو	Avocado seeds	Australia
	قشور الأفوكادو	Avocado peels	Australia
	الكيوي المجفف	Dry kiwi	Turkey
	قشور المانغوستين	Mangosteen skin	Philippines

Solvents used as in the extract natural dye from fruit are shown in Table (2).

Table (2): List the solvents used in the extraction of dye samples.

Materials	description	Formula
Methanol	Transparent liquid	CH ₃ OH Purity%:99%
Ethanol	Transparent liquid	CH ₃ CH ₂ OH Purity%:99%
Acetone	Transparent liquid	C ₃ H ₆ O Purity%:99%
Hydrochloric Acid	Transparent liquid	Formula: HCl Purity%:99%

Systems and instruments used in extraction, preparation, characterization and of dye samples are listed in Table (3).

Table (3): List the instruments and systems used in the study

Instrument and systems	Function	Specification
Laboratory tools	Pipette, beakers, filter papers, gloves.	Laboratories tools
Z-scan	Nonlinear refractive index, nonlinear absorption coefficient	
UV-VIS spectrophotometer	Absorbance spectra, transmittance spectra	Shimadzu, model UV-3101
CCD spectrometer	Florescence spectra	Edmund spectrometer
Power meter	Measuring power	
Refractometer	Linear refractive index	Kruss
Digital multimeter	Measuring current, voltage, resistance	

3.2 Natural Dyes Extraction

3.2.1 Peels

In this project, about 52 kinds of dry and fresh fruit substances were used in extraction dyes with different concentrations and solvents. The extraction method is called the immersing method as shown in Figure (15).



Figure (15): Immersion method used to extract dyes.

As presented in Figure (16) and Figure (17), the peels or seeds of the fruits (pomegranate, avocado, orange, grapefruit or mandarin) are cut into small chunks then dried at open air. After that the chunks are crushed into small pieces or powder state using electric blender. Next, the crushed sample is immersed in different solvents such as acetone, ethanol, methanol or methanol with 1% HCl for 6 days. Finally, the solution is the filtrated and stored. The chosen concentrations of samples are (0.1, 0.3, 0.6) g/ml.

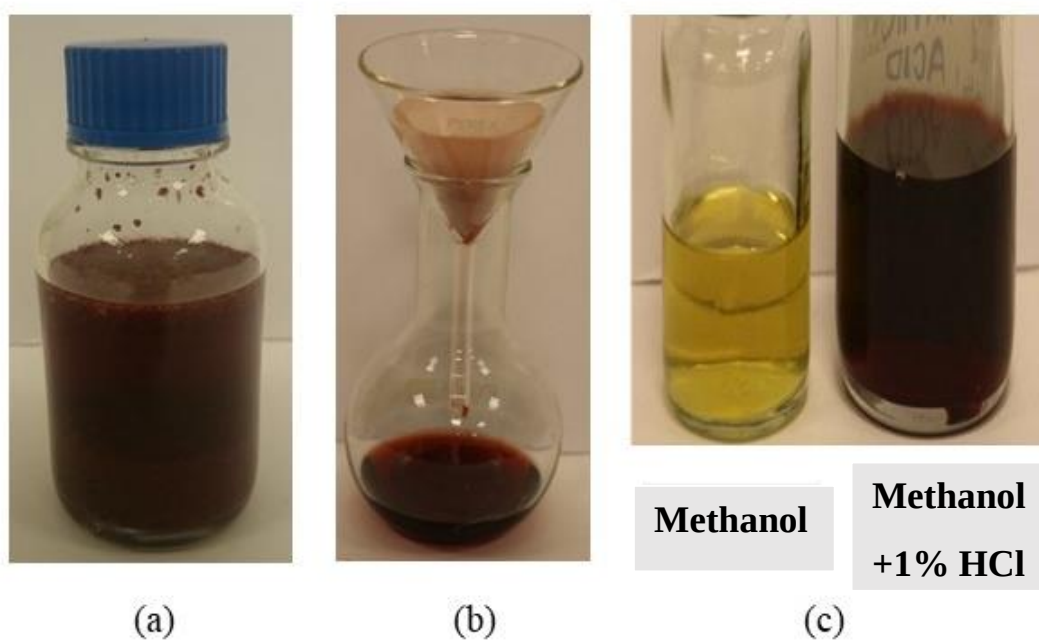


Figure (16): Almond sample (a) immersing, (b) filtration, (c) almond extracted dye in methanol and methanol with acid.

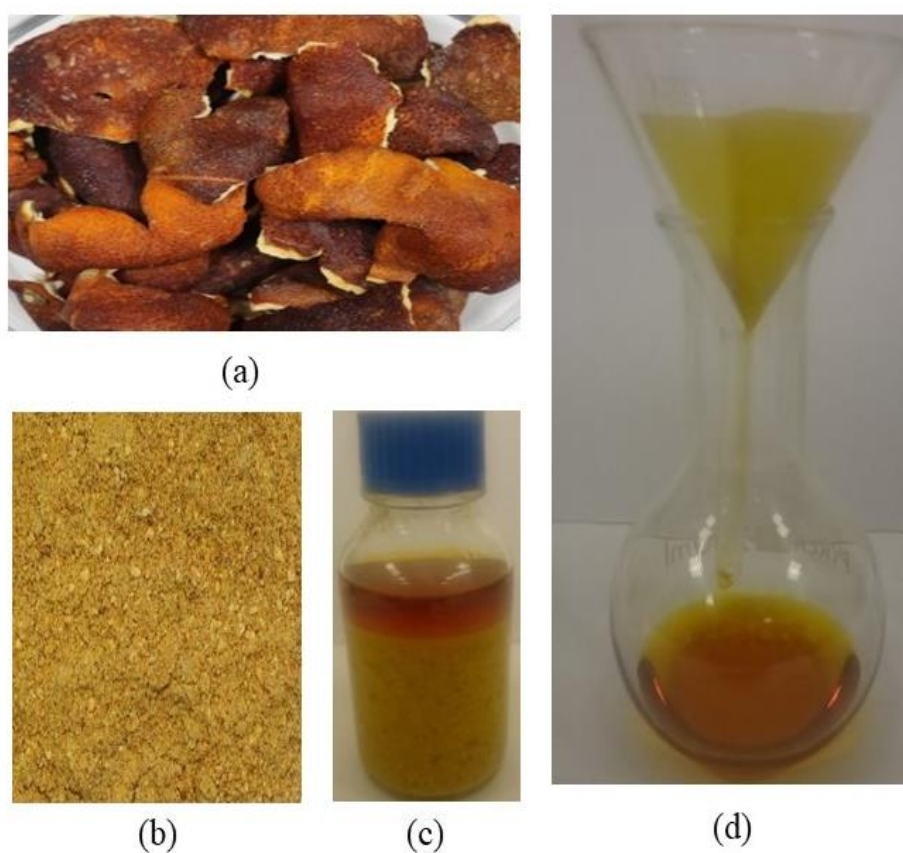


Figure (17): Mandarin peel in methanol (a) dry peel, (b) grated peel, (c) immersing, (d) filtration.

3.2.2 Pomegranate grains

Pomegranate grains were placed in the oven for 10 minutes at 160°C to get dry as shown in Figure 18. Then certain weights of the dried grains are immersed in different solvents like methanol and methanol with 1% HCl for 6 days (see Figure (19)). Then, solution is filtrated and stored. The prepared concentrations are (0.1 and 0.6) g/ml.



Figure (18): Pomegranate grains fresh and dried.



(a)



(b)



(c)

Figure (19): Pomegranate grains (a) immersing, (b) filtration, (c) pomegranate grains extracted dye in methanol.

3.2.3 Dry fruits

Dry fruits (cranberry, cherry, black raisin, prune, apricot, dry blueberry, kiwi and strawberry) samples are cut into small chunks. Next, specified mass of the sample is immersed in different solvents like methanol and methanol with 1% HCl for 6 days. Finally, the solutions are filtered and stored as shown in Figure (20) and Figure (21). Three concentrations are prepared (0.1 – 0.3 – 0.6) g/ml.

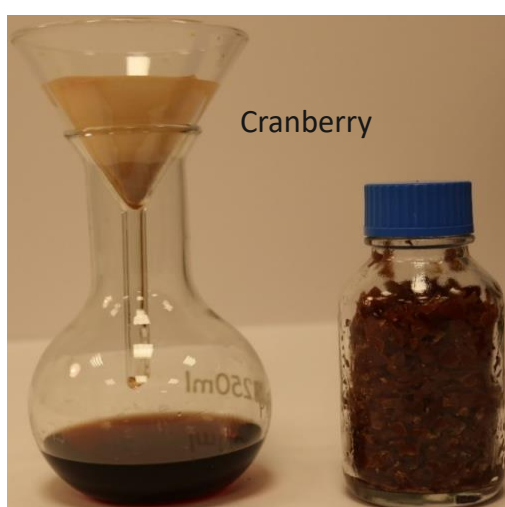


Figure (20): Dry cranberry dye extract in methanol

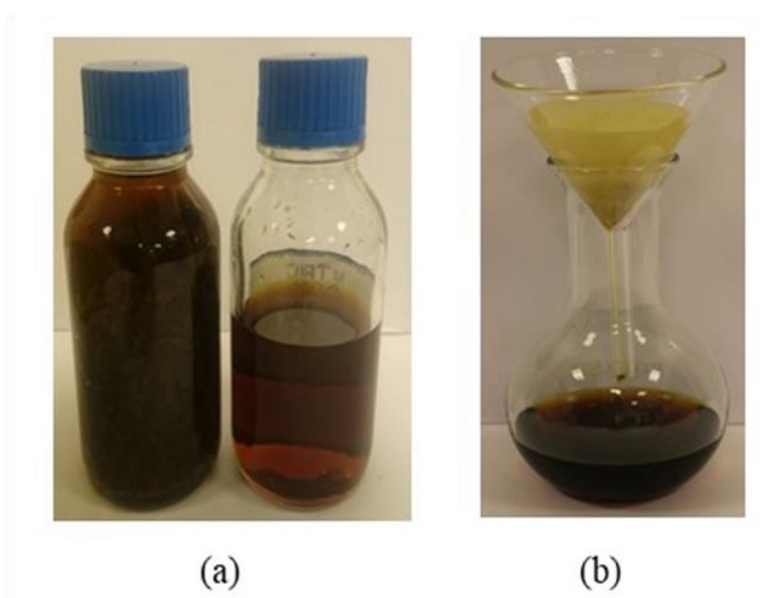


Figure (21): Prune extract in methanol (a) immersing, (b) filtrate sample.

Table (4): Extracted dyes from berry group.

Fruit	Solvent	Concentration (g/ml)
Strawberry	Methanol	0.3 and 0.6
Fresh blueberry	Acetone	0.1
	Ethanol	0.1, 0.3, and 0.6
	Methanol	0.1
Dry blueberry	Methanol	0.6
Raisin	Methanol	0.1 and 0.6
Cranberry	Methanol	0.1 and 0.6

Table (5): Extracted dyes from tropical group.

Fruit	Solvent	Concentration (g/ml)
Avocado seed peels	Methanol	0.1
Avocado seeds	Methanol	0.1 and 0.6
Avocado peels	Methanol	0.1 and 0.6
	Methanol + 1% acid	0.6
Kiwi	Methanol	0.3 and 0.6
	Methanol + 1% acid	0.6
Mangosteen peels	Methanol	0.1, 0.3, and 0.6
	Methanol + 1% acid	0.6

Table (6): Extracted dyes from prunus group.

Fruit	Solvent	Concentration (g/ml)
Almond	Acetone – Ethanol - Methanol	0.1
	Methanol + 1% HCl	0.1
Apricot	Methanol	0.6
	Methanol + 1% HCl	0.6
Brown Apricot	Methanol	0.6
Cherry	Methanol	0.6
prune	Methanol	0.6
	Methanol + 1% HCl	0.6

Table (7): Extracted dyes from pomegranate group.

Pomegranate		Solvent	Concentration (g/ml)
peels	Egypt	Acetone, Ethanol, Methanol	0.1
	Spain	Acetone, Ethanol, Methanol	
	Yemen	Acetone, Ethanol, Methanol	
	India	Methanol	0.1 and 0.3
Grains (India)		Methanol	0.1 and 0.6

Table (8): Extracted dyes from citrus group.

Fruit	Solvent	Concentration (g/ml)
Grapefruit peels	Methanol, methanol + 1% HCl	0.3
Mandarin peels	Methanol	0.3
Orange peels	Methanol	0.6

3.3 Linear Optical Properties

3.3.1 Absorbance and absorption coefficient of dye extracts

The dual beam UV-VIS spectrophotometer (Shimadzu, model UV-3101) shown in Figure (22) was used to measure absorbance of samples. Then, from the absorption spectrum, the linear absorption coefficient at wavelengths 488 nm, 514 nm and 633 nm are calculated.

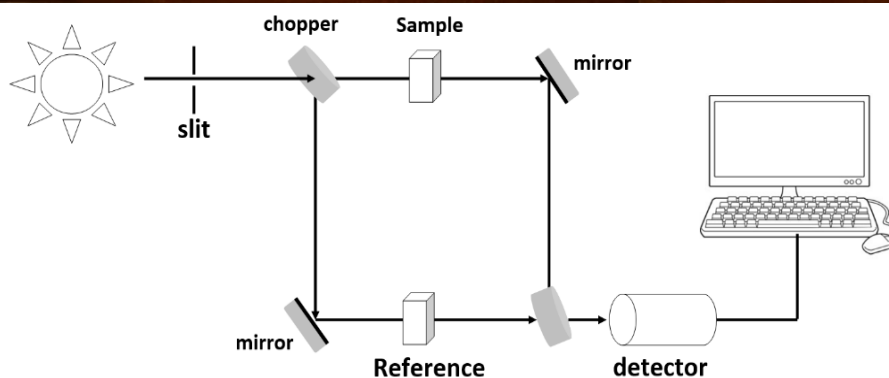


Figure (22): Image of (Shimadzu, model UV-3101), and schematic representation of the spectrophotometer.

In Figure (22), two identical cells are used for absorbance spectroscopy. One of them is filled with the reference solvent, while the other one is filled with the extracted dye sample solution. The cuvettes used have path length of 1-cm. As illustrated in Figure (22), the UV-visible light beam is divided into two beams of equivalent intensity and then directed to pass through the cells. Then, the detected signal is feed into a computer and seen as absorbance spectrum. The Absorbance is defined as:

$$A = \log_{10}\left(\frac{I_o}{I}\right) \quad (28)$$

Where I_o is the intensity of beam before irradiation and I is the intensity transmitted beam after sample irradiation.

3.3.2 Fluorescence of dye extracts

To obtain fluorescence spectra of the samples, an CCD spectrometer was used in the arrangement shown in Figure (23). The aim of fluorescence measurements is to study how active the sample as light emitter. A sample which deposit the absorbed photons as heat rather than emitting them might have large thermal lensing effect that can be observed in the z-scan spectrum. Anyhow, fluorescence spectra in combination with that of the absorbance may be used to assume certain energy levels diagram of the dye sample examined.

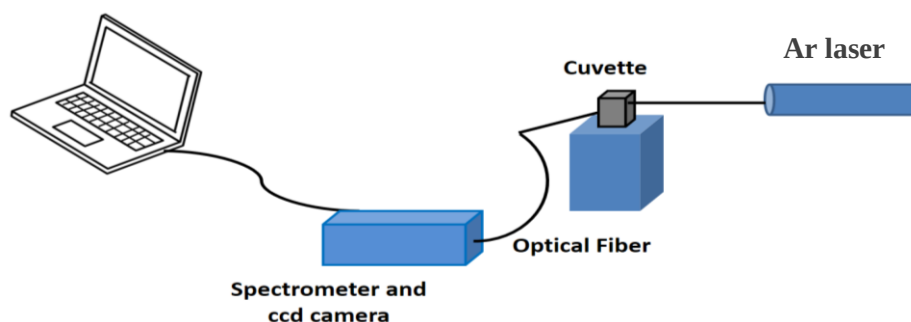


Figure (23): Schematic of the setup used in florescence measurements.

Argon-ion laser beam at wavelength 514 nm and power of 8 mW is directed to the quartz cuvette filled with the extracted dyes. The emission is collected by fibre an fed to a CCD spectrometer the signal is presented on PC as intensity versus wavelength curve.

3.3.3 Linear index of refraction measurement

Refractive index of the extracted natural dyes have been accomplished by using the digital refractometer shown in Figure (24). A drop of the solution is placed in the specified site and once the refractometer is run the index value is shown on the screen.



Figure (24): Digital Refractometer.

3.4 Constructing Z-scan Experimental Setup

Figure (11) shows schematics of experimental setup used for the close and open aperture Z-scan. which containing a spectrometer, two mirrors, 10 cm focal length lens, translation stage, thin sample, beam splitter, and light sources: HeNe laser ($\lambda = 633$ nm) or Argon ion laser ($\lambda = 488$ nm and 514 nm).

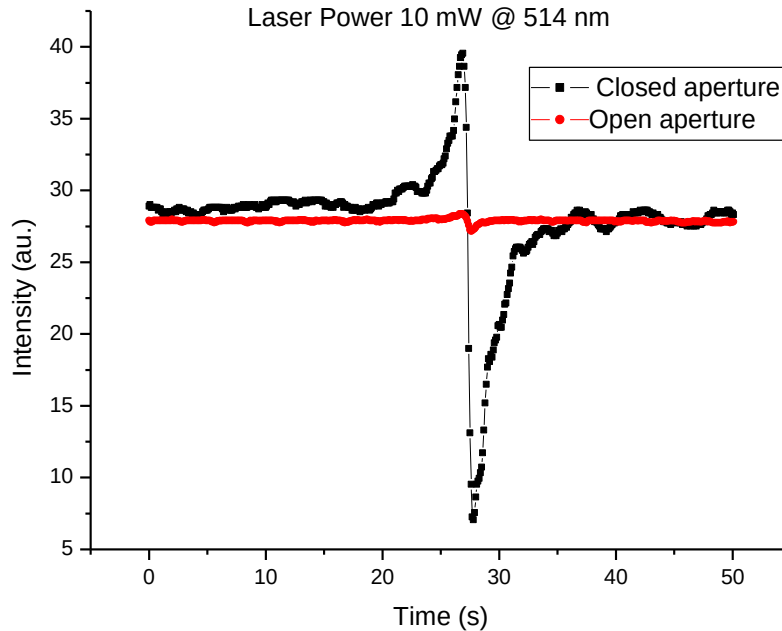


Figure (25): Z-scan transmittance versus time graph.

Laser beam power is measured using a digital light power meter. an aperture is then used to have a cleaned spot edge in order get a Gaussian laser beam. After that, the beam is aligned to a lens centre of 10 cm focal length by using two mirrors. The lens is positioned in front of the sample which is positioned on the translation stage whereby the sample would be able to move by a range of 5 cm pre-focal to 5 cm post-focal. Given that, the laser beam propagating out of the sample falls on a beam splitter which direct part of it to a lens that in turn focuses the laser beam so that all the transmitted beam will fall through the uncovered detector in order to act as open aperture arrangement. The other part of the laser beam gets directed to a detector covered with an aperture to act as closed aperture arrangement. Both detectors are interfaced to a PC which present the signals as transmittance versus time graph as shown on Figure (25).

3.5 Calculating Nonlinear Optical Parameters

In order to quantify nonlinear index of refraction, nonlinear absorption coefficient, and $\chi^{(3)}$. The raw spectrum obtained using z-scan set up (see Figure 25) is normalized and time is converted to displacement as shown in Figure 26. Next the spectrum is fitted with proper function (Equation 10) to obtain parameters that could be fed in equations as discussed in chapter 2.

As shown in Figure 26, the fitting parameters are P_1 , P_2 , and P_3 . As discussed in chapter 2, from these parameters $P_1 = \Delta\phi_o$, $P_2 = z_o$ and $P_3 = \Delta\Psi_o$ one can use equations 11, 12, 14 and 15 to calculate n_2 , β , and $\chi^{(3)}$. The calculated nonlinear parameters then can be represented graphically or in tables as function of excitation power, concentration, or excitation wavelength at specific solvent type.

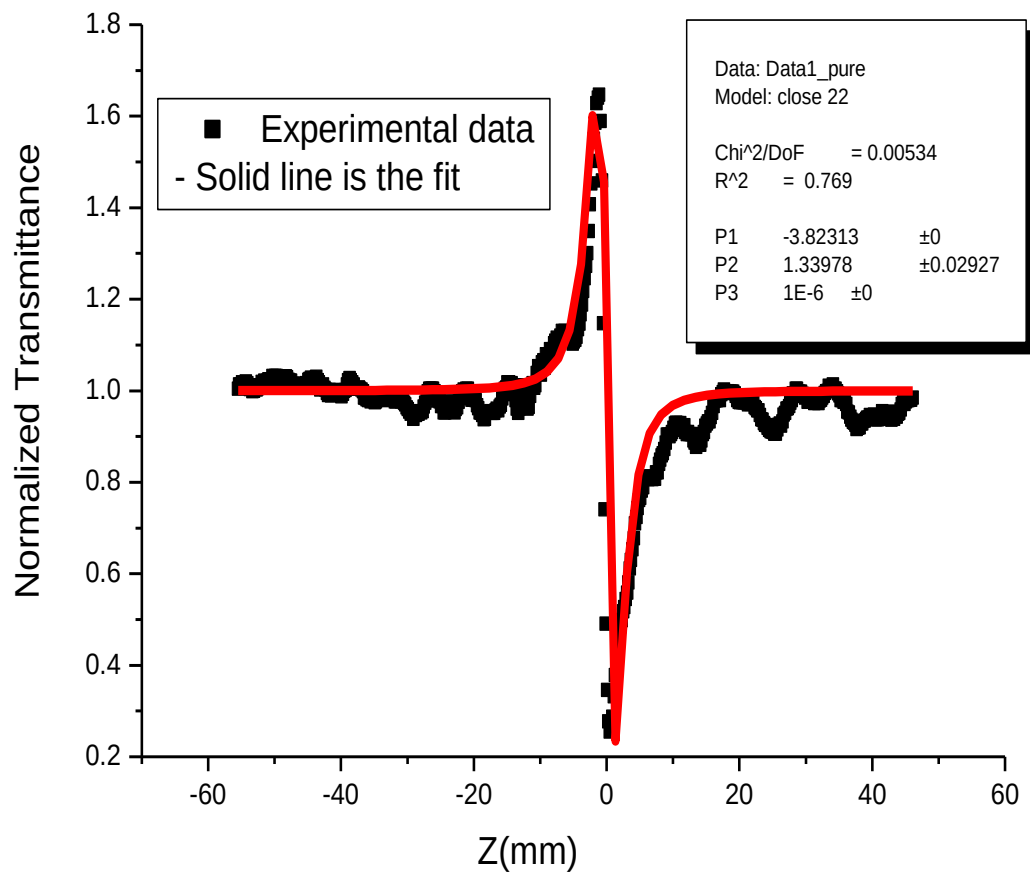


Figure (26): Normalized and fitted z-scan transmittance curve.

CHAPTER 4: RESULTS, DISSCUTION, AND RECOMMENDATIONS

4.1 Results and Discussion

4.1.1 Group 1: Berry

4.1.2 Group 2: Citrus

4.1.3 Group 3: Pomegranate

4.1.4 Group 4: Prunes

4.1.5 Group 5: Tropical

4.2 Summary of Results Analysis

4.3 Study Recommendations

CHAPTER 4: RESULTS, DISSCUTION AND RECOMMENDATIONS

Investigated samples have been classified in five groups. Each group has some common characteristics. All samples are z-scanned at room temperature. Over heating of sample due to laser beam has been avoided. Moreover, fresh sample is used in each z-scan measurement. Sample is used for one time to avoid effects of optically damaged or degraded material. Used sample is not returned back to the storing bottle to avoid any contaminations.

4.1 Group 1: Berry

In group 1, five materials extracted in different solvents, with concentrations and excited with three different wavelengths and at different beam power are investigated. These materials are fresh blueberry, dry blueberry, cranberry, and strawberry (Vainio, 2003). The linear absorption spectra for blueberry in ethanol at different concentrations is shown in Figure (27).

4.1.1 Linear Absorption Spectroscopy

4.1.1.1 Effect of concentration

Linear absorption spectroscopy of blueberry samples shown in Figure (27) at wavelengths beyond 700 nm absorbance is very weak. However, as wavelength is blue shifted towards 500 nm sample absorbance increases reaching a characteristic peak at wavelength 540 nm. After wavelength of 460 nm, sample absorbance gradually increases

without showing any other characteristic peaks. Moreover, increasing sample concentration enhances absorbance peak values mainly due to increased number of absorbers.

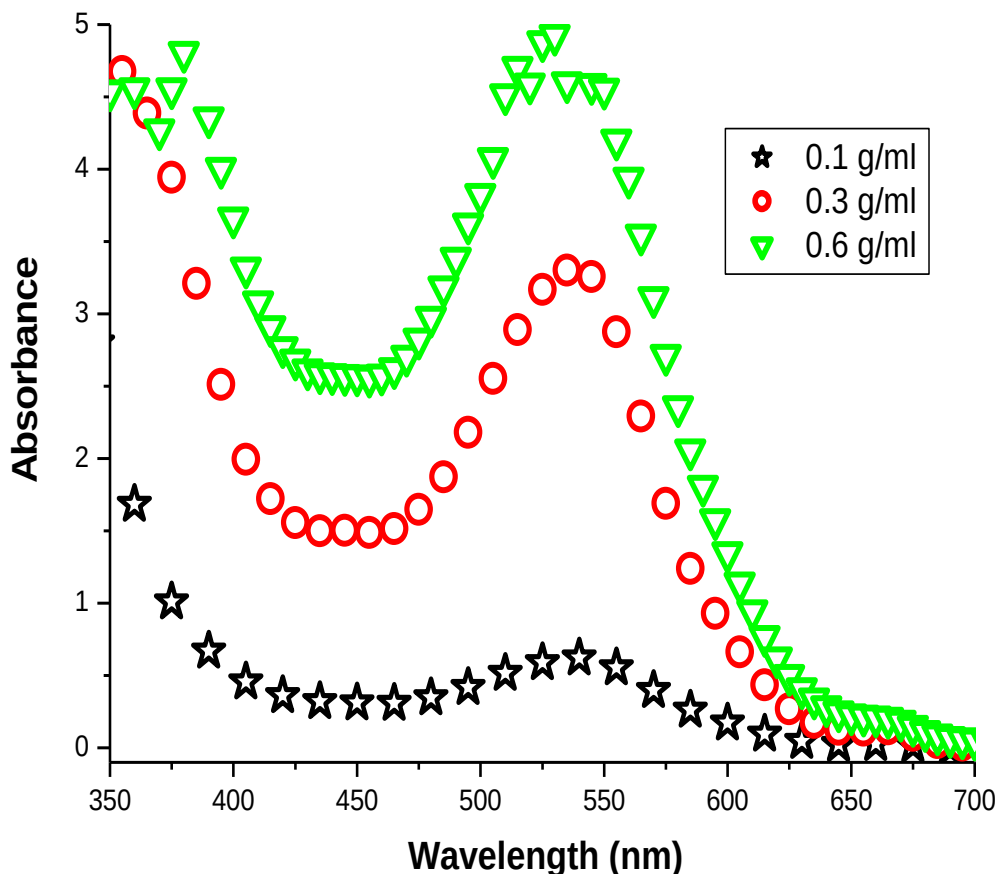


Figure (27): Linear absorption of blueberry extracted in ethanol at different concentrations.

Figure (28) presents the linear absorption spectroscopy of raisin and cranberry in methanol with different concentrations. Each dye extract has a characteristic peak, for raisins at $\lambda = 550$ nm and cranberry at $\lambda = 520$ nm. Moreover, increasing sample concentration enhances absorbance peak values. Also, at infrared range of the spectrum they show similar behaviour as blueberry and strawberry.

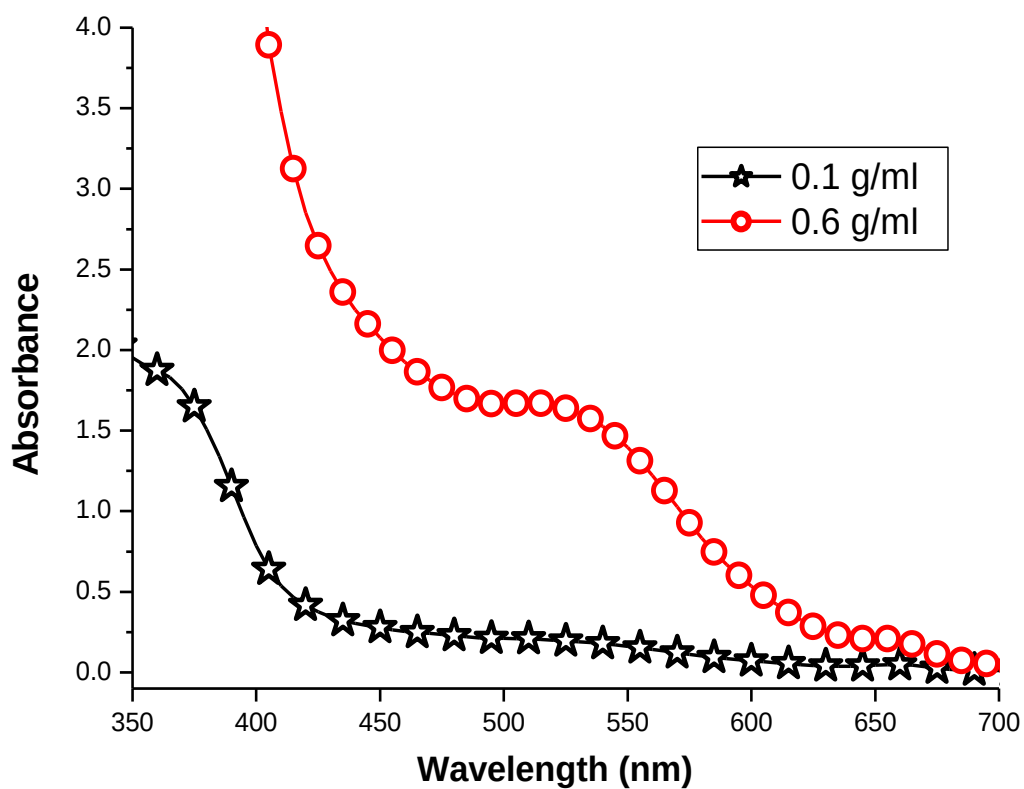
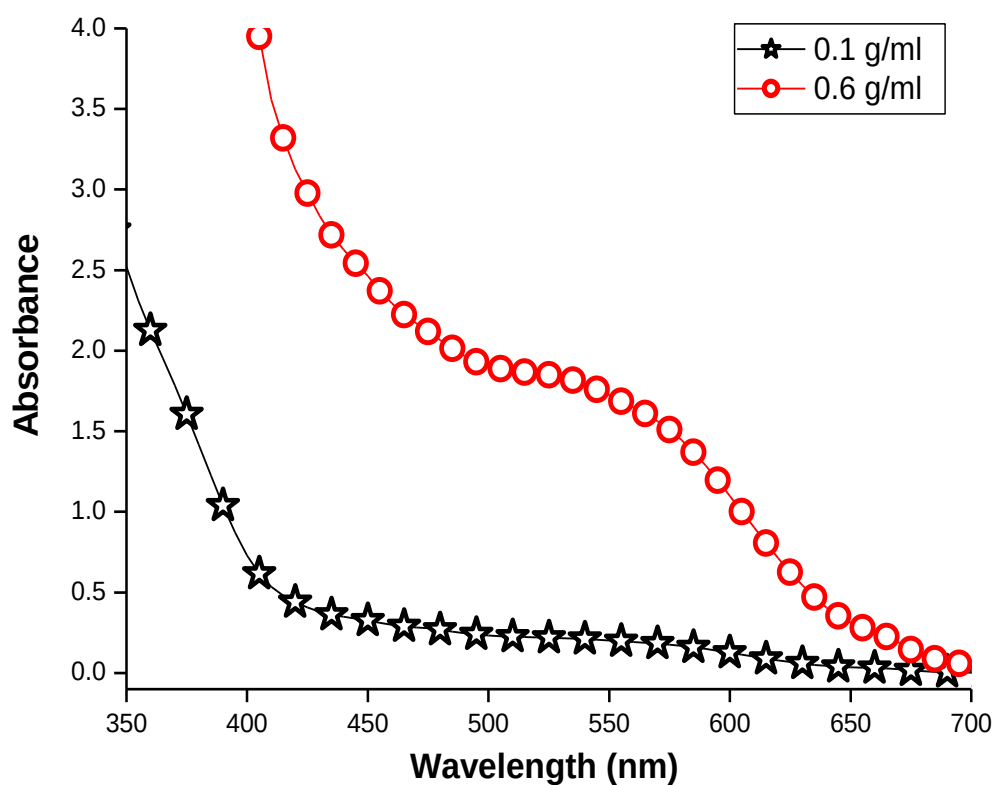


Figure28 a) Linear absorption spectra of raisin and b) Linear absorption spectra of cranberry extracted in methanol at two different concentrations.

Figure (29) shows the linear absorption spectroscopy of strawberry in methanol in different concentrations. Strawberry sample has good absorbance in visible range which starts absorption at 700 nm, small characteristic peak at 660 nm. As the concentration increases absorbance enhances. As in the case with blueberry, the infrared ($\lambda > 800$ nm) absorbance is very weak, while in visible and UV ranges absorbance is clearly very high.

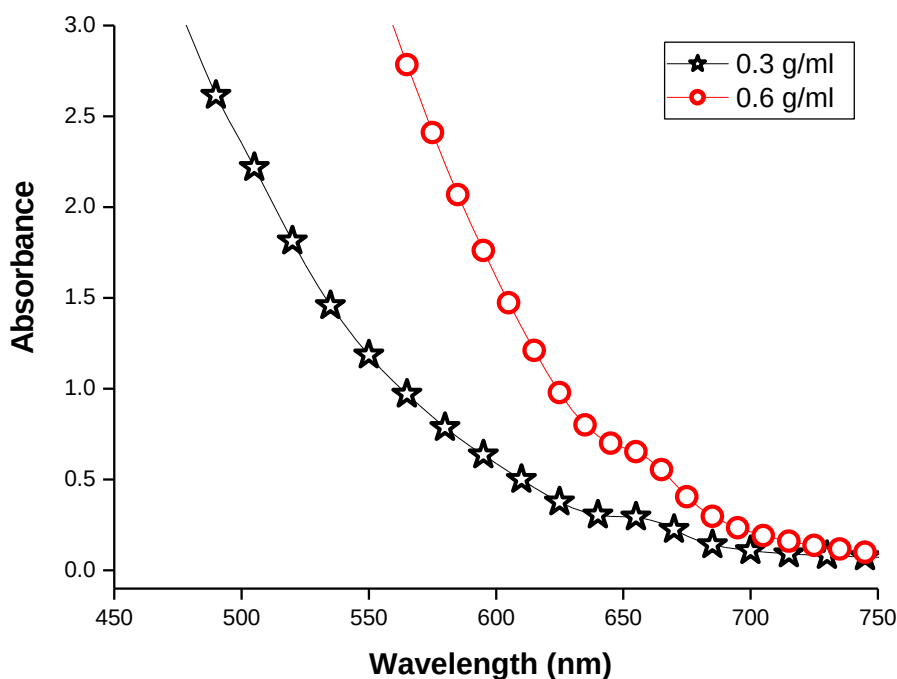


Figure (29): Linear absorption spectra of strawberry extracted in methanol at two different concentrations.

4.1.1.2 Effect of solvent

Effect of solvent used to extract samples have been studied and shows a remarkable difference in absorption spectrum. As an example, Figure (30) shows the effect of solvent on absorbance of the sample at specific concentration 0.1 g/ml. Addition of small amount of HCl acid to ethanol enhances the absorbance of the sample such that characteristic absorption peak at 540 nm is overwhelmed. With acetone the absorbance

peak shifted to 350 nm. On the other hand, both methanol and ethanol have absorbance peak at wavelength of 540 nm with weaker one for methanol sample.

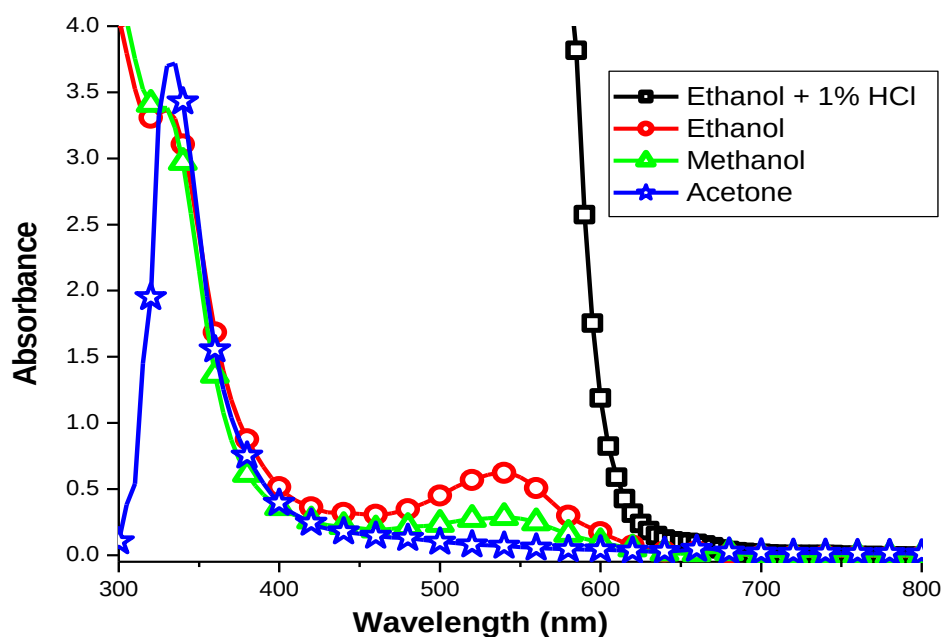


Figure (30): Linear absorption spectra of blueberry extracted in ethanol with 1% HCl acid, ethanol methanol and acetone at specific concentration of 0.1 g/ml.

4.1.1.3 Effect of materials

Effect of extracted dye source (material) at same concentration using the same solvent is presented in Figure (31). Berry in methanol as blueberry, raisin and cranberry at 0.1 g/ml of concentration have similar absorbance spectrum as shown in figure (31-a). There is a slight difference in the peak wavelength at 580 nm and 350. In figure (31-b) materials show different absorption level, but the behaviour is almost the same where above 750 nm its very weak. At the visible range it has its own characteristic absorption peak and quite good level of absorbance.

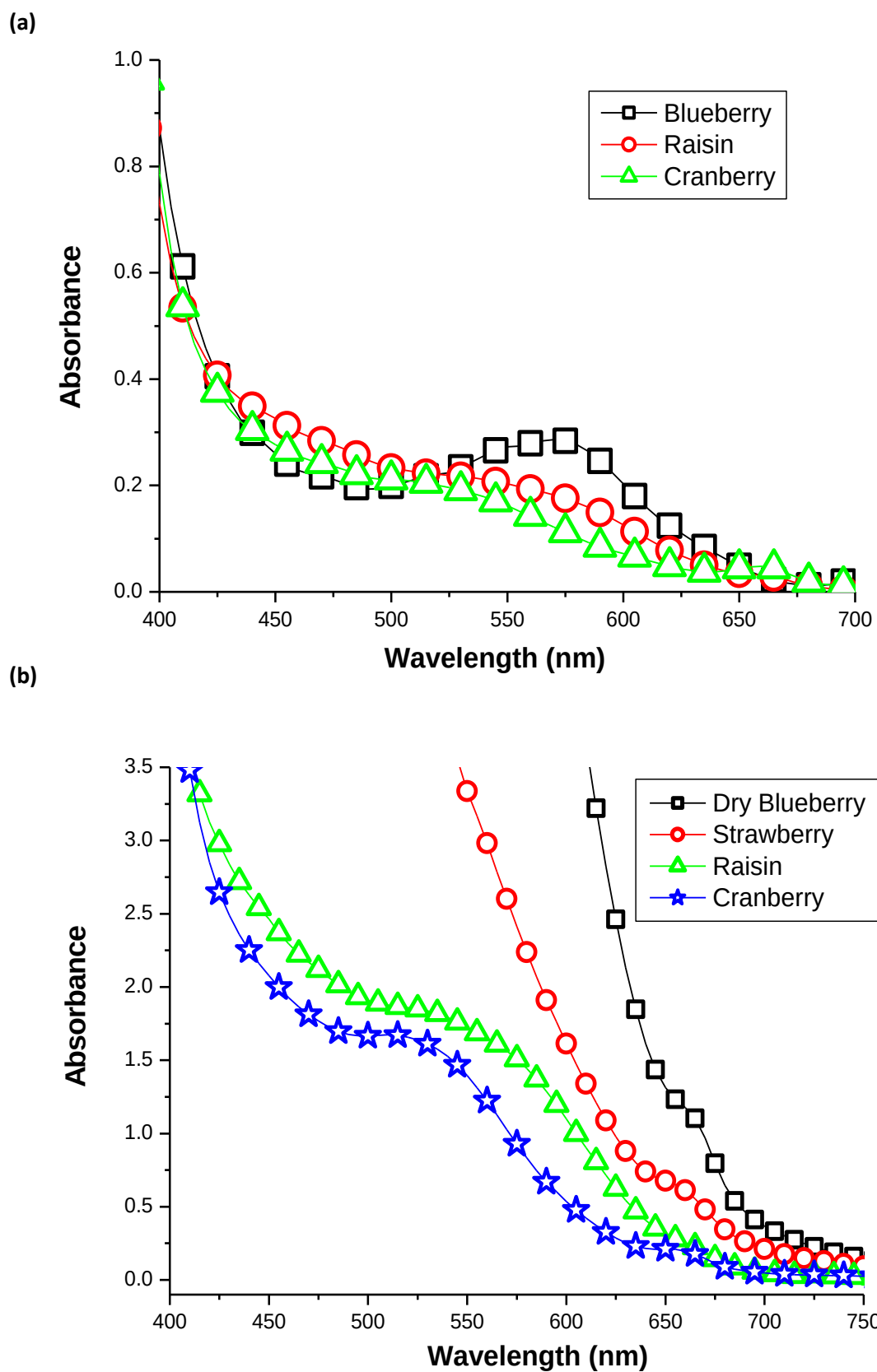


Figure (31): Linear absorption spectra of berry extracted in methanol at a) 0.1 g/ml concentration, and b) 0.6 g/ml concentration.

4.1.2 Fluorescence Spectroscopy

While exciting samples during Z-scan measurements, it has been found that samples are fluorescing at different strength depending on the extract. Below is the investigation carried out to study the fluorescence spectra of each sample under different conditions.

4.1.2.1 Effect of concentration

Figure (32) shows the fluorescence spectra for blueberry in ethanol at different concentrations. The samples shown remarkable fluorescence activity with a characteristic peak wavelength at 672 nm irrespective of concentration. As the concentration increases fluorescence intensity increases due to increased number of emitters. However, higher concentration of sample enhances absorption of the emitted photons and hence lower level of recorded intensity as presented in Figure (33).

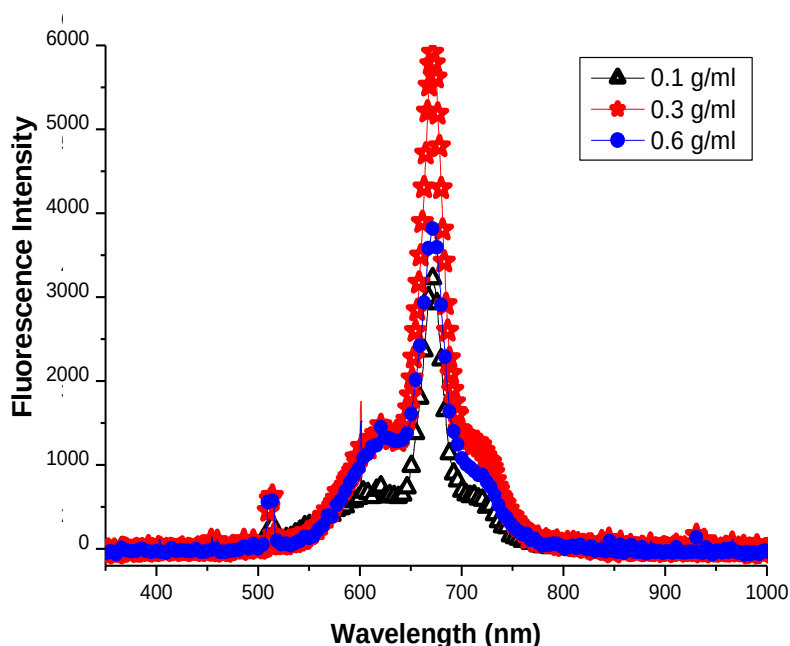


Figure (32): Fluorescence spectra of blueberry extracted in ethanol at three different concentrations.

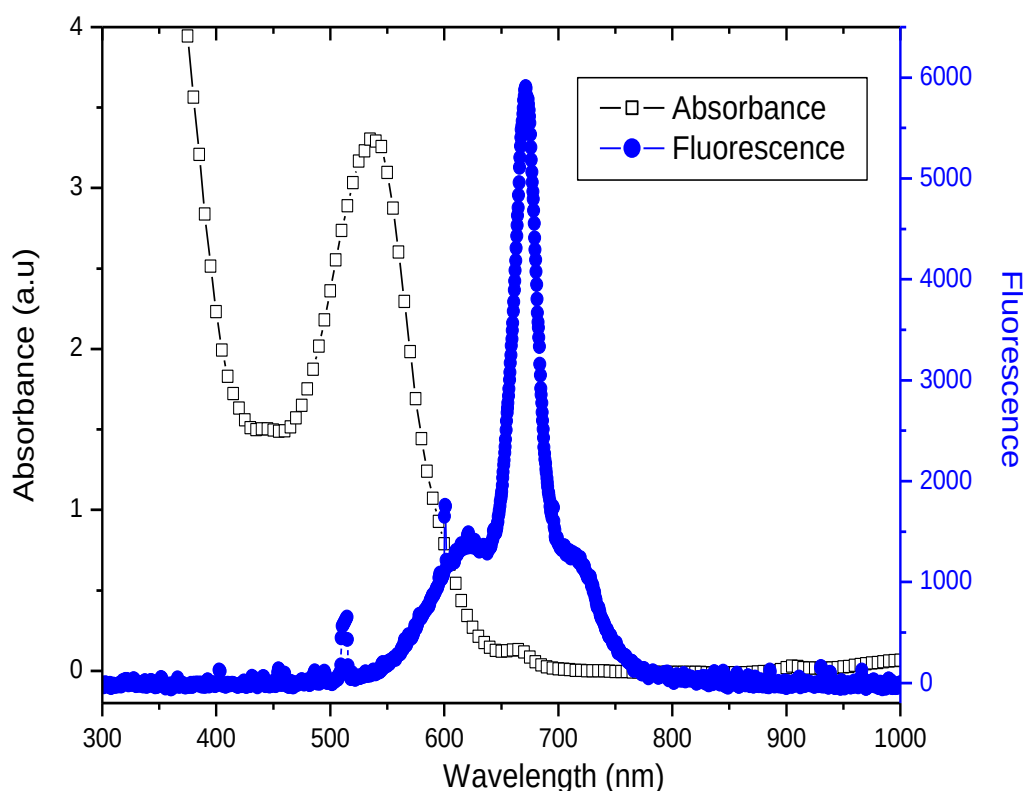


Figure (33): Fluorescence and absorption spectra of extract of concentration 0.3 g/ml from blueberry extracted in ethanol.

Figure (33) shows the overlapping between the absorbance and fluorescence curve is very little. photon emitted by fluorescence at the excitation wavelength is weak. So, the contribution due to fluorescence of material is negligible.

Figure (34) shows the fluorescence spectra for strawberry extracted in methanol at two different concentrations. The sample shows remarkable fluorescence behaviour with a main peak at 650 nm and shoulder peak at 725 nm. As the concentration increases (0.6 g/ml) fluorescence intensity decreases due to enhanced absorbance at this concentration.

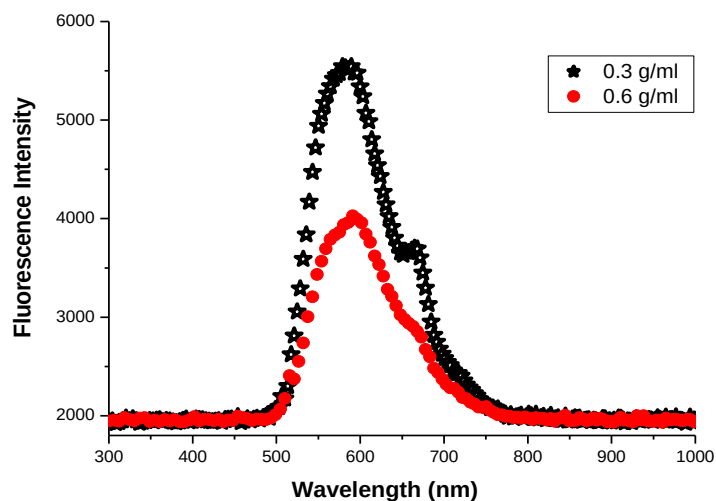


Figure (34): Fluorescence spectra of strawberry extracted in methanol at two different concentration.

For raisin extracted in methanol at different concentrations, Figure (35) shows the fluorescence spectra. At 0.1 g/ml concentration a remarkable fluorescence behaviour is seen with peak wavelength at 625 nm and a shoulder one at 723 nm. While, with 0.6 g/ml concentration a fluorescence behaviour with peak at 647 nm and 723 nm. We think after referring to Figure (28-a), the fluorescence peak at 625 nm/647 nm are much higher than that at 735 nm mainly due to higher absorbance of samples below 700 nm.

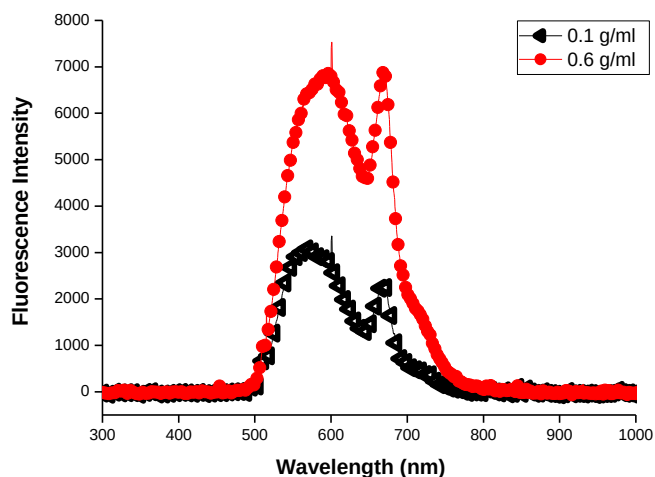


Figure (35): Fluorescence spectra of raisin extracted in methanol at two different concentrations.

Figure (36) shows the fluorescence spectra for cranberry in methanol at different concentration. The samples show remarkable fluorescence behaviour with peak wavelength at 655 nm and 725 nm. Moreover, as the concentration increases fluorescence intensity increases.

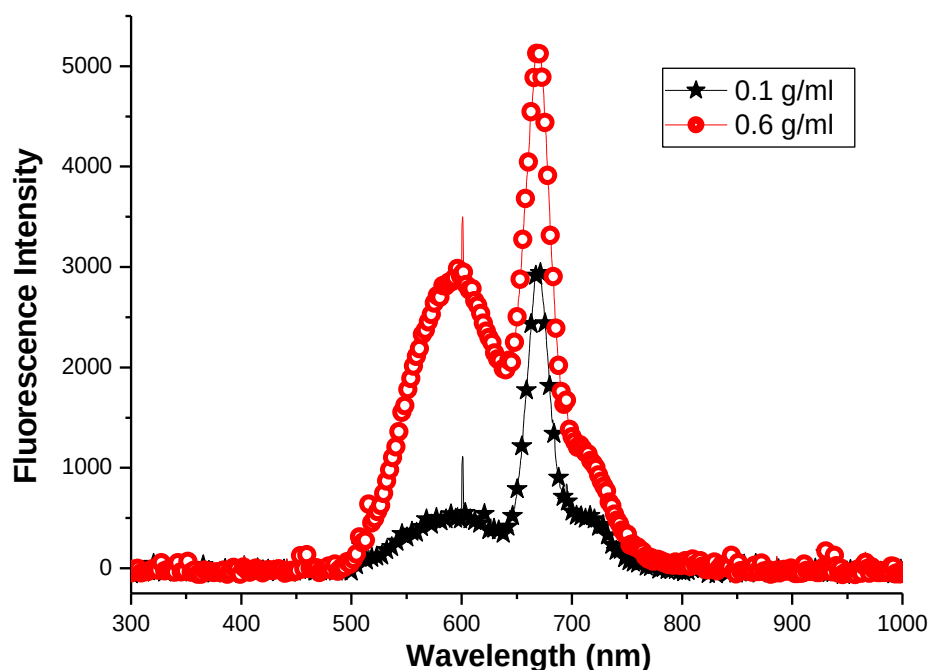


Figure (36): Fluorescence spectra of cranberry extracted in methanol at two different concentrations.

4.1.2.2 Effect of solvent

Choice of solvent shows a remarkable effect on fluorescence behaviour of the sample as shown in Figure (37-a). Addition of acid to ethanol as solvent not only affected the absorbance of the sample (e.g. 0.1 g/ml) but also resulted in clear quenching of fluorescence intensity as can be visually noticed in Figure (37-a).

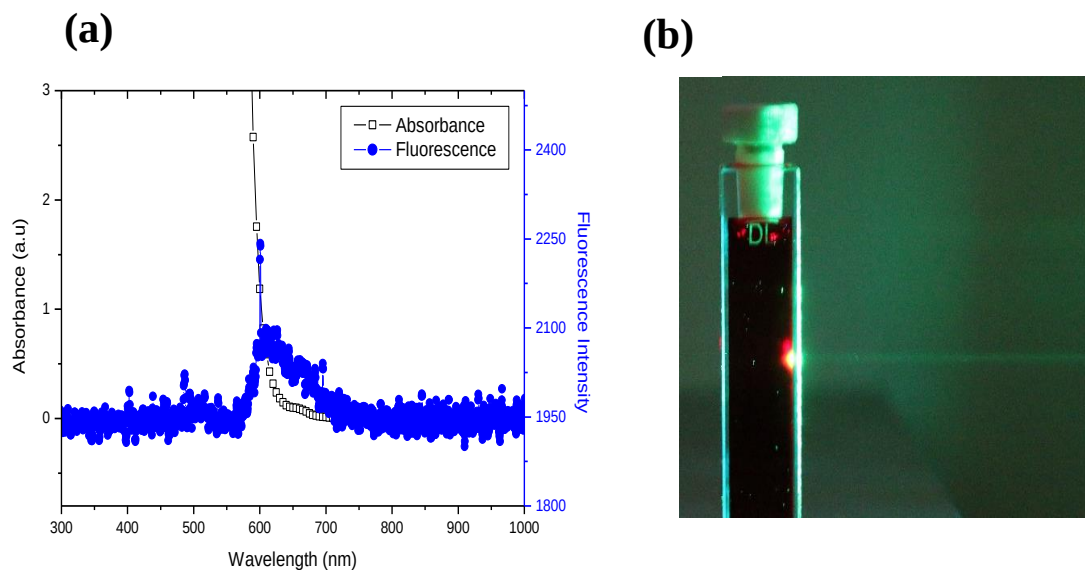


Figure (37): Fluorescence and absorbance of blueberry in Methanol and Acid.

Figure (38) shows the fluorescence spectra for blueberry at 0.1 g/ml with different solvent. The sample shows remarkable fluorescence behaviour with peak at 672 nm. Ethanol solvent enhances fluorescence intensity while addition of HCl acid to ethanol suppresses the fluorescence intensity.

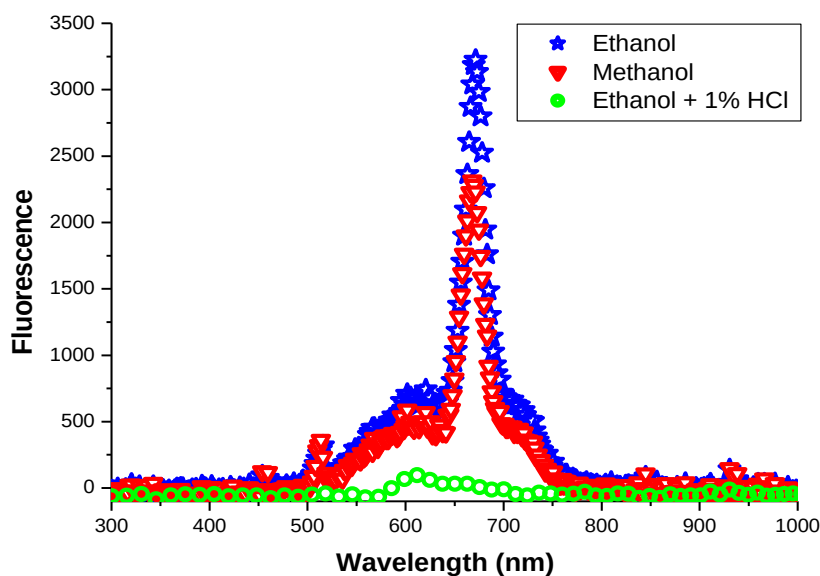


Figure (38): Fluorescence spectra of blueberry at concentration of 0.1 g/ml in three different solvent.

4.1.2.3 Effect of material

Each material shows characteristic fluorescence spectra when excited at same beam power and laser, typical example is presented in Figure (39).

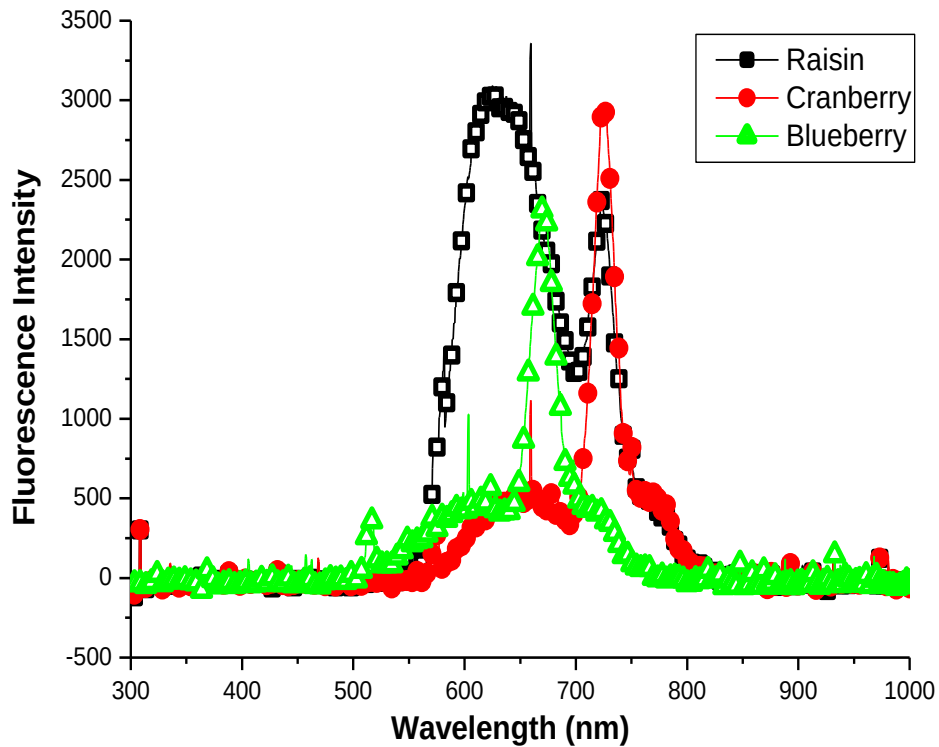


Figure (39): Fluorescence spectra of different extracts in methanol with concentration of 0.1 g/ml.

4.1.3 Nonlinear Index of Refraction

Using Z-scan technique to characterize nonlinear index of refraction, investigation of many factors is detailed below. The calculated value of n_2 is presented. Raw data has been fitted with one of the proper model suggested in the literatures as detailed in chapter 2.

4.1.3.1 Effect of excitation power level

For sample extracts in methanol, ethanol and acetone at fixed concentration of 0.1 g/ml, Figure (40-a and 40-b), show the variation of nonlinear index of refraction versus excitation power at $\lambda = 514$ nm. As excitation power increases n_2 value decreases in a nonlinear way and beyond 6 mW the variation in n_2 value vanishes such that it reaches a constant value. This behaviour is a clear indication of capability of sample to be used as an optical limiter (Henari and Jasim, 2012, Henari, et al., 2013). This mechanism for optical limiting might arise from thermal lens effect as it could be concluded from Figure (41).

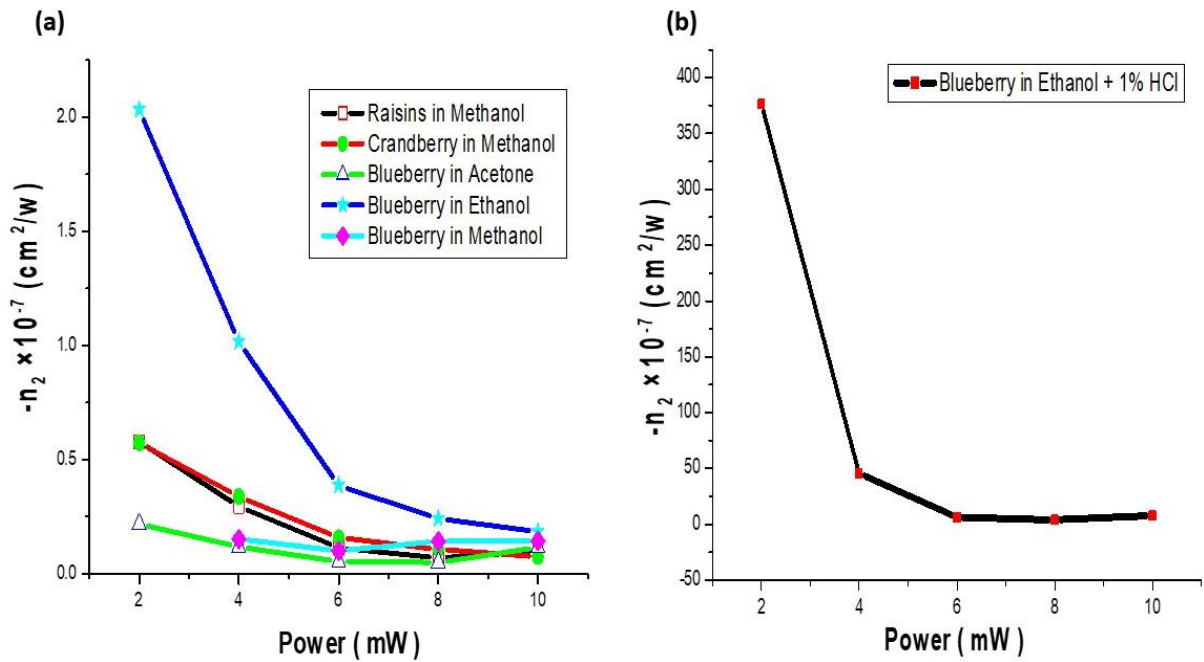


Figure (40): Variation of n_2 as function of excitation power ($\lambda = 514$ nm) with extract concentration 0.1 g/ml.

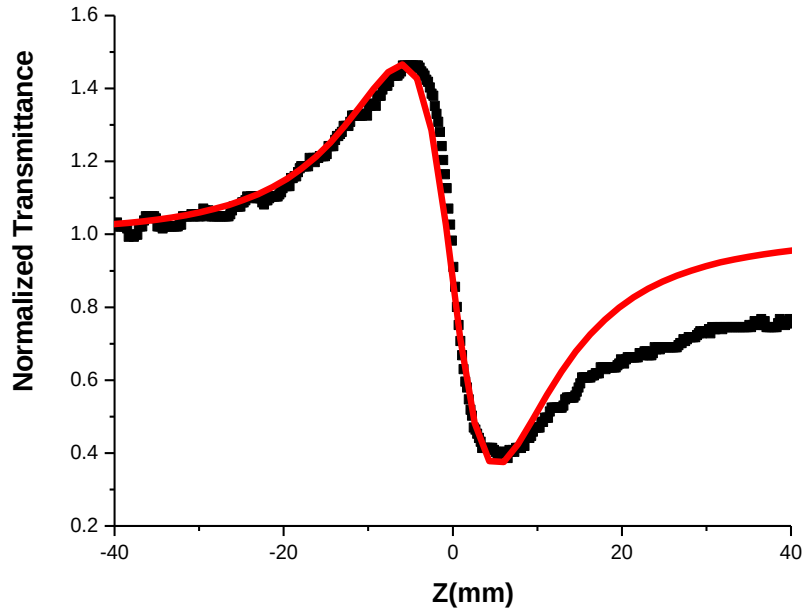


Figure (41): Normalized transmittance curve, dots are the data while solid line is the fit.

Similar behaviour observed in Figure (40) have been observed with other concentrations of extracts as summaries in Table 9 and Table 10.

Table (9): Nonlinear parameters for berries with concentration of 0.1g/ml extracted in methanol and scanned using Ar ion laser at 514 nm for closed aperture configuration.

Power mW	Sample	Fitting parameter $P_1(\Delta\phi)$	Fitting parameter $P_2(z_0)$ mm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m ²	$n_2 \times 10^{-7}$ cm ² /W
2	Raisins	-0.712	0.750	1.110	1.040	-0.578
	Cranberry	-0.672	0.790	1.140	0.984	-0.573
4	Raisins	-0.720	0.757	1.110	2.050	-0.295
	Cranberry	-0.979	0.639	1.020	2.430	-0.338
6	Raisins	-0.453	0.698	1.070	3.340	-0.114
	Cranberry	-0.672	0.653	1.030	3.570	-0.158
8	Raisins	-0.345	0.740	1.100	4.200	-0.069
	Cranberry	-0.425	0.930	1.230	3.340	-0.107
10	Raisins	-0.619	0.732	1.100	5.310	-0.098
	Cranberry	-0.425	0.930	1.230	3.340	-0.107

At concentration of 0.6 g/ml Table (10) shows that dry blueberry extract has the largest n_2 values under different excitation power and strawberry extract comes second.

Table (10): Nonlinear parameters for berries with concentration of 0.6 g/ml extracted in methanol and scanned using Ar ion laser at 514 nm for closed aperture configuration.

Power mW	Sample	Fitting parameter $P_1(\Delta\Phi)$	Fitting parameter $P_2(z_0)$ mm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m ²	$n_2 \times 10^{-7}$ cm ² /W
2	Raisins	- 7.857	0.669	1.050	1.160	- 6.818
	Cranberry	- 5.299	0.602	0.993	1.290	- 4.052
	Dry blueberry	-10.880	0.701	1.070	1.110	- 12.870
	Strawberry	- 7.430	0.711	1.080	1.090	- 8.594
4	Raisins	- 5.457	0.720	1.090	2.160	- 2.548
	Cranberry	- 6.111	0.954	1.250	1.630	- 3.700
	Dry blueberry	-16.796	0.682	1.060	2.280	- 9.662
	Strawberry	-15.099	0.731	1.090	2.130	- 8.973
6	Raisins	-3.992	1.411	1.520	1.650	- 2.435
	Cranberry	- 4.092	1.204	1.400	1.940	- 2.085
	Dry blueberry	-16.655	0.769	1.120	3.030	- 7.200
	Strawberry	-12.936	1.075	1.330	2.170	- 7.541
8	Raisins	- 3.600	1.567	1.600	1.980	- 1.828
	Cranberry	- 3.985	1.248	1.430	2.490	- 1.579
	Dry blueberry	-15.606	1.046	1.310	2.970	- 6.886
	Strawberry	- 8.591	1.536	1.590	2.020	- 5.367
10	Raisins	- 2.923	0.833	1.170	4.670	- 0.631
	Cranberry	- 1.997	0.943	1.240	4.120	- 0.478
	Dry blueberry	- 11.006	0.856	1.180	4.540	- 3.178
	Strawberry	- 7.637	1.897	1.760	2.050	- 4.713

Calculations presented in Tables (9) and (10), clearly indicate that this group of berry posse negative value of nonlinear index of refraction n_2 demonstrating self-defocusing effect (see Figure (41) as an example). In Table (9), it has been that at excitation power of 2 mW both raisins and cranberry extract have similar n_2 . However, as excitation power increases below cranberry n_2 value become larger than that for raisins.

4.1.3.2 Effect of concentration

Figure (42) shows n_2 increasing as the concentration increases. This is due to the increase in the density (number) of dye molecules. These findings are in good agreement with the reported resulted (Dhinaa and Pallnisamy, 2010; Rashidian, et al., 2008). The optical nonlinearity of berry dyes attributed to thermal effect of laser (Rekha and Ramalingam, 2009; Yakop & Badran, 2014).

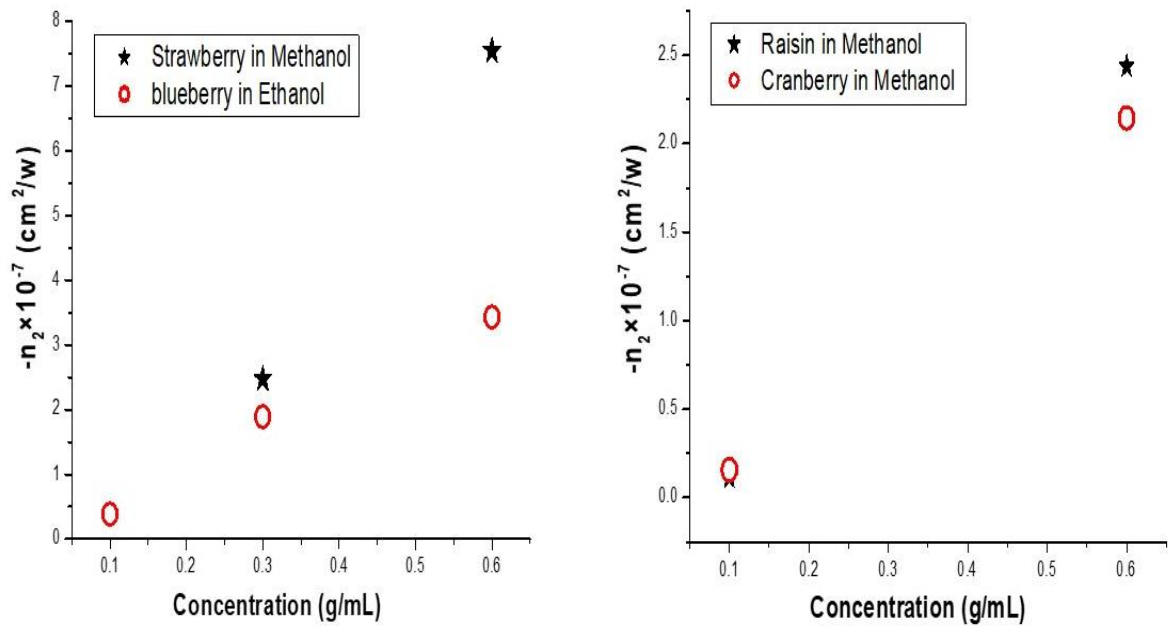


Figure (42): Plot of n_2 versus concentration for barriers extracts.

4.1.3.3 Effect of excitation wavelength

Different excitation wavelengths at beam power of 6 mW have been used to investigate extracts nonlinear index of refraction are presented in Tables (11, 12, and 13). No distinct behaviour has been noticed. Therefore, each wavelength has its own effect regardless the change in extracted dye concentrations. Values of n_2 for berry at 0.1 g/ml concentration are very close because of similarity of linear absorption as presented in Figure (29-a).

Table (11): Calculated nonlinear parameters for berries at concentration of 0.1 g/ml extracted in methanol and scanned by Ar ion laser ($\lambda = 488$ nm and 514 nm) and HeNe laser ($\lambda = 633$ nm). $P = 6$ mW for closed aperture configuration.

Sample	Excitation wavelength nm	Fitting parameter $P_1 (\Delta\phi)$	Fitting parameter $P_2 (z_0)$ mm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m ²	$n_2 \times 10^{-7}$ cm ² /W
Cranberry	488	- 0.992	0.675	1.020	3.640	- 0.217
	514	- 0.672	0.653	1.030	3.570	- 0.158
Raisin	488	- 1.628	0.570	0.941	4.310	- 0.302
	514	- 0.453	0.698	1.070	3.340	- 0.114
Blueberry	488	-1.727	0.534	0.911	4.600	- 0.299
	514	-0.221	1.255	1.430	1.860	- 0.101

Table (12): Nonlinear parameters for blueberry at 0.1 concentration in ethanol with acid scanned using Ar laser at (514 – 488) nm and HeNe laser ($P = 6$ mW) for closed aperture configuration.

λ nm	Fitting parameter $P_1 (\Delta\phi)$	Fitting parameter $P_2 (z_0)$ mm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ (W/m ²)	α_0 m ⁻¹	$n_2 \times 10^{-7}$ cm ² /W
488	-9.960	0.931	1.200	2.640	1381.56	- 5.403
514	-26.41	0.442	0.851	5.270	944.30	- 6.339
633	-0.858	5.315	3.270	0.315	33.85	- 2.790

Table (12) shows that for blueberry extract, n_2 has higher value at $\lambda = 514$ nm than at 633 nm. In table (13), values of n_2 for berry at 0.6 g/ml concentration change by changing the excitation wavelength. Dry blueberry samples have higher value of n_2 than strawberry, raisin and cranberry at wavelength 488 nm, 514 nm and 633 nm this is because the dry blueberry have higher value of linear absorption as shown in Figure (31).

Table (13): Nonlinear parameters for berry extract at 0.6 g/ml concentration in methanol scanned using Ar laser at (514 – 488) nm and HeNe laser ($P = 6$ mW) for closed aperture configuration.

Sample	Excitation wavelength nm	Fitting parameter $P_1(\Delta\Phi)$	Fitting parameter $P_2(z_0)$ mm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m ²	$n_2 \times 10^{-7}$ cm ² /W
Cranberry	488	- 3.838	0.665	1.020	3.700	- 0.972
	514	- 4.092	1.204	1.404	1.940	- 2.085
	633	- 0.801	1.328	1.640	1.260	- 0.664
Raisin	488	- 7.939	0.556	0.929	4.420	- 1.733
	514	- 3.992	1.411	1.520	1.650	- 2.435
	633	- 1.570	0.848	1.310	1.970	- 0.846
Strawberry	488	-37.806	0.642	0.999	3.830	- 11.960
	514	-12.936	1.075	1.330	2.170	- 7.541
	633	-4.104	7.075	3.780	0.237	- 19.130
Dry blueberry	488	-13.208	0.904	1.190	2.720	- 6.202
	514	-16.655	0.769	1.120	3.030	- 7.203
	633	- 6.668	7.855	3.980	0.213	- 38.69

Table (14) shows that at excitation wavelength of 514 nm and 633 nm, nonlinear refractive index increases as concentration increases (see Figure (42)). While, at $\lambda = 488$ nm n_2 increases with increasing concentration from 0.1 g/ml to 0.3 g/ml, but decreases at 0.6 g/ml.

Table (14): Nonlinear parameters blueberry in ethanol at different concentration by using Ar laser at (514 – 488) nm and HeNe laser (P = 6mW) at for closed aperture configuration.

Concentration	Excitation wavelength nm	Fitting parameter $P_1 (\Delta\phi)$	Fitting parameter $P_2 (z_0)$ mm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m ²	α_0 m ⁻¹	$n_2 \times 10^{-7}$ cm ² /W
0.1 g/ml	488	-1.258	0.839	1.140	2.930	90.0	- 0.349
	514	-0.607	1.703	1.670	1.370	125.3	- 0.387
	633	-0.537	2.471	2.230	0.678	8.3	- 0.802
0.3 g/ml	488	-4.270	1.080	1.300	2.280	464.7	- 1.821
	514	-2.569	1.527	1.580	1.530	665.5	- 1.888
	633	-0.836	6.798	3.700	0.246	40.1	- 3.490
0.6 g/ml	488	-3.315	0.999	1.250	2.460	778.5	- 1.505
	514	-3.320	1.795	1.710	1.300	1082.5	- 3.427
	633	-1.231	8.915	4.240	0.188	77.1	- 6.862

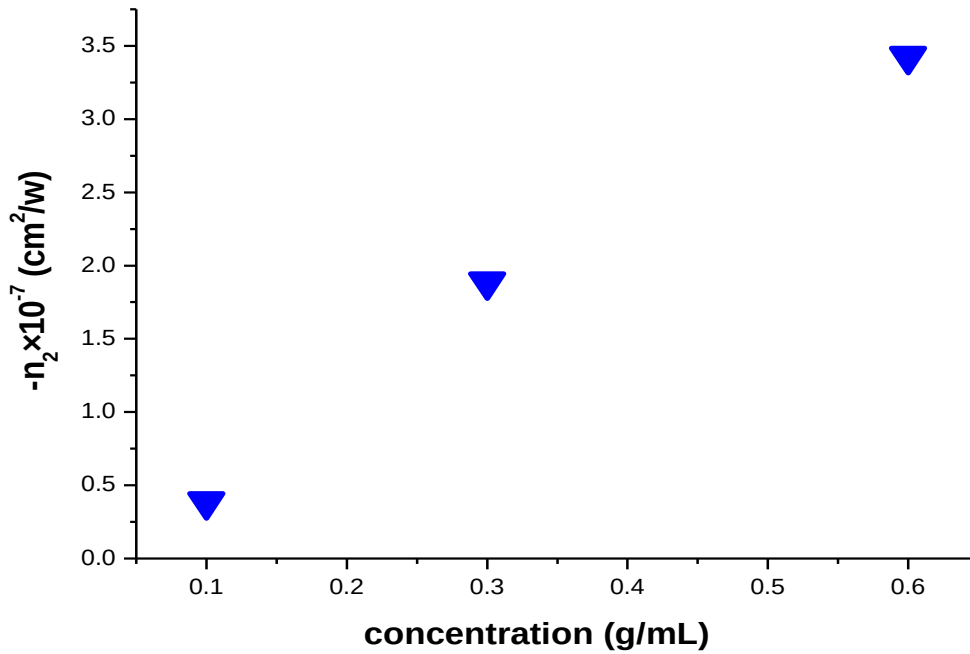


Figure 43: Variation of n_2 with concentration extracted in ethanol excited at 514 nm (P= 6 mW).

Table (15), shows that strawberry dye extracted in methanol at concentration of 0.3 g/ml possess comparable value of n_2 when sample scanned at 488 nm and 514 nm, but, when 633 nm excitation wavelength is used n_2 value is more than 4 times those at 488 nm and 514 nm.

Table (15): Nonlinear parameters strawberry extracted in methanol at concentration 0.3 g/ml ($P = 6\text{mW}$) for closed aperture configuration.

Excitation wavelength nm	Fitting parameter $P_1 (\Delta\phi)$	Fitting parameter $P_2 (z_0)$ mm	$w_0 \times 10^{-5}\text{m}$	$I \times 10^7 \text{ W/m}^2$	$\alpha_0 \text{ m}^{-1}$	$n_2 \times 10^{-7} \text{ cm}^2/\text{W}$
488	-5.880	0.993	1.240	2.480	602.1	- 2.456
514	-3.852	1.470	1.550	1.590	448.6	- 2.468
633	-2.149	8.512	4.140	0.197	73.9	- 11.420

Figure (44) shows examples of the fitted z-scan plectra for strawberry sample (0.3 g/ml) when z-scanned with beam wavelength 488 nm, 514 nm, and 633 nm and excitation power of 6 mW.

To sum up the findings, one can conclude from the above tabulated measured and calculated data:

- Nonlinear refractive index increases as the excitation beam power increases.
- Nonlinear refractive index increases as sample concentration increases.
- For beam wavelength 633 nm: At 0.1 g/ml no effect has been observed. The case of blueberry extract in ethanol with acid n_2 has smaller value.
- The n_2 values for at excitation wavelength 488 nm are comparable to those at 514 nm.

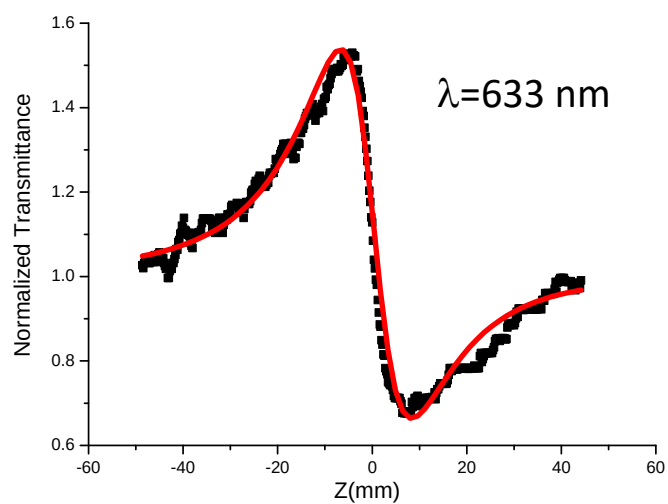
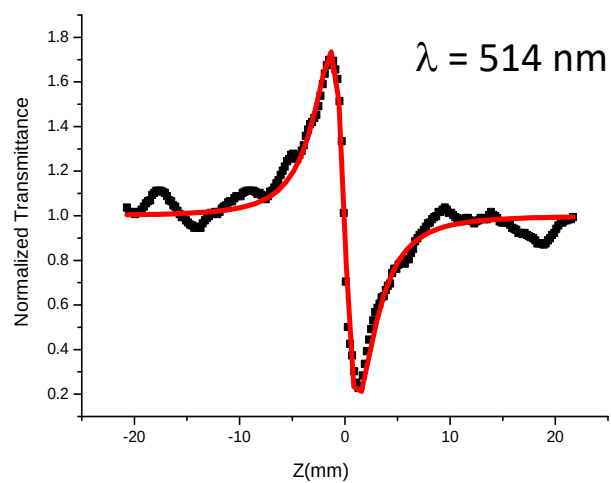
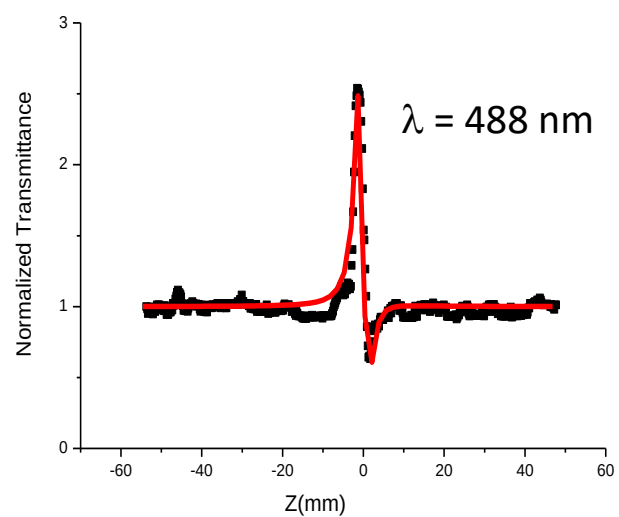


Figure (44): Fitted z-scan transmittance curves for strawberry sample (0.3 g/ml) when z-scanned with beam of wavelengths 488 nm, 514 nm, and 633 nm and excitation power of 6 mW.

Figure (45) presents images of the laser spot while scanning the sample at wavelength 514 nm and laser beam power 6 mW. The n_2 sign can be visually figured out from the variation of the beam spot size.

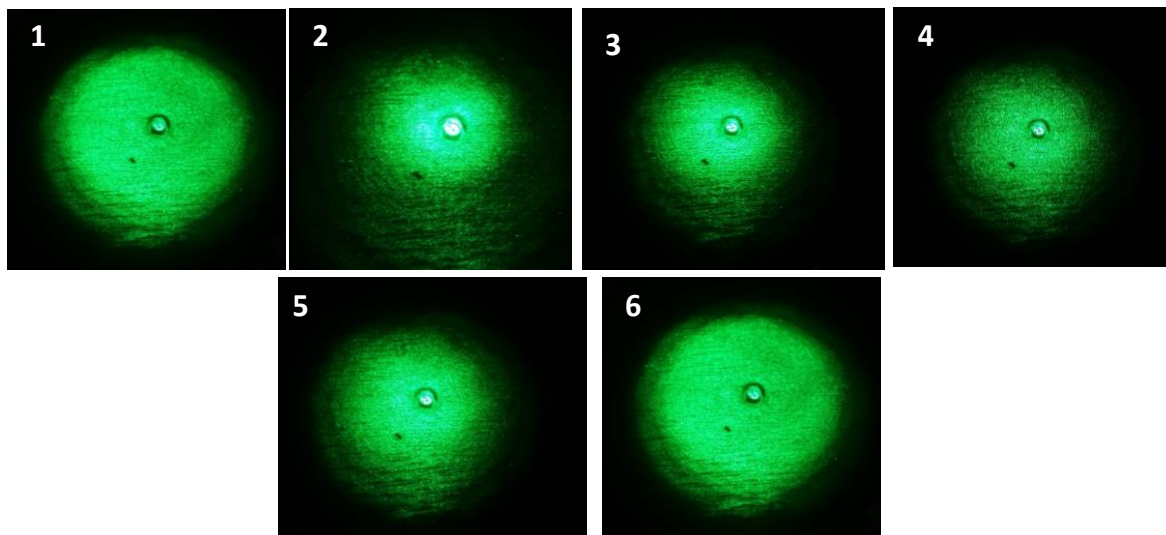


Figure (45): Images of laser spot size as the sample scanned with beam of wavelength 514 nm and power 6 mW.

4.1.4 Nonlinear Absorption Coefficient

4.1.4.1 Effect of excitation power level

Figure (46) shows the variation of nonlinear absorption coefficient with excitation power at fixed $\lambda = 514$ nm. The samples have concentration of 0.3 g/ml in which methanol is used to extract strawberry, while ethanol is used to extract blueberry. As excitation power increases β value decreases. These results are in good agreement with the reported resulted (Pramodini, et al., 2013). However, beyond 6 mW excitation power, the change in β become very small. Blueberry shows saturable absorption (SA) behaviour at excitation power of 2 mW, However, at power ranges between 4 mW to 10 mW reverses saturable absorption

(RSA) behaviour is dominating. For strawberry dye extracts SA at power ranges between (2-4) mW are clear, but RSA at power ranges between (6–10) mw is observed. These results are in good agreement with what was reported by (Srinivas, et al., 2003).

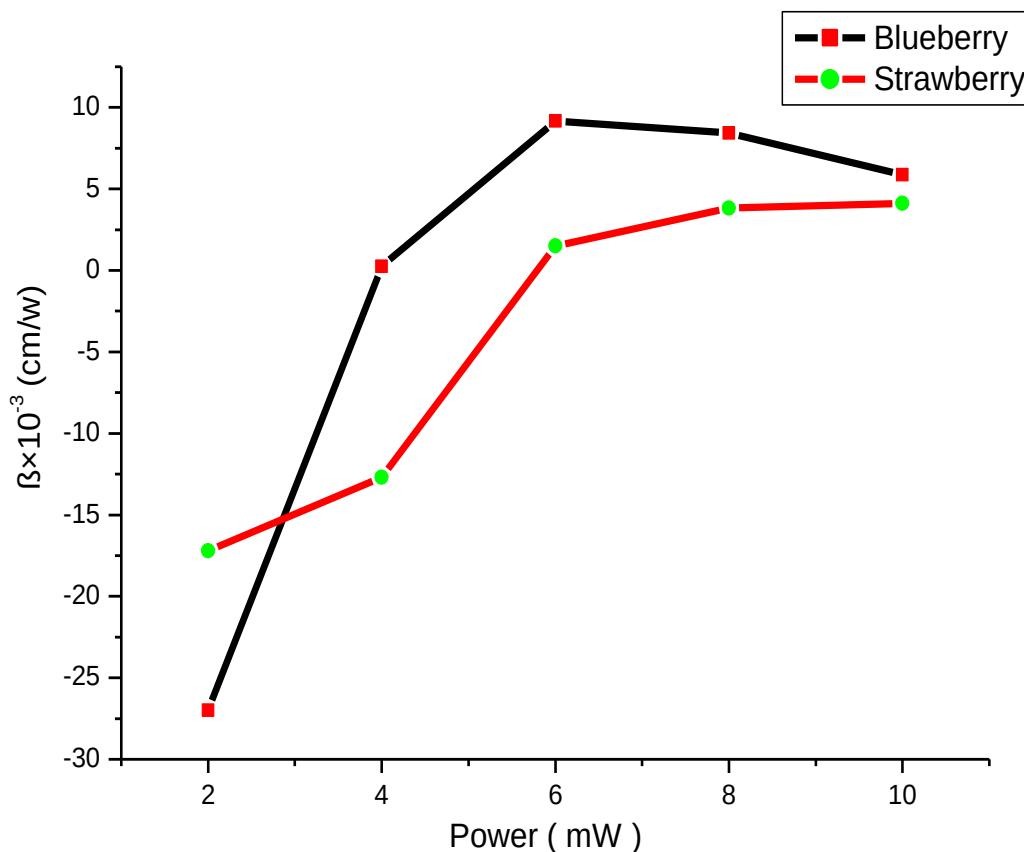
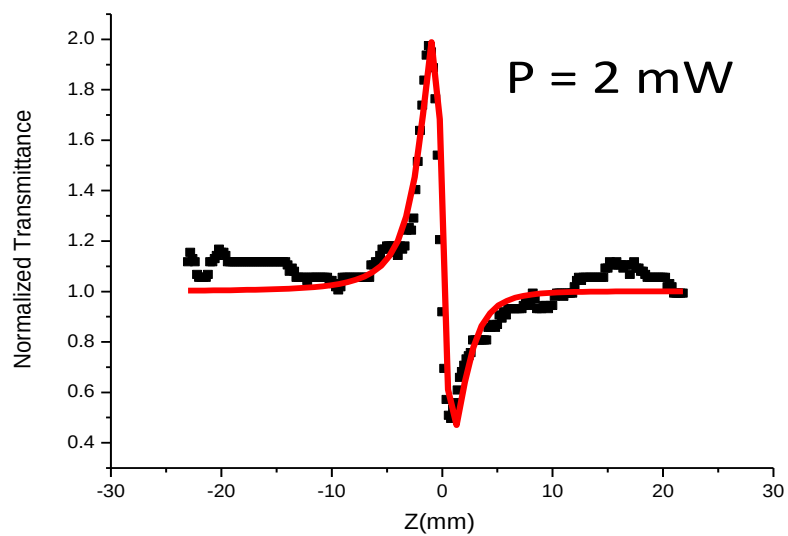


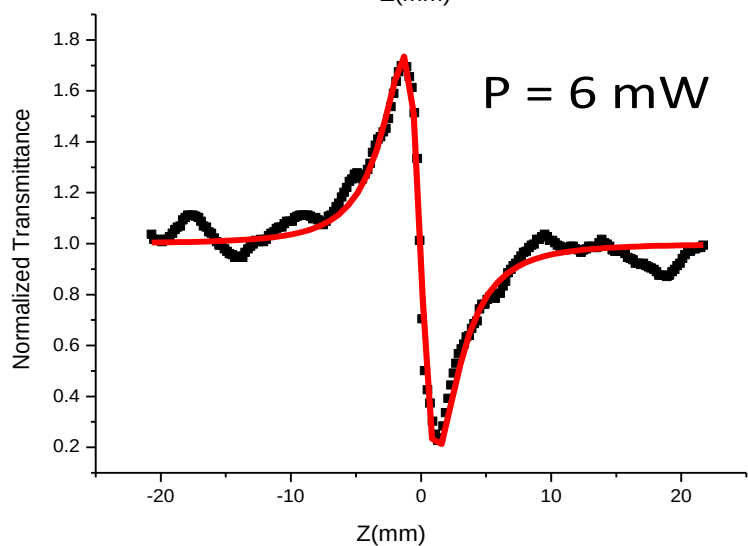
Figure (46): Variation of β as function of excitation power ($\lambda = 514 \text{ nm}$) with sample extracted in methanol at concentration of 0.3g/ml.

To distinguish between sample with saturable absorption behaviour (SA) and that with reverse saturable absorption (RAS), one must observe the size of the peak and valley for the normalized Z-scan transmittance curve, examples are shown in Figure (47). If the peak size is larger than that of the valley (Figure 47-a) SA is the dominate behaviour. On the other hand, when the valley size is larger than the peak (Figure 47-b,c), RSA is the dominate behaviour.

(a)



(b)



(c)

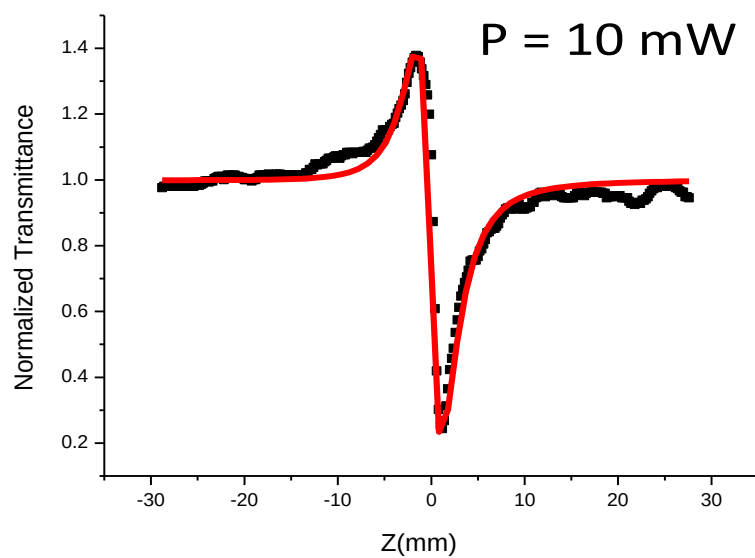


Figure (47): Fitted z-scan transmission curves to determine both the sign and magnitude of β .

In Table (16), sample from raisin extract in methanol at concentration of 0.1 g/ml behaves as SA between power 2 mW and 4 mW. However, above 6 mW it behaves as RSA. For the same concentration and solvent, cranberry dye extract shows SA behaviour under all applied excitation power used (2-10 mW). Also, third order susceptibility and both of its parts the real and imaginary are listed in Table (16). The real part of $\chi^{(3)}$ is two orders of magnitude higher than the imaginary part.

Table (16): Nonlinear parameters for berries extracted in methanol at concentration of 0.1 g/ml and scanned by Ar ion laser at 514 nm at different power for closed aperture configuration.

Power mW	Sample	$\beta \times 10^{-4}$ cm/W	Re $\chi^{(3)}$ $\times 10^{-6}$ esu	Im $\chi^{(3)}$ $\times 10^{-8}$ esu	$\chi^{(3)}$ $\times 10^{-6}$ esu
2	Raisins	4.545	- 2.644	8.509	2.640
	Cranberry	- 1.082	- 2.621	- 2.028	2.620
4	Raisins	3.258	- 1.348	6.099	1.350
	Cranberry	- 17.560	- 1.544	- 32.904	1.580
6	Raisins	- 2.501	- 0.520	- 4.682	0.523
	Cranberry	- 3.367	- 0.723	- 6.308	0.725
8	Raisins	- 1.306	- 0.315	- 2.445	0.316
	Cranberry	- 2.764	- 0.488	- 5.178	0.490
10	Raisins	- 1.069	- 0.448	- 2.001	0.448
	Cranberry	- 2.764	- 0.488	- 5.178	0.490

Table (17) shows nonlinear parameters for berries dye extract at concentration of 0.6 g/ml in methanol excited using Ar laser at 514 nm for closed aperture configurations. Raisin and cranberry dye extracts act as SA between excitation power 2 mW and 6 mW. This behaviour is

different than that observed at 0.1 g/ml concentrations. However, above 8 mW it behaves as RSA. Dry blueberry and strawberry extracts shows SA action for all the excitation power used. Also it could be concluded from table (17) that $\chi^{(3)}$ decreases as excitation power is increases see Figure (48).

Table (17): Nonlinear parameters for berries extracted in methanol at concentration of 0.6 g/ml and excited by Ar laser at 514 nm at different power for closed aperture.

Power mw	Sample	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)}$ $\times 10^{-5}$ esu	$\text{Im } \chi^{(3)}$ $\times 10^{-6}$ esu	$\chi^{(3)}$ $\times 10^{-6}$ esu
2	Raisins	- 2.465	- 3.301	- 4.889	33.40
	Cranberry	- 0.177	- 1.971	- 0.352	19.70
	Dry blueberry	- 10.50	- 6.200	- 20.710	65.40
	Strawberry	- 6.218	- 4.091	- 12.120	42.70
4	Raisins	- 0.770	- 1.234	- 1.527	12.40
	Cranberry	- 1.371	- 1.800	- 2.733	18.20
	Dry blueberry	- 8.006	- 4.655	- 15.800	49.20
	Strawberry	- 6.666	- 4.272	- 13.000	44.70
6	Raisins	- 0.231	- 1.179	- 0.458	11.80
	Cranberry	- 0.149	- 1.014	- 0.298	10.15
	Dry blueberry	- 6.458	- 3.468	- 12.740	37.00
	Strawberry	- 6.233	- 3.590	- 12.150	37.90
8	Raisins	0.067	- 0.885	0.133	8.85
	Cranberry	- 0.143	- 0.768	- 0.284	7.69
	Dry blueberry	- 6.033	- 3.317	- 11.900	35.20
	Strawberry	- 3.374	- 2.555	- 6.578	26.40
10	Raisins	0.068	- 0.306	0.135	3.06
	Cranberry	- 0.049	- 0.233	- 0.097	2.33
	Dry blueberry	- 2.108	- 1.531	- 4.159	15.90
	Strawberry	- 2.372	- 2.244	- 4.625	22.90

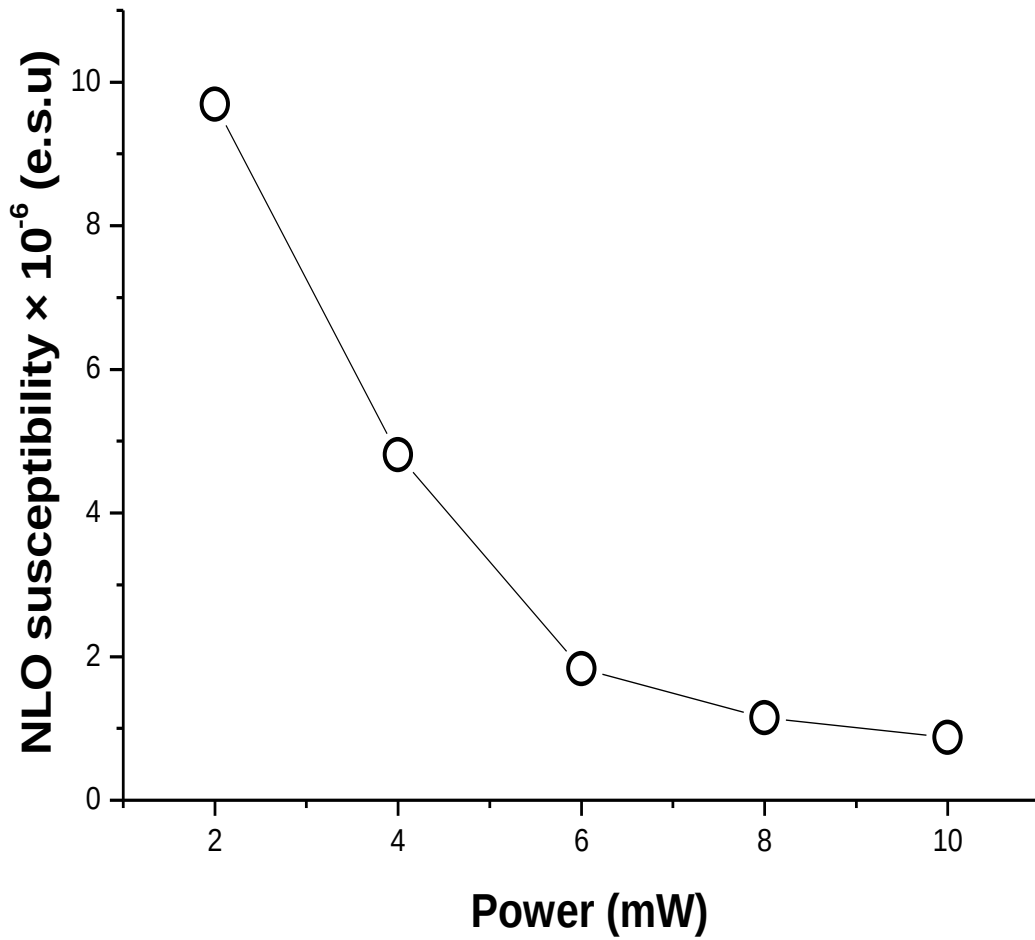


Figure (48): variation of $\chi(3)$ with excitation power for blueberry extracted in ethanol at concentration 0.1 g/ml.

As listed in Table (18), SA is the dominating nonlinear absorption behaviour for the blueberry extracted using acetone and ethanol with acid. While, in methanol they act as RSA. Moreover, the blueberry samples in ethanol at excitation power below 4 mW they act as SA, while behave as RSA for excitation powers form 4 mW to 10 mW. In most of the listed values the real part of $\chi^{(3)}$ is one order of magnitude larger than the imaginary part.

Table (18): Nonlinear parameters for berries at 0.1 g/ml concentration and scanned using Ar ion laser at 514 nm for closed aperture configuration.

Power mw	Solvent	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)}$ $\times 10^{-5}$ esu	$\text{Im } \chi^{(3)}$ $\times 10^{-6}$ esu	$\chi^{(3)}$ $\times 10^{-6}$ esu
2	Acetone	- 0.056	- 0.102	- 0.107	1.030
	Ethanol	- 0.594	- 0.962	- 1.150	9.690
	Ethanol+ 1% HCl	- 128.30	- 187.1	- 261.2	1,890
4	Acetone	- 0.010	- 0.055	- 0.020	0.553
	Methanol	0.058	- 0.069	0.107	0.696
	Ethanol	0.143	- 0.481	0.277	4.810
	Ethanol+ 1% HCl	- 59.380	- 22.710	- 120.9	257.0
6	Acetone	- 0.016	- 0.025	- 0.031	0.252
	Methanol	0.013	- 0.046	0.024	0.456
	Ethanol	0.071	- 0.183	0.137	1.830
	Ethanol+ 1% HCl	- 4.766	- 3.152	- 9.704	33.00
8	Acetone	- 0.004	- 0.023	- 0.007	0.234
	Methanol	0.022	- 0.064	0.041	0.644
	Ethanol	0.058	- 0.114	0.111	1.150
	Ethanol+ 1% HCl	- 1.964	- 1.958	- 3.999	20.00
10	Acetone	- 0.029	- 0.054	- 0.055	0.541
	Methanol	0.013	- 0.065	0.024	0.652
	Ethanol	0.038	- 0.087	0.073	0.874
	Ethanol+ 1% HCl	- 3.430	- 3.923	- 6.985	39.80

4.1.4.2 Effect of concentration

Investigation of concentration effect on nonlinear absorption of blueberry dye extracts in ethanol, an example is summarized in Table (19). Generally speaking, for all concentration at excitation power less

than 4 mW, samples show SA behaviour. While, when the excitation is above 4 mW samples act as RSA these results are in good agreement with the reported results in (Srinivas, et al., 2003).

Table (19): Nonlinear parameters for blueberry in ethanol at different Concentrations of dye scanned using Ar laser at 514 nm for closed aperture configurations.

Power mw	Concentration g/ml	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)}$ $\times 10^{-5}$ esu	$\text{Im } \chi^{(3)}$ $\times 10^{-6}$ esu	$\chi^{(3)}$ $\times 10^{-6}$ esu
2	0.1	- 0.594	- 0.962	- 1.150	9.690
	0.3	- 2.699	- 2.564	- 5.240	26.20
	0.6	- 1.036	- 1.989	- 2.021	20.00
4	0.1	0.143	- 0.481	0.277	4.810
	0.3	0.026	- 1.362	0.050	13.60
	0.6	- 1.793	- 2.112	- 3.496	21.40
6	0.1	0.071	- 0.183	0.137	1.830
	0.3	0.917	- 0.895	1.781	9.120
	0.6	0.071	- 1.632	0.139	16.30
8	0.1	0.058	- 0.114	0.111	1.150
	0.3	0.844	- 0.565	1.639	5.880
	0.6	0.703	1.253	1.371	12.60
10	0.1	0.038	- 0.087	0.073	0.874
	0.3	0.587	- 0.424	1.140	4.390
	0.6	0.686	- 0.925	1.338	9.350

4.1.4.3 Effect of excitation wavelength

When different excitation wavelengths are used to scan samples at specific power and concentration, their nonlinear absorption behaviour

may change from SA to RSA. For example, as listed in Table (20), cranberry, raisin and strawberry at wavelength 633 nm act as RSA while at 488 nm and 514 nm they act as SA. Dry blueberry samples nonlinear absorption behaviour did not change and remain as SA at all excitation wavelengths.

Table (20): Nonlinear parameters for berries at 0.6 g/ml concentrations extracted in methanol and scanned using Ar laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.

Sample	Excitation wavelength nm	$\beta \times 10^{-2}$ cm/W	α_0 m ⁻¹	Re $\chi^{(3)}$ $\times 10^{-5}$ esu	Im $\chi^{(3)}$ $\times 10^{-6}$ esu	$\chi^{(3)}$ $\times 10^{-6}$ esu
Cranberry	488	- 0.337	386.2	- 4.728	-0.637	0.477
	514	- 0.149	384.5	- 10.144	-0.298	1.015
	633	0.024	53.0	- 3.232	0.058	0.323
Raisin	488	- 1.659	453.2	- 8.394	-3.120	0.896
	514	- 0.231	429.9	- 11.790	-0.458	1.180
	633	0.051	108.5	- 4.094	0.126	0.410
Strawberry	488	- 14.01	966.4	- 56.960	-25.90	6.257
	514	- 6.233	940.8	- 35.900	-12.15	3.790
	633	0.009	184.2	- 91.050	0.020	9.105
Dry Blueberry	488	- 6.958	1092.6	- 29.880	-13.02	3.259
	514	- 6.458	1028.6	- 34.680	-12.74	3.695
	633	- 11.86	425.5	- 186.40	-28.77	18.86

A similar behaviour experienced by dye extracts that noted in Table (6) have been observed with them at low concentrations as presented in Table (21). However, the values of β are less. Also, at wavelength of 633 nm samples showed no response.

Table (21): Nonlinear parameters for berries at 0.1 g/ml concentration extraced in methanol and scanned using Ar laser at (514 – 488) nm for closed aperture configuration.

Sample	Excitation wavelength nm	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)} \times 10^{-5}$ esu	$\text{Im } \chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
Cranberry	488	- 0.084	- 0.099	- 0.149	1.000
	514	- 0.034	- 0.072	- 0.063	0.725
Raisin	488	- 0.082	- 0.138	- 0.145	1.390
	514	- 0.025	- 0.052	- 0.047	0.523
Blueberry	488	- 0.170	- 0.135	- 0.299	1.390
	514	0.013	- 0.046	0.024	0.456

Table (22): Nonlinear parameters for blueberry at different concentrations of dye in ethanol by using Ar laser at (514 – 488) nm for closed aperture configuration.

Concentration	Excitation wavelength (nm)	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)} \times 10^{-5}$ esu	$\text{Im } \chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
0.1 g/ml	488	- 0.090	- 0.165	- 0.165	1.657
	514	0.071	- 0.183	0.137	1.834
	633	0.118	- 0.379	0.282	3.802
0.3 g/ml	488	- 1.098	- 0.863	- 2.021	8.864
	514	0.917	- 0.895	1.78	9.123
	633	- 0.377	- 1.644	- 0.900	16.768
0.6 g/ml	488	- 0.760	- 0.717	- 1.405	7.302
	514	0.071	- 1.632	0.14	16.320
	633	- 0.269	- 3.267	- 0.65	32.680

Investigating the effects of other solvents with and without addition of acid has revealed that the nonlinear absorption behaviour remains the same, but the β value has enhanced in acidic solvent as shown in Tables (23) and (24).

Table (23): Nonlinear parameters for blueberry at 0.1 g/ml concentrations extracted in methanol with acid and scanned using Ar ion laser at (514 – 488) nm for closed aperture configuration.

Excitation Wavelength nm	$\beta \times 10^{-2}$ cm/W	Re $\chi^{(3)}$ $\times 10^{-5}$ esu	Im $\chi^{(3)}$ $\times 10^{-6}$ esu	$\chi^{(3)}$ $\times 10^{-6}$ esu
488	- 2.956	- 2.686	- 5.707	27.460
514	- 4.766	- 3.152	- 9.704	32.980
633	0.493	- 1.387	1.235	13.930

Table (24): Nonlinear parameters for Strawberry at 0.3 g/ml Concentrations of dye in methanol by using Ar laser at (514 – 488) nm for closed aperture.

Excitation Wavelength nm	$\beta \times 10^{-2}$ cm/W	Re $\chi^{(3)}$ $\times 10^{-5}$ esu	Im $\chi^{(3)}$ $\times 10^{-6}$ esu	$\chi^{(3)}$ $\times 10^{-6}$ esu
488	- 1.473	- 1.135	- 2.644	11.700
514	0.150	- 1.141	0.283	11.400
633	- 2.598	- 5.278	- 6.050	53.100

To conclude this part, the conditions required for RSA are as follows:

- 1- Incident photons with the same wavelength can be absorbed by molecules in the ground state and also by excited states.
- 2- The absorption of the excited states must be larger than that of the ground state (Henari & Patil, 2014)

Addition of HCl to a solvent resulted in enhancement of magnitude of both n_2 and β . But only absorption behaviour has changed (see for example Figure (49))

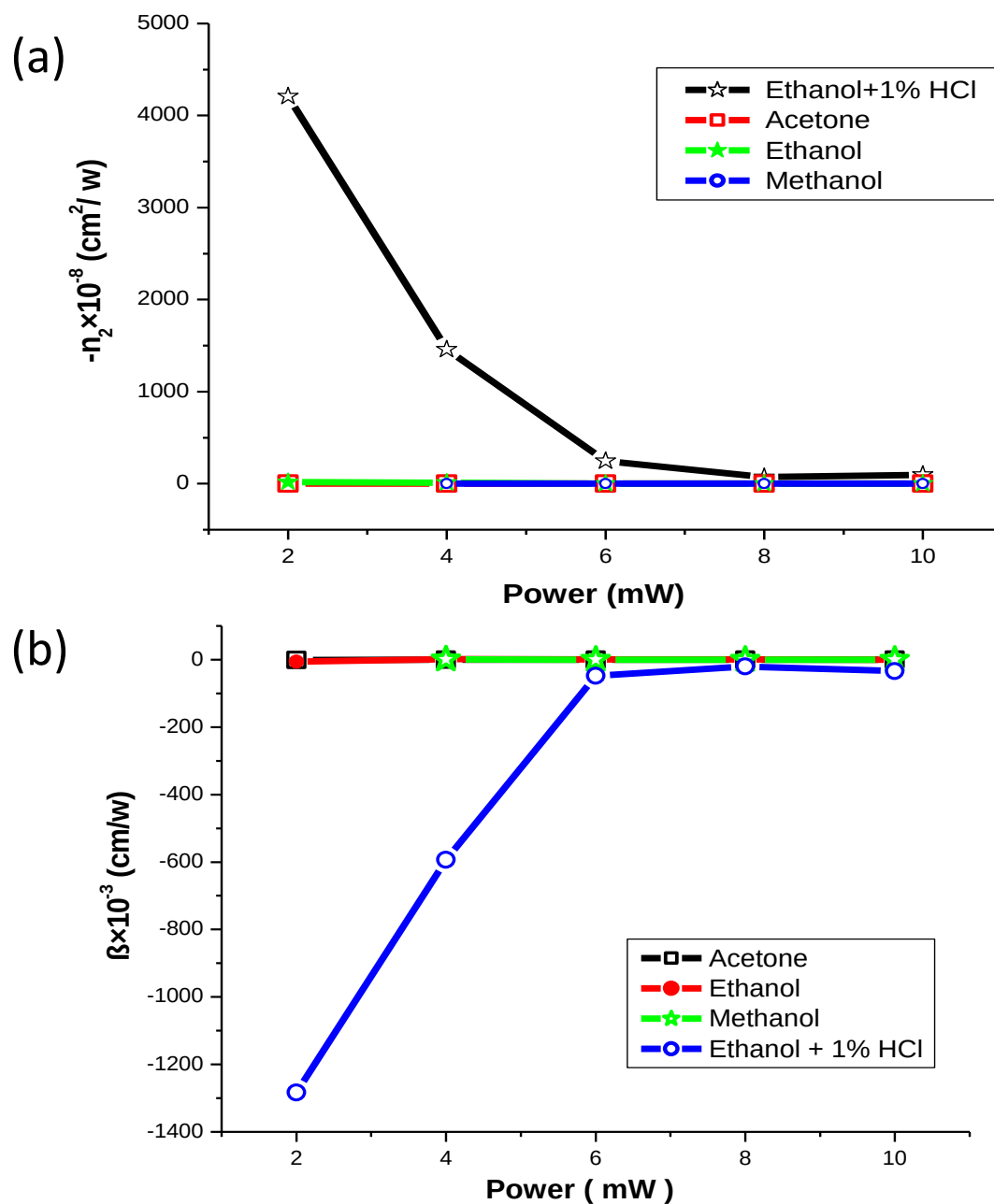


Figure (49): Variation of n_2 and β as function of power with and without addition of HCl acid to extraction solvent.

4.2 Group 2: Citrus

As have been done with group 1, in group 2, three materials prepared with different solvents, at three different concentrations and irradiated with beams of three different wavelengths are investigated. These materials are fresh mandarin, orange and grapefruit peels (Vainio, 2003).

4.2.1 Linear Absorption Spectroscopy

4.2.1.1 Effect of solvent

Linear absorption spectra for mandarin is shown in Figure (50). It is broad, there is no characteristic peak. The onset of absorption starts at 800 nm while for mandarin in methanol with acid and 620 nm for mandarin in methanol.

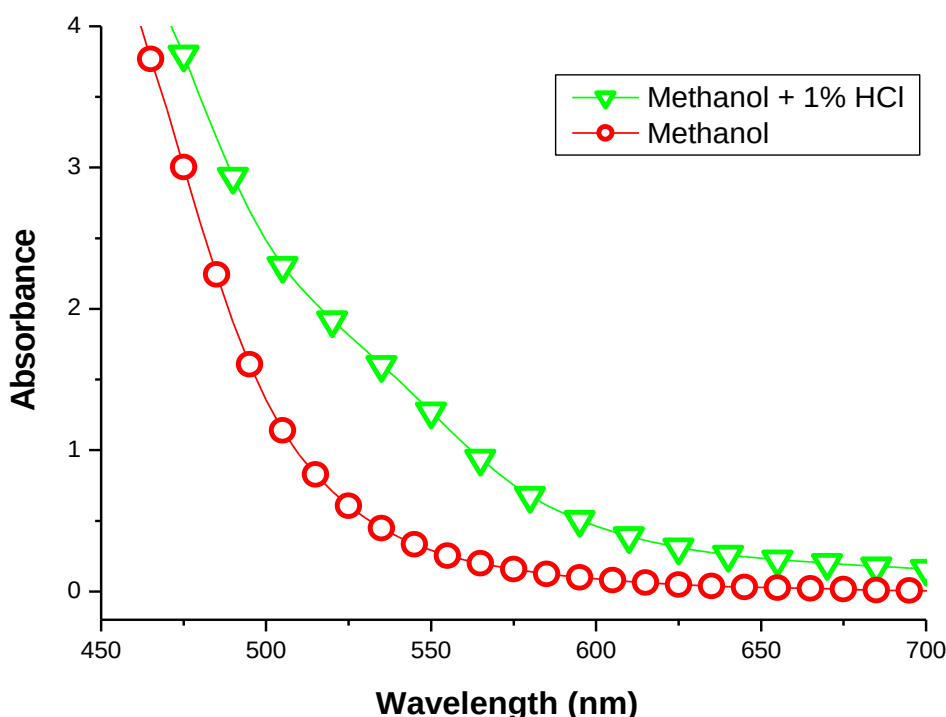


Figure (50): Absorption spectrum of mandarin at 0.3 g/ml concentration extracted in methanol and 1% HCl acid.

4.2.1.2 Effect of materials

Linear absorption spectroscopy of citrus samples extracted using methanol as solvent is shown in Figure (51). Generally speaking they have similar absorption behaviour, none have characteristic absorption peak. However, the only difference between them is in the onset of absorption which starts at 620 nm for mandarin and orange, while grapefruit starts from 570 nm.

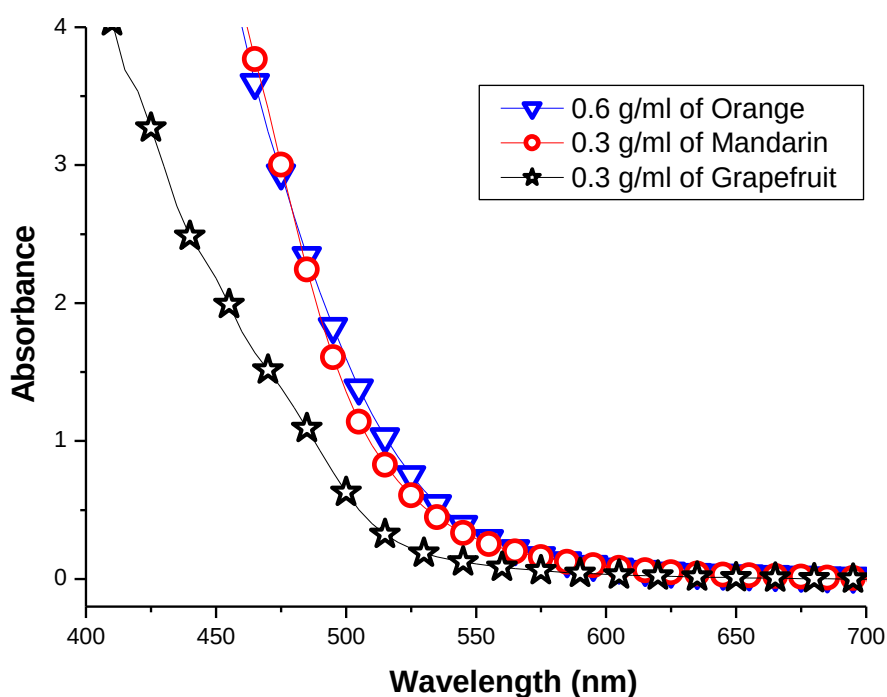


Figure (51): Linear absorption spectra of citrus samples extracted in methanol.

4.2.2 Fluorescence Spectroscopy

4.2.2.1 Effect of solvent

Figure (52) presents the effect of solvent choice on fluorescence of the sample at specific concentration 0.3 g/ml. Addition of HCl acid to methanol suppress the fluorescence peak of the sample at 580 nm.

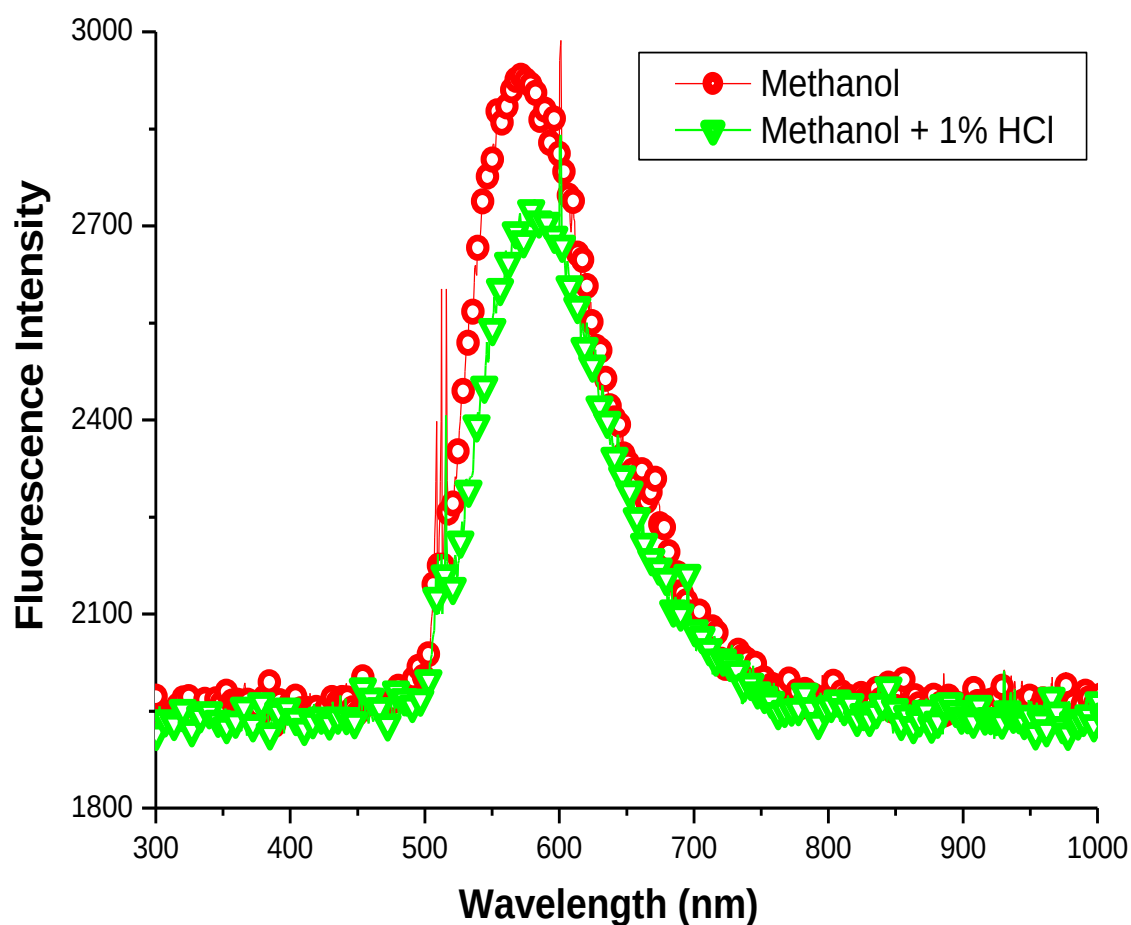


Figure (52): Fluorescence spectra of mandarin extracted in methanol at concentration of 0.3 g/ml.

4.2.2.2 Effect of materials

Figure (53) shows the effect of materials on fluorescence of the sample at 0.3 g/ml and 0.6 g/ml concentrations extracted in methanol. The fluorescence spectra for citrus group shows remarkable fluorescence behaviour with approximate peak of 565 nm for grapefruit in methanol and 583 nm for mandarin in acid. The highest fluorescence peak for highest concentration is for orange at 0.6 g/ml.

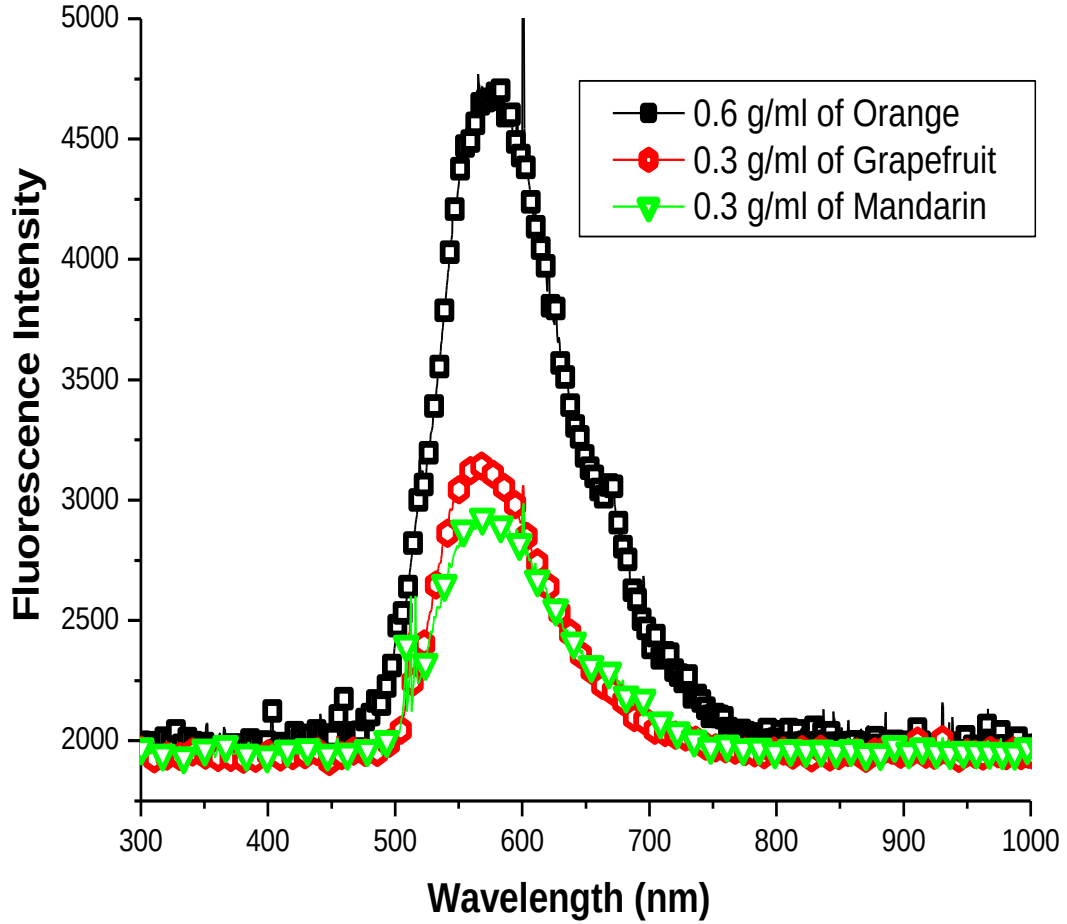


Figure (53): Fluorescence spectra of citrus extracted in methanol.

4.2.3 Nonlinear Index of Refraction

4.2.3.1 Effect of excitation power level

Figure (54) shows variation of nonlinear index of refraction versus excitation power at excitation $\lambda = 514$ nm for mandarin, orange and grapefruit peels. As the excitation power increases, n_2 value decreases in a nonlinear manner. Mandarin have the highest nonlinear refractive index of $-50 \times 10^{-8} \text{ cm}^2/\text{W}$.

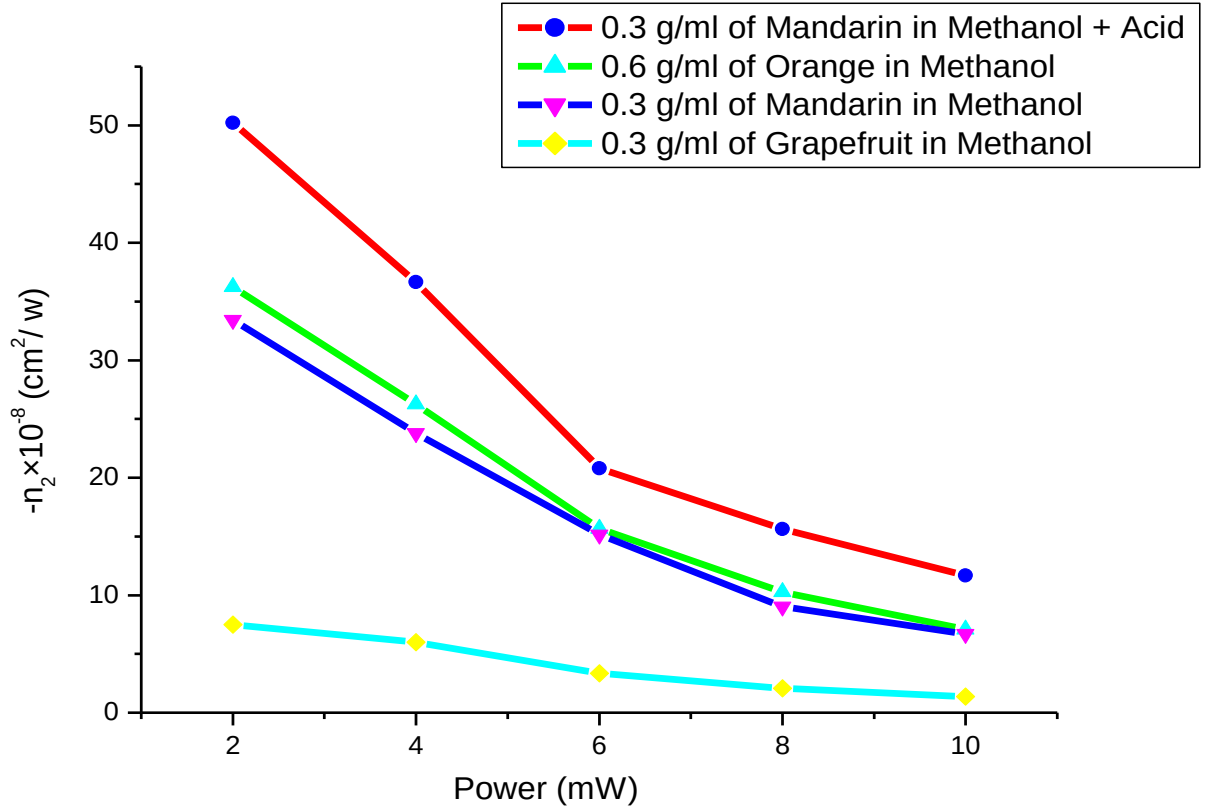


Figure (54): Variation of n_2 values as function of excitation power level ($\lambda = 514$ nm) for citrus.

4.2.3.2 Effect of excitation wavelength

Three different excitation wavelengths (488, 514, and 633 nm) at beam power of 6 mW have been used to investigate the citrus extracts nonlinear index of refraction are listed in Tables (25). No distinct behaviour has been noticed. Therefore, each wavelength has its own effect regardless the change in concentrations. The mandarin dye extracted in methanol with acid possess higher value of n_2 at $\lambda = 633$ nm. While, no effect has been observed at same wavelength for mandarin in methanol this attributed to weak linear absorption at 633 nm which equals to 8.75 m^{-1} . Values of n_2 almost are close. Moreover, mandarin at 514 have smaller values of n_2

Table (25): Nonlinear parameters for mandarin at 0.3 g/ml concentration and scanned using Ar laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.

Sample	Excitation wavelength nm	Fitting parameter $P_1 (\Delta\phi)$	Fitting parameter $P_2 (z_0)$ mm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m ²	$n_2 \times 10^{-7}$ cm ² /W
Mandarin 0.3 g/ml + Acid	488	-11.818	0.751	1.080	3.280	- 3.854
	514	-4.088	1.141	1.370	2.040	- 2.081
	633	-0.989	8.019	4.020	0.209	- 4.923
Mandarin 0.3 g/ml	488	-4.070	1.139	1.330	2.160	- 1.808
	514	-2.732	1.435	1.530	1.620	- 1.514

Because of weak linear absorption level at 633 nm (see Figure 51) orange and grapefruit peels extract showed no clear variation in n_2 . As shown in Table (26) the value of n_2 for orange extracts at excitation wavelength 488 nm is almost close to that at 514 nm. But, for grapefruit peels extract n_2 value at excitation wavelength 514 nm has smaller value than that at 488 nm.

Table (26): Nonlinear parameters for citrus at different concentrations and scanned using Ar ion laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.

Sample	Excitation wavelength nm	Fitting parameter $P_1 (\Delta\phi)$	Fitting parameter $P_2 (z_0)$ mm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m ²	$n_2 \times 10^{-7}$ cm ² /W
orange 0.6 g/ml	488	-6.901	0.630	0.989	3.910	- 1.727
	514	-3.339	1.188	1.400	1.960	- 1.566
Grapefruit 0.3 g/ml	488	-7.933	0.672	1.020	3.660	- 1.870
	514	-0.939	0.978	1.270	2.380	- 0.335

4.2.4 Nonlinear Absorption Coefficient

4.2.4.1 Effect of excitation power level

Figure (55) shows the nonlinear absorption coefficient (β) as function of excitation power level. The β value decreases as the excitation power level increases. Mandarin peels in methanol with acid have the highest β value equal -2.5×10^{-3} cm/W. Mandarin peels extracts in methanol, mandarin in methanol with acid and orange shows SA action at low power levels. But, at $P = 10$ mw it demonstrates RSA effect. Grapefruit peels extract shows RSA effect at all applied excitation power levels.

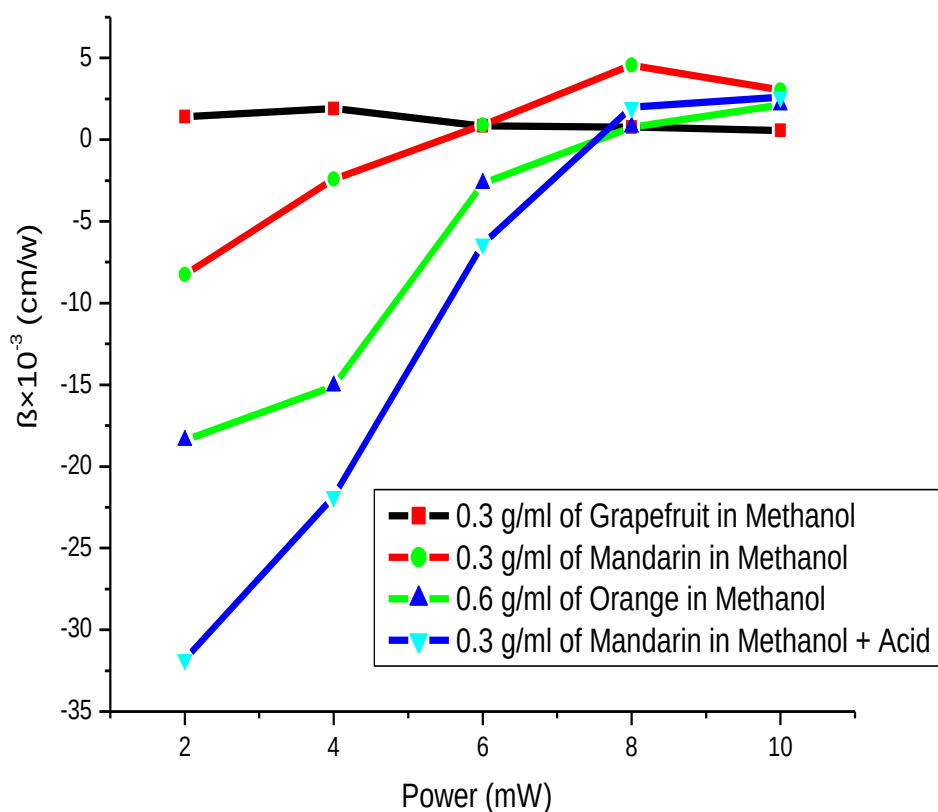


Figure (55): Variation of β as function of excitation power level ($\lambda = 514$ nm) at fixed concentration.

As a matter of fact, whenever the excitation wavelength is near the peak of the absorption spectrum, the effect of saturable absorption (SA) is observed because of high optical density. The presence of SA enhances the peak along with the relative inhibition of the valley in the measured profile. Likewise, if the excitation wavelength is far from the peak of the absorption (low optical density region) then either the effects of two-photon absorption (TPA) or the excited state absorption (ESA) can take place. These effects suppress the peak and somewhat enhances the valley in the measured profile. This is generally known as reverse saturation of absorption (RSA) (Tripathy & Bisht, 2015).

4.2.4.2 Effect of excitation wavelength

As listed in Table (27) β value as well as the sign are affected by excitation wavelength. β at excitation wavelength of 514 nm switched from SA in methanol to RSA in methanol with acid. With 488 nm SA is enhanced when acid is added to methanol as solvent. It has been found that excitation with 633 nm produced RSA effect only when acid has been added to methanol as solvent.

Table (27): Nonlinear parameters for mandarin peels at different concentrations scanned using Ar ion laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.

Sample	Excitation wavelength nm	$\beta \times 10^{-2}$ cm/W	Re $\chi^{(3)}$ $\times 10^{-5}$ esu	Im $\chi^{(3)}$ $\times 10^{-6}$ esu	$\chi^{(3)}$ $\times 10^{-6}$ esu
0.3 g/ml methanol+ 1% HCl	488	- 3.732	- 1.808	- 6.799	19.320
	514	- 0.639	- 0.976	- 1.228	9.840
	633	0.002	- 2.310	0.006	23.100
0.3 g/ml methanol	488	- 0.883	- 0.824	- 1.562	8.383
	514	0.089	- 0.689	0.166	6.895

For both orange and grapefruit peels, Table (28) list values of β when samples are excited with Ar ion laser when $\lambda = 488$ nm both samples exhibited SA behaviour. When excited with $\lambda = 514$ nm orange peels samples exhibited SA while grapefruit peels showed RSA action. However, samples show no clear SA or RSA when excited 633 nm.

Table (28): Nonlinear parameters for citrus extracted in methanol at different concentrations and scanned using Ar ion laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.

Sample	Excitation wavelength nm	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)} \times 10^{-5}$ esu	$\text{Im } \chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
Orange peels 0.6 g/ml	488	- 1.462	- 0.798	- 2.623	8.396
	514	- 0.268	- 0.724	- 0.507	7.253
Grapefruit peels 0.3 g/ml	488	- 0.849	- 0.852	- 1.502	8.648
	514	0.086	- 0.153	0.160	1.533

4.3 Group 3: Pomegranate

Following the same approach used with groups 1 and 2, in group 3, extracts from pomegranate peel (Egyptian, Indian, Yamani and Spanish origin) and grains (Indian origin) are investigated using different solvents, concentrations and wavelengths.

4.3.1 Linear Absorption Spectroscopy

4.3.1.1 Effect of concentration

Linear absorption spectra for Indian pomegranate is shown in Figure (56), in the near infrared part of the spectrum absorbance is very shallow. However, sample absorbance increases at wavelength shorter than 650 nm. Moreover, absorbance level gets enhanced with increasing sample concentration.

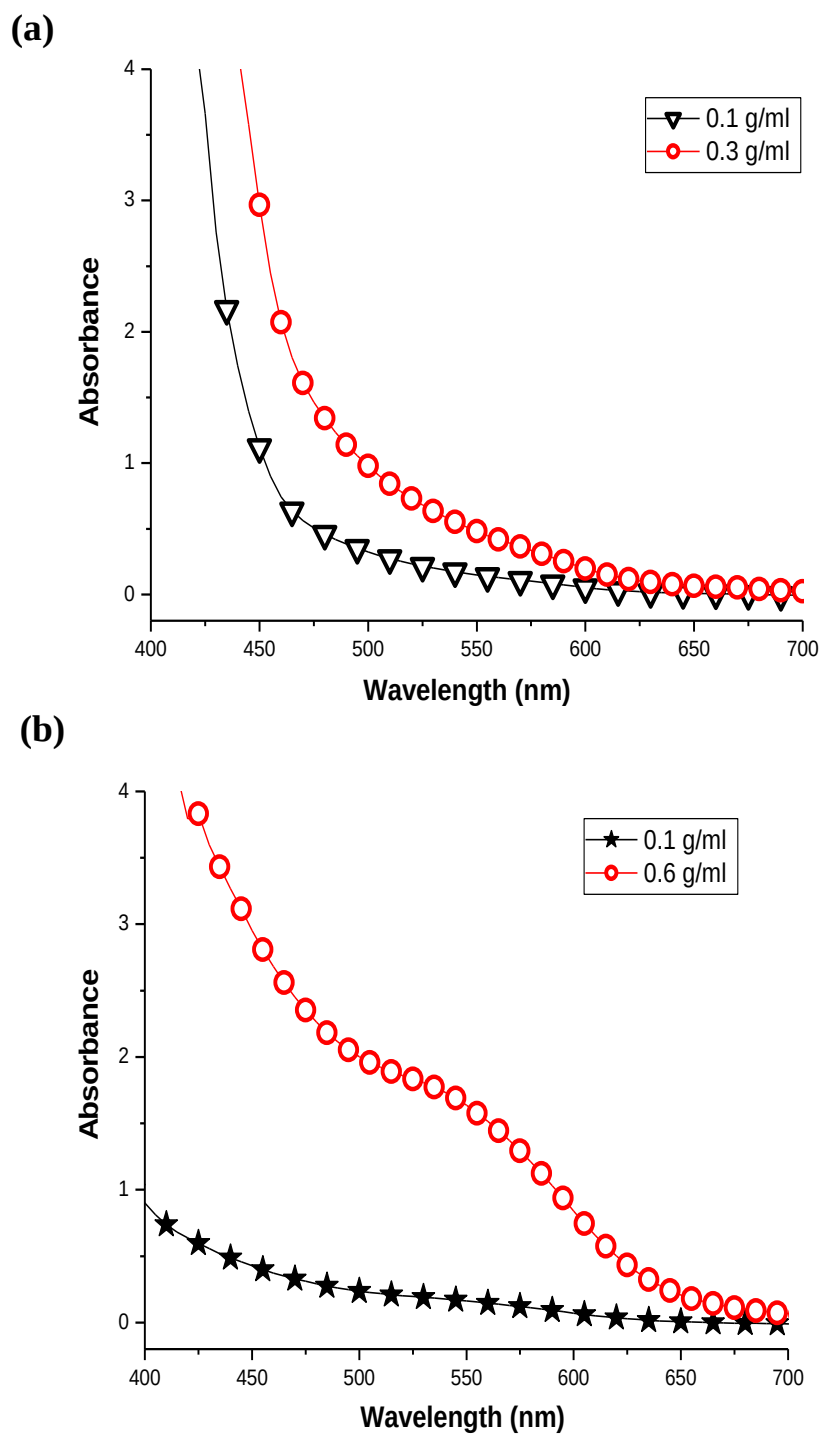


Figure (56): Linear absorption spectra of Indian pomegranate extracted in methanol at different concentrations for a) peels, and b) grains.

4.3.1.2 Effect of solvent

Figure (57) shows the effect of the solvent on the absorbance of the sample at specific concentration (say, 0.1 g/ml.). Addition of HCl acid to

methanol enhances the absorption of Indian pomegranate grains. However, the linear absorption spectroscopy of Egyptian and Yemeni pomegranate peel is almost similar in different solvents as shown in parts b and c.

As demonstrated in Figure (57), there is almost no difference in the effect of the solvent on Yemini and Egyptian pomegranate peel. However, the effect is more explicit in the Spanish pomegranate peel.

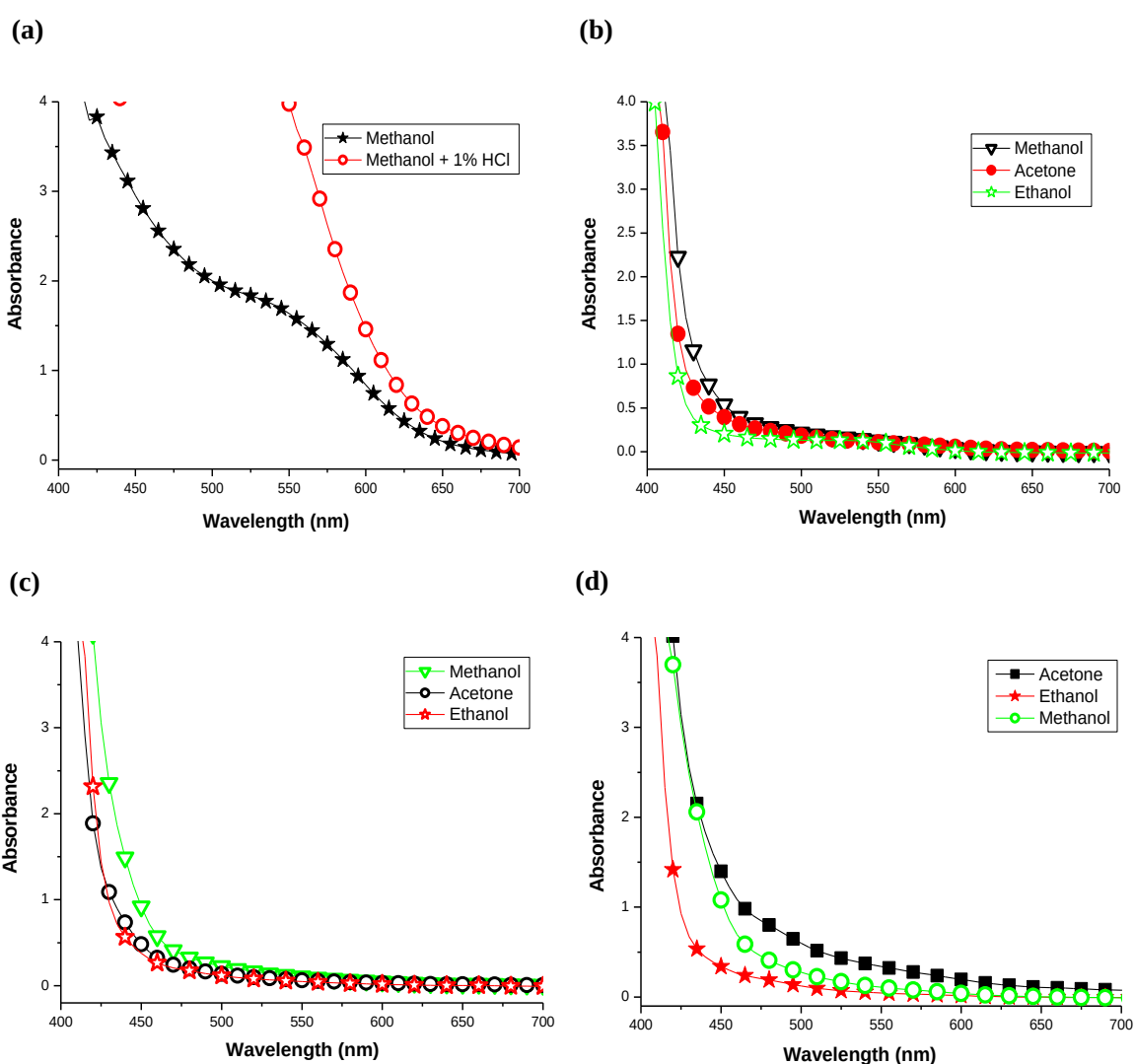


Figure (57): Linear absorption spectra in different solvent of a) Indian pomegranate grains at 0.6 g/ml b) Egyptian pomegranate peels at 0.1 g/ml c) Yamani pomegranate peels at 0.1 g/ml d) Spanish pomegranate peels at 0.1 g/ml.

4.3.1.3 Effect of materials

Figure (58) shows the effect of the material on the absorbance of the sample at specific concentration (0.1 g/ml.). In this figure different kinds of pomegranate peels show similar spectra. However, pomegranate grains showed a minor linear absorption spectra difference.

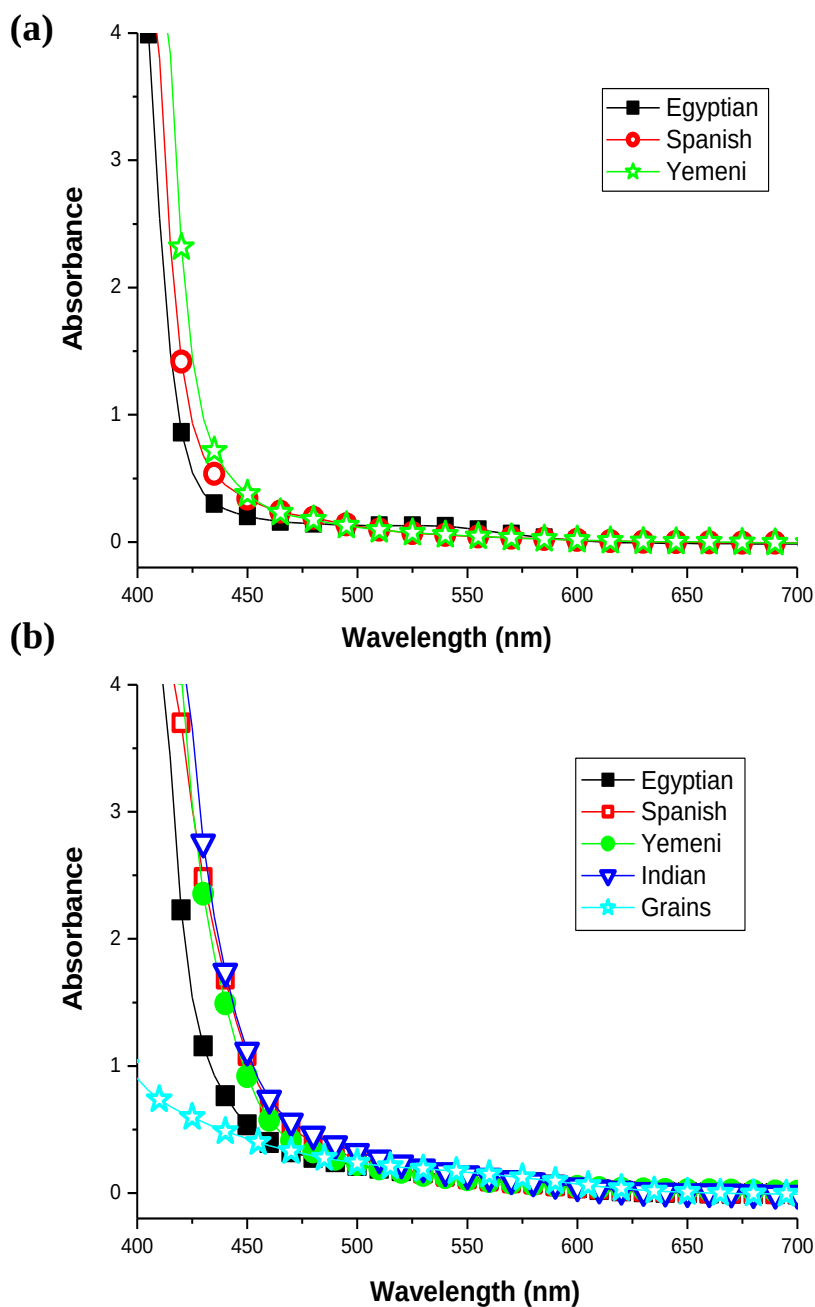


Figure (58): Linear absorption spectra at concentration of 0.1 g/ml for a) pomegranate peels in ethanol b) pomegranate peels and grains in methanol.

4.3.2 Fluorescence Spectroscopy

4.3.2.1 Effect of concentration

Figure (59) shows the fluorescence spectra for Indian pomegranate peel and grains in methanol at different concentrations. At 0.1 and 0.3 g/ml concentrations of peel a remarkable fluorescence behaviour is seen with a peak wavelength of about 590 nm and a shoulder one at 670 nm. While, with 0.1 g/ml and 0.6 g/ml concentrations of grains fluorescence behaviour with peak at 580 nm and 600 nm are seen respectively. As the concentration increases fluorescence intensity increases due to increased number of light emitters.

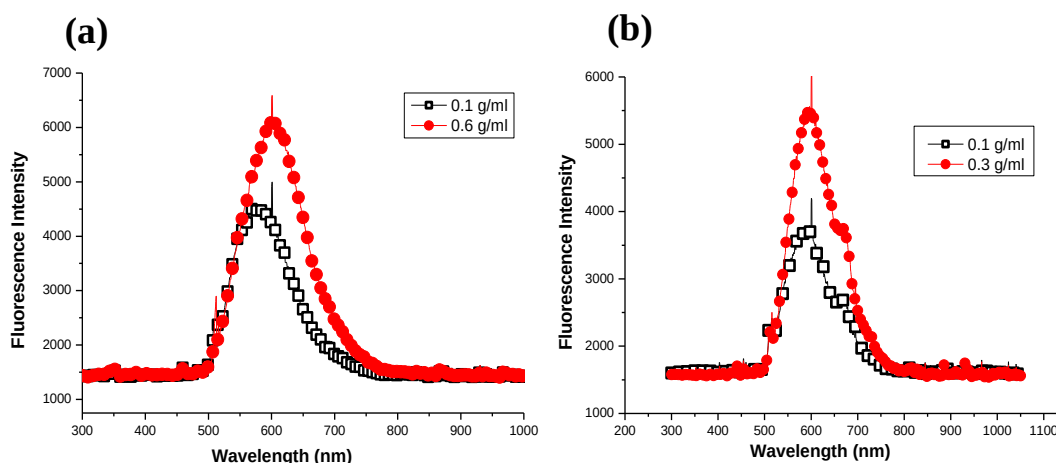


Figure (59): Fluorescence spectra of a) Indian pomegranate grains b) Indian pomegranate peels in methanol at different concentrations.

4.3.2.2 Effect of solvent

Figure (60-a) presents fluorescence spectra for Indian pomegranate grains at concentration of 0.6 g/ml using different extraction solvents. Samples show remarkable fluorescence behaviour with characteristic peak at $\lambda = 600$ nm. Addition of acid to methanol suppresses the fluorescence intensity. While, in methanol solvent fluorescence intensity

get enhanced. The effect of methanol solvent is the same on the extracts from Egyptian, Yemeni, and Spanish pomegranate peels. Sample have remarkable fluorescence behaviour with characteristic peak at about $\lambda = 580$ nm for Egyptian, Yemeni, and Spanish pomegranate peels.

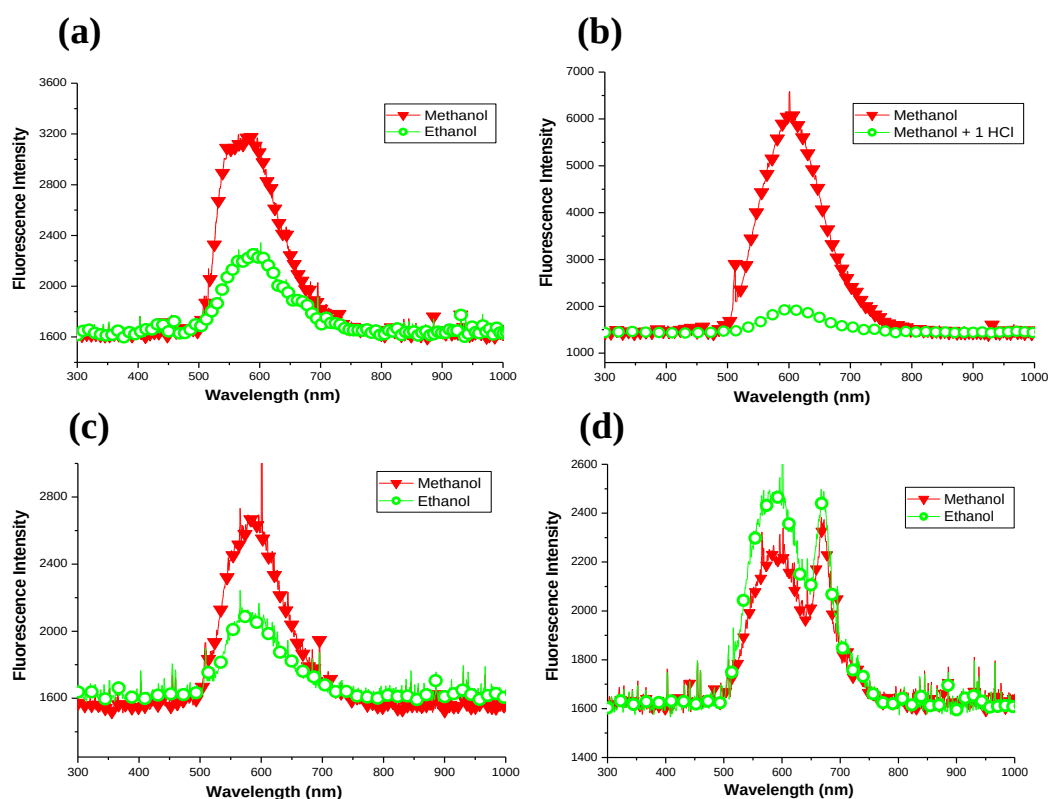


Figure (60): Fluorescence spectra of a) Indian pomegranate grains extracted in methanol at specific concentrations 0.6 g/ml. b) Spanish pomegranate peels c) Egyptian pomegranate peels d) Yemeni pomegranate peels extracted in methanol at specific concentrations 0.1 g/ml.

4.3.2.3 Effect of material

Figure (61) shows the effect of materials choice on fluorescence of the sample at specific concentration of 0.1 g/ml. As demonstrated in Figure (61-a), there are almost no difference in the fluorescence spectra due to Egyptian or Spanish pomegranate peels extracts which show remarkable fluorescence behaviour at characteristic peak of $\lambda = 585$ nm.

Whilst Yamani pomegranate peels show remarkable fluorescence behaviour with peak at 587 nm and at 672 nm. Yamani pomegranate peels extracts own the highest fluorescent intensity. Figure (61-b) shows the fluorescence spectra for pomegranate peel extracted in methanol group with notable fluorescence behaviour at peak of $\lambda = 580$ nm for both peels and grains. However, Indian and Yamani pomegranate peel shows remarkable fluorescence behaviour with approximate peak of 588nm and 672nm. Indian pomegranate grains have highest fluorescent intensity.

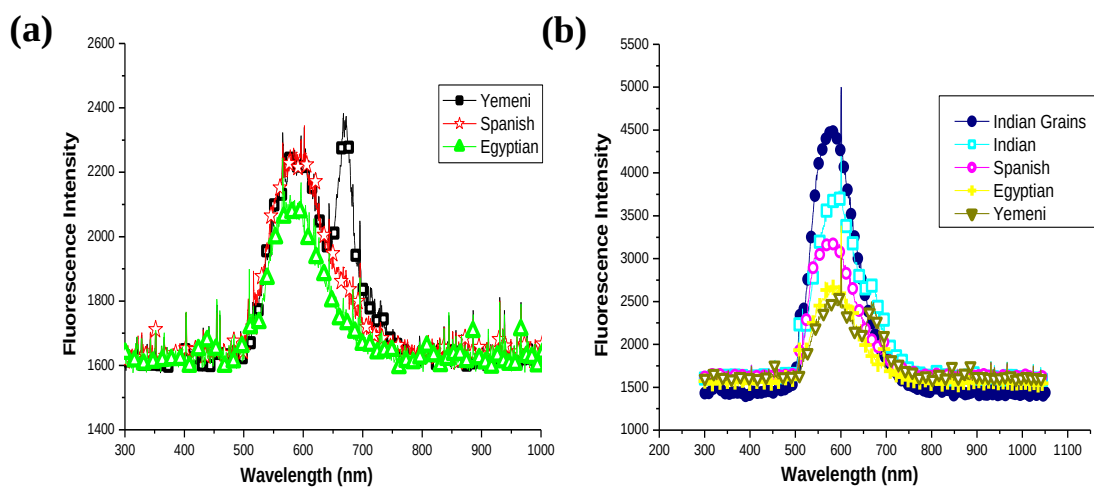


Figure (61): Fluorescence spectra at specific concentration of 0.1 g/ml of a) pomegranate peels extracts in ethanol, b) pomegranate peels extracts and grains in methanol.

4.2.1 Nonlinear Index of Refraction

4.3.2.4 Effect of exciting power level

Figure (62) shows the variation of nonlinear absorption coefficient with excitation power at fixed $\lambda = 514$ nm, at different concentration using methanol to extract Indian pomegranate peels and grains extracts and methanol with acid to extract grains. As excitation power increases, n_2 magnitude decreases in a nonlinear mode. As it has been noted with those of group 1.

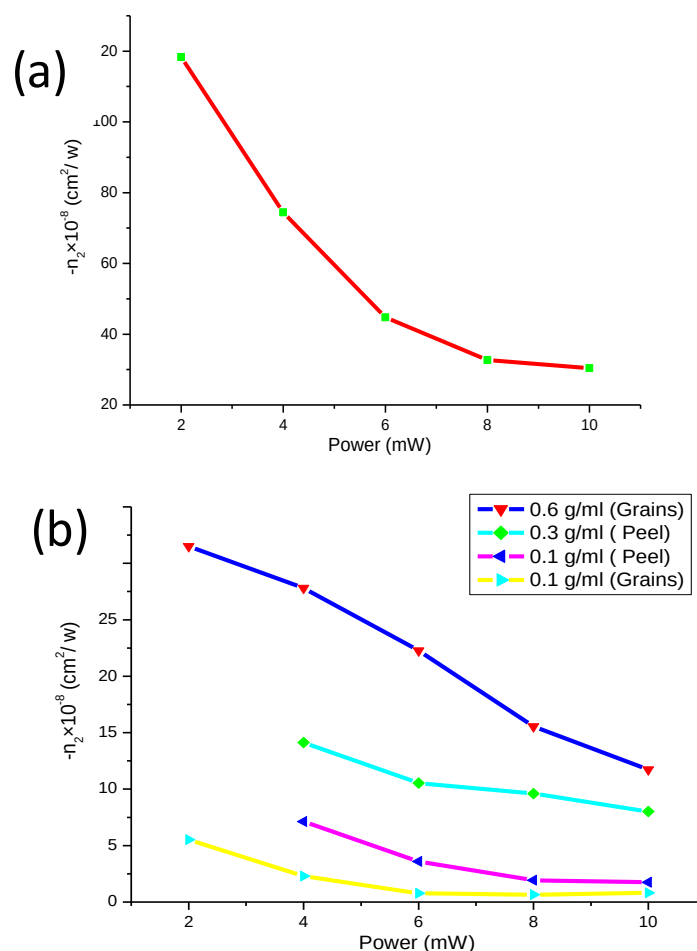


Figure (62): Variation of n_2 as function of excitation power level ($\lambda = 514 \text{ nm}$) for Indian pomegranate a) grains extracted in methanol with acid b) grains and peels extracted in methanol only.

Similar behaviour observed in Figure (62) have been found with other concentrations of extracts and numerical values are presented in Table (29). In Table (29), It has been found that values of n_2 are almost the same. at excitation power of 2 mW the Indian pomegranate grains have higher value of n_2 . while, at other values of powers the Indian pomegranate peel have the higher value of n_2 .

In Tables (29), (30), and (31) one can observe the effect solvent choice on the calculated value of n_2 even if the tested sample has specific concentration (for example, 0.1g/ml) and is excited with the same power level.

Table (29): Nonlinear parameters for pomegranate extracted in methanol with concentration of 0.1 g/ml for peel and 0.6 g/ml for grains scanned using Ar ion laser at 514 nm for closed aperture configuration.

Power mW	Pomegranate		$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m²	$n_2 \times 10^{-7}$ cm²/W
2	peel	Egyptian	1.090	1.070	-0.180
		Yamani	0.828	1.860	-0.215
		Spanish	1.055	1.145	-0.115
		Indian	1.270	0.793	-0.349
	grains	Indian	1.260	0.798	-0.551
4	peel	Egyptian	1.410	1.280	-0.157
		Yamani	1.060	2.270	-0.238
		Spanish	1.550	1.060	-0.174
		Indian	1.610	0.987	-0.713
	grains	Indian	1.210	1.740	-0.229
6	peel	Egyptian	1.700	1.320	- 0.152
		Yamani	1.010	3.780	- 0.128
		Spanish	1.200	2.630	-0.071
		Indian	1.540	1.620	-0.360
	grains	Indian	1.250	2.430	-0.077
8	peel	Egyptian	1.320	2.920	-0.077
		Yamani	1.090	4.280	-0.088
		Spanish	1.200	3.540	-0.048
		Indian	1.480	2.330	-0.192
	grains	Indian	1.210	3.480	-0.065
10	peel	Egyptian	1.210	4.380	-0.057
		Yamani	1.210	4.370	-0.076
		Spanish	1.080	5.410	-0.048
		Indian	1.480	2.890	-0.175
	grains	Indian	1.100	5.230	-0.081

In Table (30) one can observe that when acetone is used as solvent and at each exciting power level, small variations in the calculated values of n_2 at concentration of 0.1 g/ml irrespective of the origin of pomegranate fruit. However, n_2 magnitude decreases for both Yamani and Egyptian pomegranate peels as exciting power changed from 2 to 10 mW. Spanish pomegranate peels show no clear trend as power increases.

Table (30): Nonlinear parameters for pomegranate extracted in acetone with concentration of 0.1g/ml and scanned using Ar ion laser at 514 nm for closed aperture configuration.

P (mW)	Pomegranate peels origin	w_0 $\times 10^{-5}\text{m}$	$I \times 10^7$ W/m^2	$n_2 \times 10^{-7}$ cm^2/W
2	Yamani	1.180	0.912	-0.427
	Spanish	1.170	0.935	-0.453
4	Egyptian	1.160	1.890	-0.064
	Yamani	1.160	1.900	-0.169
	Spanish	1.100	2.090	-0.075
6	Egyptian	0.983	3.950	-0.043
	Yamani	1.210	2.630	-0.102
	Spanish	1.270	2.350	-0.258
8	Egyptian	1.030	4.840	-0.038
	Yamani	1.190	3.580	-0.084
	Spanish	1.290	3.040	-0.368
10	Egyptian	1.050	5.740	-0.069
	Yamani	1.170	4.680	-0.071
	Spanish	1.210	4.320	-0.285

In Table 31, following the same approach of exciting power level with sample concentration of 0.1 g/ml and ethanol as extraction solvent, Egyptian pomegranate peels extract have higher value of n_2 in all excitation power. But, Spanish pomegranate peels extract shows no clear trend in n_2 magnitudes as exciting power level increased.

Table (31): Nonlinear parameters for pomegranate extracted in ethanol with concentration of 0.1g/ml and scanned using Ar ion laser at 514 nm for closed aperture.

P mW	Pomegranate	w₀ × 10⁻⁵m	I × 10⁷ (W/m²)	n₂ × 10⁻⁷ cm²/W
2	Egyptian	1.090	1.070	-0.233
	Yamani	0.887	1.620	-0.143
	Spanish	1.060	1.140	-0.031
4	Egyptian	1.360	1.380	-0.181
	Yamani	0.941	2.880	-0.084
	Spanish	1.420	1.260	-0.068
6	Egyptian	1.100	3.130	-0.133
	Yamani	1.050	3.460	-0.051
	Spanish	1.240	2.500	-0.129
8	Egyptian	1.180	3.680	-0.071
	Yamani	1.150	3.870	-0.057
	Spanish	0.948	5.670	-0.022
10	Egyptian	1.250	4.060	-0.061
	Yamani	1.280	3.910	-0.038
	Spanish	0.972	6.730	-0.016

In summary, One need to observe the effect of choice of both exciting power level and extraction solvent on the magnitude of the calculated n₂. More conclusions about the effect of solvent choice on calculated n₂ can be deduced from Tables (32), and (33)

4.3.2.5 Effect of concentration

Figure (63) presents an example of results obtained where n_2 magnitude increases as sample concentration is increased. This is probably due to the increase in the number of dye molecules.

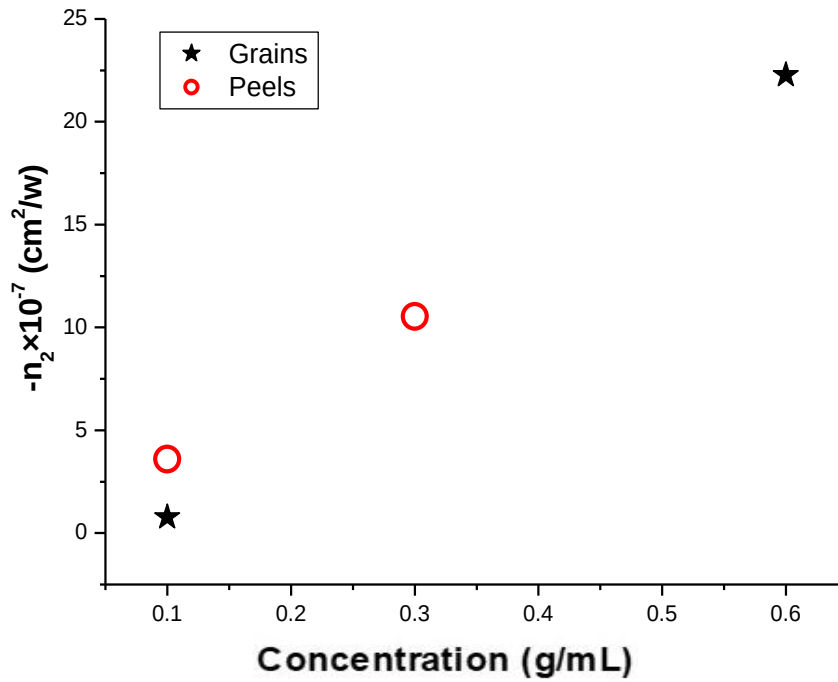


Figure (63): Variation of n_2 as function of concentration ($\lambda = 514 \text{ nm}$, 6 mW) for Indian pomegranate extracts.

4.3.2.6 Effect of excitation wavelength

Tables (32) and (33) show that the role of excitation wavelength on determining n_2 magnitude requires consideration of both concentration and extraction solvent type. For example, n_2 magnitude is increasing as the sample concentration is increased. The higher value of n_2 for peels at is found at $\lambda = 633 \text{ nm}$. While, the lower value is at $\lambda = 514 \text{ nm}$.

For grains extracts at concentration of 0.1 g/ml there are variation in magnitude of n_2 for each excitation wavelength. At 514 nm n_2 magnitude is lower by a factor of 42.3 compared to that at 633nm and 488 nm. Therefore, each case when quantifying sample's n_2 magnitude one must be specifically stating not only excitation wavelength, but also concentration, extraction solvent used and excitation power level. Each of these variables (concentration, solvent, wavelength, power) has its unique effect in determining magnitude of n_2 .

Table (32): Nonlinear parameters for Indian pomegranate at different concentrations in methanol and scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) at for closed aperture configuration.

Indian Pomegranate	Solvent	Excitation wavelength nm	$n_2 \times 10^{-7}$ cm ² /W
Peel (0.1 g/ml)	Methanol	488	-0.667
		514	-0.360
		633	-1.197
Peel (0.3 g/ml)	Methanol	488	-2.075
		514	-1.054
		633	-4.777
Grains (0.1 g/ml)	Methanol	488	-0.374
		514	-0.077
		633	-3.259
Grains (0.6 g/ml)	Methanol	488	-1.760
		514	-2.228
		633	-5.754
Grains (0.6 g/ml)	Methanol + 1% HCl	488	-0.683
		514	-0.439
		633	-1.255

Table (33): Nonlinear parameters for pomegranate at 0.1 g/ml concentration and scanned using Ar ion laser at (514 – 488 nm, P = 6mW) for closed aperture configuration.

Pomegranate	Excitation wavelength nm	$n_2 \times 10^{-7}$ cm^2/W
Egyptian Ethanol	488	-0.070
	514	-0.133
Egyptian Methanol	488	-0.399
	514	-0.152
Yamani Ethanol	488	-0.132
	514	-0.051
Yamani Methanol	488	-0.593
	514	-0.128
Spanish Ethanol	488	-0.143
	514	-0.129
Spanish Methanol	488	-0.829
	514	-0.071

4.3.3 Nonlinear Absorption Coefficient

4.3.3.1 Effect of excitation power level

Figure (64) shows the variation of nonlinear absorption coefficient with excitation power at fixed $\lambda = 514$ nm. The samples have concentration of 0.6 g/ml in methanol and methanol with acid. The sample shows SA at power ranges between (2– 6) mw and as excitation power increases β value decreases. While the sample shows RSA at power ranges between (8– 10) mw and as excitation power increases β value increases. However, the Indian pomegranate grains extract at same concentration in methanol with acid acts as SA in all excitation power. Also, beyond 6 mW power β value clamped to constant value.

For pomegranate peels extracted in acetone and ethanol, values of β are listed in Tables (34) and (35). One must be aware of effect of solvent in combination with variation of excitation power. Also, note the signs of β is not the same in each excitation power level for different peels origin. As we have seen in groups 1 and 2, the magnitude of the real part of $\chi^{(3)}$ almost one order of magnitude larger than the imaginary part.

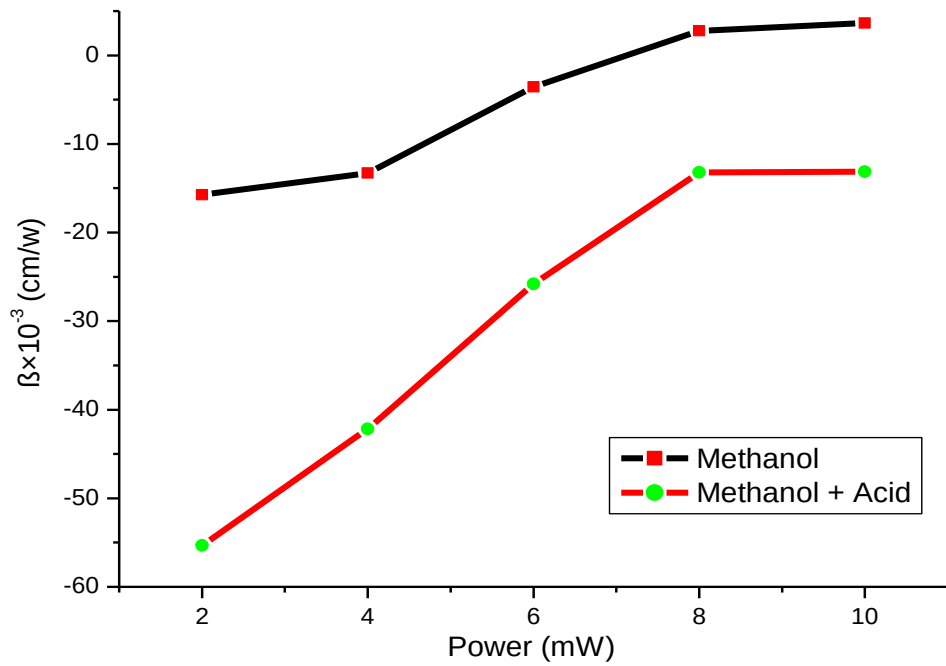


Figure (64): Variation of β as function of excitation power ($\lambda = 514$ nm) for Indian pomegranate grains extract at concentration of 0.6 g/ml.

Table (34): Nonlinear parameters for pomegranate extracted in acetone with concentration of 0.1 g/ml for scanned using Ar ion laser at 514 nm for closed aperture configuration.

P mW	Pomegranate peels	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)}$ $\times 10^{-5}$ esu	$\text{Im } \chi^{(3)}$ $\times 10^{-6}$ esu	$\chi^{(3)}$ $\times 10^{-6}$ esu
2	Yamani	- 0.079	- 0.201	- 0.153	2.018
	Spanish	0.126	- 0.214	0.244	2.155
4	Egyptian	- 0.005	- 0.030	- 0.009	0.305
	Yamani	0.002	- 0.080	0.004	0.798
	Spanish	- 0.018	- 0.035	- 0.035	0.357
6	Egyptian	0.007	- 0.021	0.014	0.207
	Yamani	0.006	- 0.048	0.011	0.483
	Spanish	- 0.058	- 0.122	- 0.112	1.224
8	Egyptian	0.013	- 0.018	0.026	0.182
	Yamani	0.010	- 0.040	0.019	0.399
	Spanish	- 0.062	- 0.174	- 0.120	1.745
10	Egyptian	0.018	- 0.033	0.034	0.331
	Yamani	0.002	- 0.033	0.004	0.332
	Spanish	- 0.068	- 0.135	- 0.133	1.353

Table (35): Nonlinear parameters for pomegranate extracted in ethanol with concentration of 0.1 g/ml and scanned using Ar ion laser at 514 nm for closed aperture configuration.

P mW	Pomegranate peels	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)}$ $\times 10^{-5}$ esu	$\text{Im } \chi^{(3)}$ $\times 10^{-6}$ esu	$\chi^{(3)}$ $\times 10^{-6}$ esu
2	Egyptian	0.035	- 0.110	0.068	1.105
	Yamani	- 0.082	- 0.067	- 0.158	0.691
	Spanish	- 0.000	- 0.015	- 0.001	0.147
4	Egyptian	0.000	- 0.086	0.000	0.856
	Yamani	0.012	- 0.040	0.022	0.398
	Spanish	0.057	- 0.032	0.110	0.341
6	Egyptian	0.005	- 0.063	0.010	0.627
	Yamani	0.005	- 0.024	0.010	0.240
	Spanish	- 0.006	- 0.061	- 0.012	0.608
8	Egyptian	0.012	- 0.034	0.024	0.339
	Yamani	0.005	- 0.027	0.009	0.271
	Spanish	- 0.003	- 0.010	- 0.005	0.102
10	Egyptian	0.004	- 0.029	0.007	0.291
	Yamani	0.004	- 0.018	0.008	0.177
	Spanish	- 0.002	- 0.007	- 0.004	0.075

4.3.3.2 Effect of concentration

As expected concentration of extract does affect values of β . Figure (65) illustrate one of the typical results that has been obtained. The sign of the β in the figure indicates the nature of saturation process as detailed in the chapter 2 and discussion of results of group 1. Moreover, Table (36) makes it clear to conclude that as extract concentration increases value of β increases. Addition of acid to methanol as solvent enhanced β value in dramatic way.

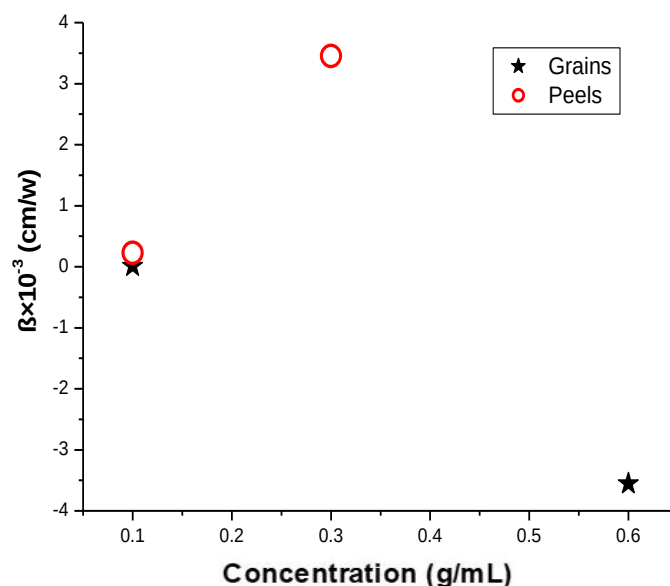


Figure (65): Variation of β as function of concentration ($\lambda = 514$ nm) for Indian pomegranate grains and peels extracts.

Table (36): Nonlinear parameters for Indian pomegranate at different concentration extracted in methanol and scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.

Indian Pomegranate	Solvent	Excitation wavelength (nm)	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)} \times 10^{-5}$ esu	$\text{Im } \chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
Peel (0.1 g/ml)	Methanol	488	- 0.226	- 0.303	- 0.399	3.058
		514	0.023	- 0.163	0.042	1.635
		633	0.005	- 0.544	0.011	5.440
Peel (0.3 g/ml)	Methanol	488	- 1.925	- 0.961	- 3.462	10.210
		514	0.345	- 0.488	0.655	4.925
		633	- 0.355	- 2.212	- 0.828	22.140
Grains (0.1 g/ml)	Methanol	488	- 0.372	- 0.170	- 0.656	1.821
		514	0.001	- 0.035	0.002	0.351
		633	- 0.517	- 1.482	- 1.185	14.870
Grains (0.6 g/ml)	Methanol	488	- 0.556	- 0.815	- 0.999	8.211
		514	- 0.356	- 1.032	- 0.674	10.340
		633	1.546	- 2.665	3.606	26.890
Grains (0.6 g/ml)	Methanol + 1% HCl	488	- 79.730	- 0.327	-148.100	148.100
		514	- 28.160	- 0.210	- 55.170	55.210
		633	18.980	- 0.600	45.740	46.130

4.3.3.3 Effect of excitation wavelength

Excitation wavelength choice does affect the obtained value of β keeping in mind controlling solvent type, extract concentration, and excitation power level as presented in Tables (36) and (37).

Table (37): Nonlinear parameters for pomegranate at 0.1 g/ml concentration extracted in methanol and scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6 mW) at for closed aperture configuration.

Pomegranate	Excitation wavelength (nm)	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)} \times 10^{-5}$ esu	$\text{Im } \chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
Egyptian Ethanol	488	- 0.013	- 0.033	- 0.002	0.332
	514	0.005	- 0.063	0.010	0.627
Egyptian Methanol	488	- 0.052	- 0.182	0.009	1.815
	514	0.001	- 0.069	0.003	0.691
Yamani Ethanol	488	- 0.092	- 0.063	- 0.169	0.651
	514	0.005	- 0.024	0.010	0.242
Yamani Methanol	488	- 0.516	- 0.269	- 0.909	2.844
	514	- 0.020	- 0.058	- 0.037	0.584
Spanish Ethanol	488	- 0.097	- 0.067	- 0.177	0.697
	514	- 0.006	- 0.061	- 0.012	0.608
Spanish Methanol	488	- 0.763	- 0.376	- 1.344	3.995
	514	0.018	- 0.032	0.033	0.324

4.4 Group 4: Prunes

4.4.1 Linear Absorption Spectroscopy

As we have done with the previous groups, in group 4, five materials with different solvents, concentrations and excitation wavelengths were investigated. These materials are almond, dry apricot, dry brown apricot, cherry, and prune (Biswajit Das, 2011).

4.4.1.1 Effect of concentration

Figure (66) shows linear absorption spectroscopy of prune in methanol at different concentrations. Prune extracts have a good absorbance in visible range, it starts absorption at $\lambda = 500$ nm for concentration of 0.1 g/ml, but at $\lambda = 660$ nm for the extract with concentration of 0.6 g/ml. It's obvious from Figure (66) that increasing extracts concentration results in enhanced absorbance level. Anyway, in the near infrared wavelength absorbance is very weak, while below 400 nm wavelength absorbance is very high.

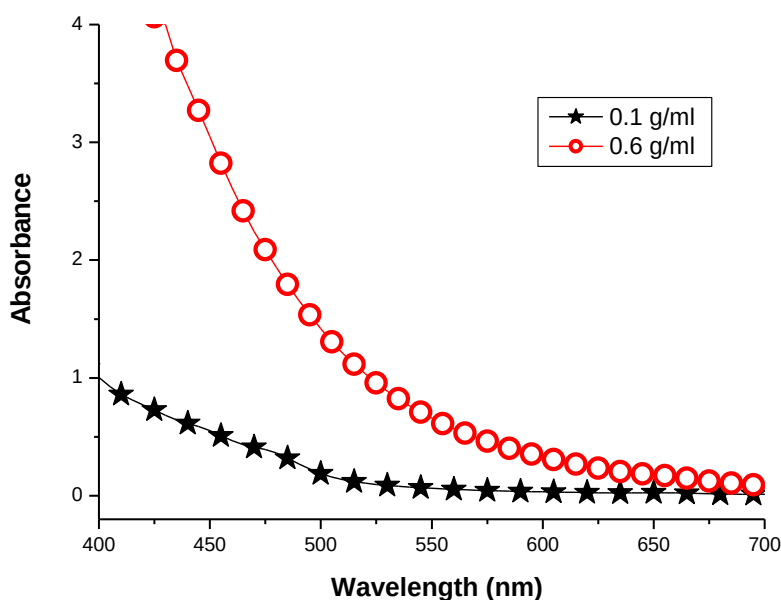


Figure (66): Linear absorption spectra of prune extracted in methanol at two different concentrations.

4.4.1.2 Effect of solvent

Figure (67) shows the effect of solvent on absorbance of the sample at specific concentration (0.1 g/ml). Addition of HCl acid to methanol enhances the absorbance of the sample such that characteristic

absorption peak at $\lambda = 525$ nm is overwhelmed. With acetone the absorbance peak shifted to 365 nm. On the other hand, both methanol and ethanol have absorbance peak almost at wavelength of 350 nm with weaker one for methanol sample.

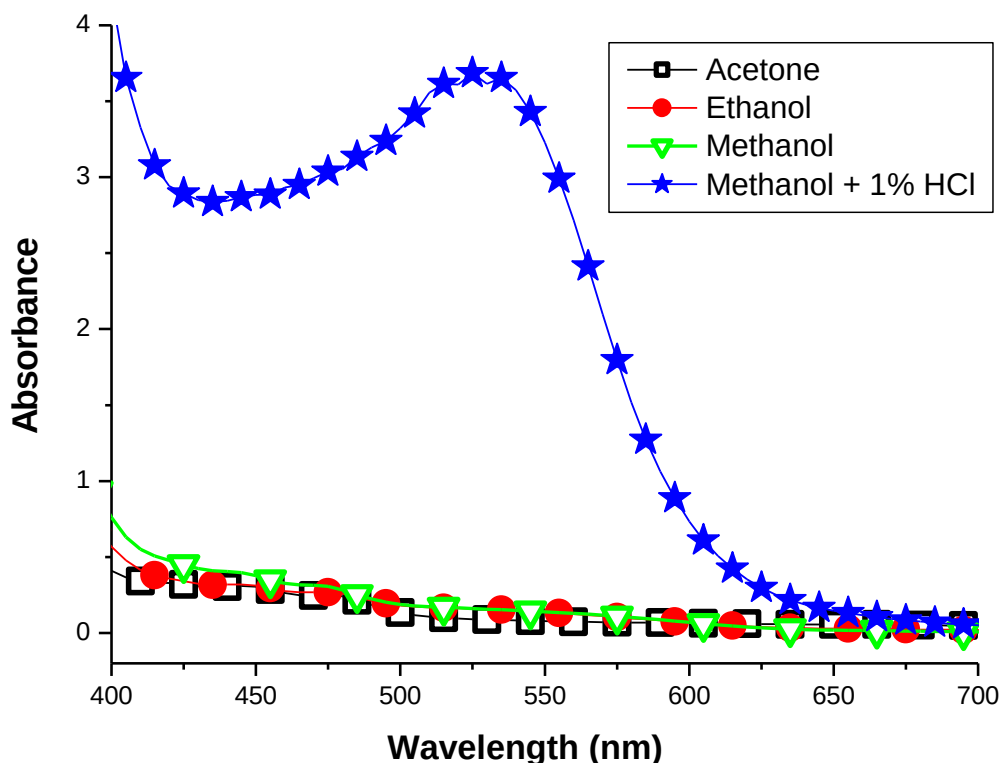


Figure (67): Linear absorption spectra of almond extracted in methanol with 1% HCl acid, ethanol, methanol, and acetone.

4.4.1.3 Effect of materials

Effect of extract material at same concentration using the same solvent is presented in Figure (68) none of the samples demonstrated absorption peak. Prunes and almond in methanol with concentration of 0.1 g/ml, have similar absorbance spectra shown in (Figure 68-a) where absorption is very low in the infrared part and low in the visible part of

the spectrum. In Figure (68-b) materials are extracted in methanol with 1% HCl acid at concentration of 0.6 g/ml demonstrated different absorption levels, but the absorbance behaviours of both are almost the same above wavelength of 750 nm its very weak. Prune and brown apricot extracted in in methanol at concentration of 0.6 g/ml of have similar absorption spectrum as shown in Figure (68-c).

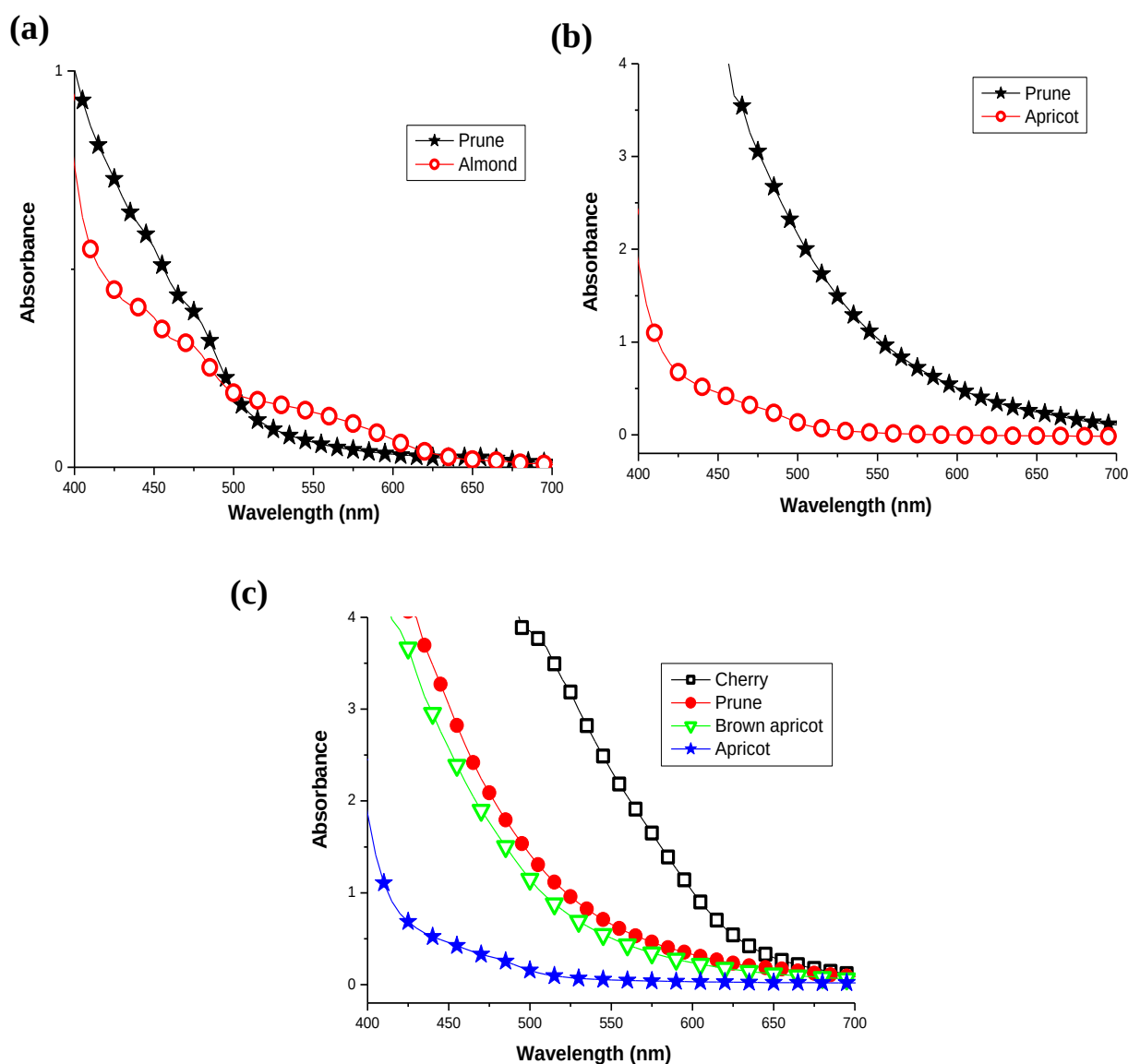


Figure (68): Linear absorption spectra of prunes extracted a) in methanol at concentration of 0.1 g/ml b) in methanol with acid at concentration of 0.6 g/ml of concentration c) in methanol at concentration of 0.6 g/ml.

4.4.2 Fluorescence Spectroscopy

4.4.2.1 Effect of concentration

Figure (69) shows the fluorescence spectra for prune extracted using methanol. The sample shows remarkable fluorescence behaviour with emission characteristic peak at 672 nm. As the concentration increases fluorescence intensity increases as well. However, higher concentration of sample enhances absorption of the emitted photons as presented in Figure (68-b).

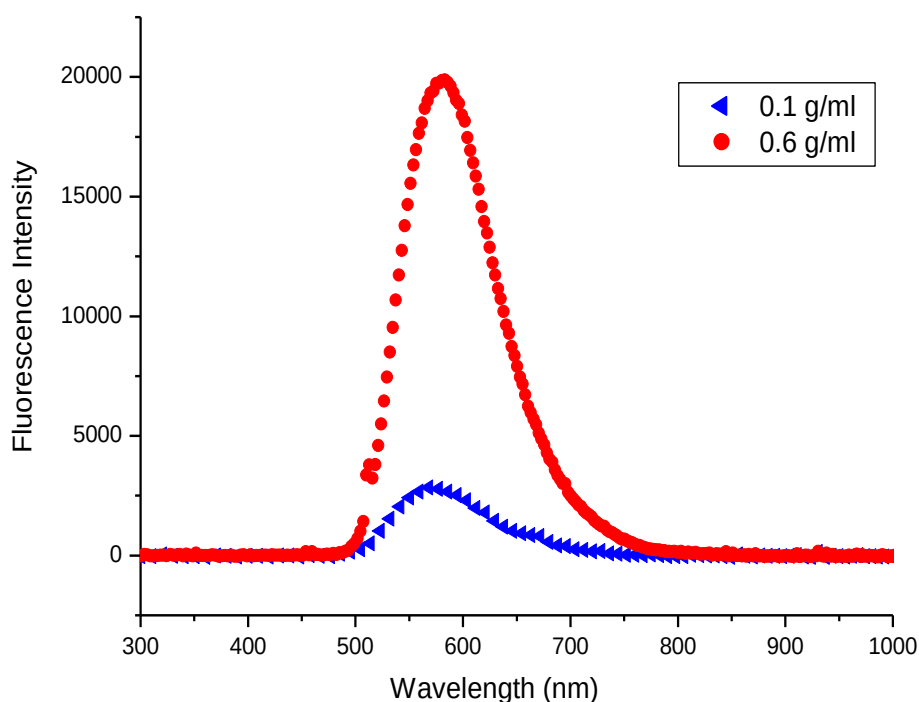


Figure (69): Fluorescence spectra of prune extracted using methanol at two different concentrations.

4.4.2.2 Effect of solvent

Figure (70) shows the fluorescence spectra for almond at concentration of 0.1 g/ml using different solvents. The extracted samples using methanol and ethanol as solvents, exhibited low intensity

fluorescence behaviour with emission characteristic peak at $\lambda \cong 582$ nm. On the other hand, samples extracted using methanol with acid, resulted in a very low fluorescence action with emission characteristic peak at $\lambda \cong 625$ nm. Ethanol as solvent enhances fluorescence intensity while addition of acid to methanol suppresses the fluorescence intensity and red shifted the emission peak.

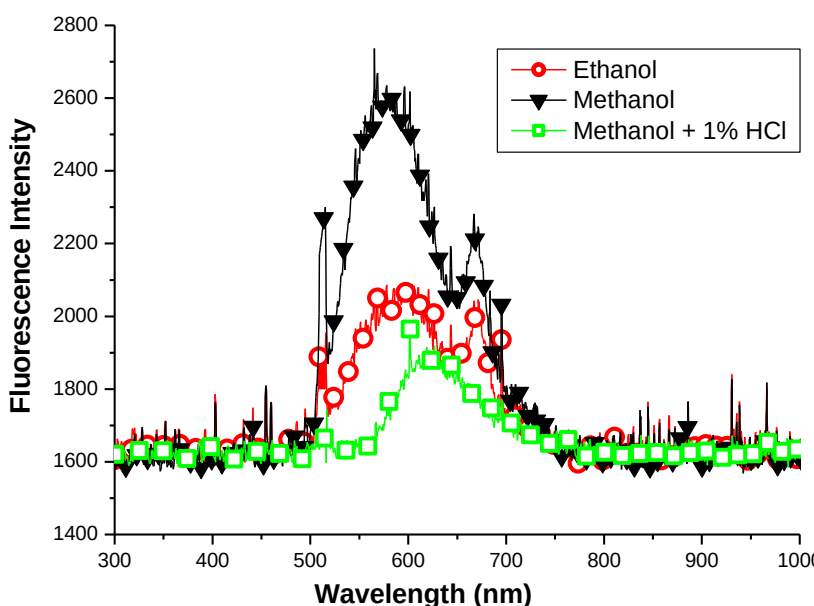


Figure (70): Fluorescence spectra of almond at concentration of 0.1 g/ml extracted with different solvents.

4.4.2.3 Effect of materials

Figure (71) shows the effect of extract materials on fluorescence of the prunes at 0.1 g/ml and 0.6 g/ml concentrations. The fluorescence spectra (Figure (71-a)) for prunes at 0.1 g/ml concentration using methanol shows remarkable fluorescence behaviour with approximate emission characteristic peak at 575 nm for prune and almond. The highest fluorescence peak is for prune extract. Also, prune have higher fluorescence peak in methanol and acid as depicted in Figure (71-b).

While Figure (71-c) show the brown apricot have higher fluorescence peak in methanol at 0.6 g/ml of concentration and apricot the lower fluorescence peak.

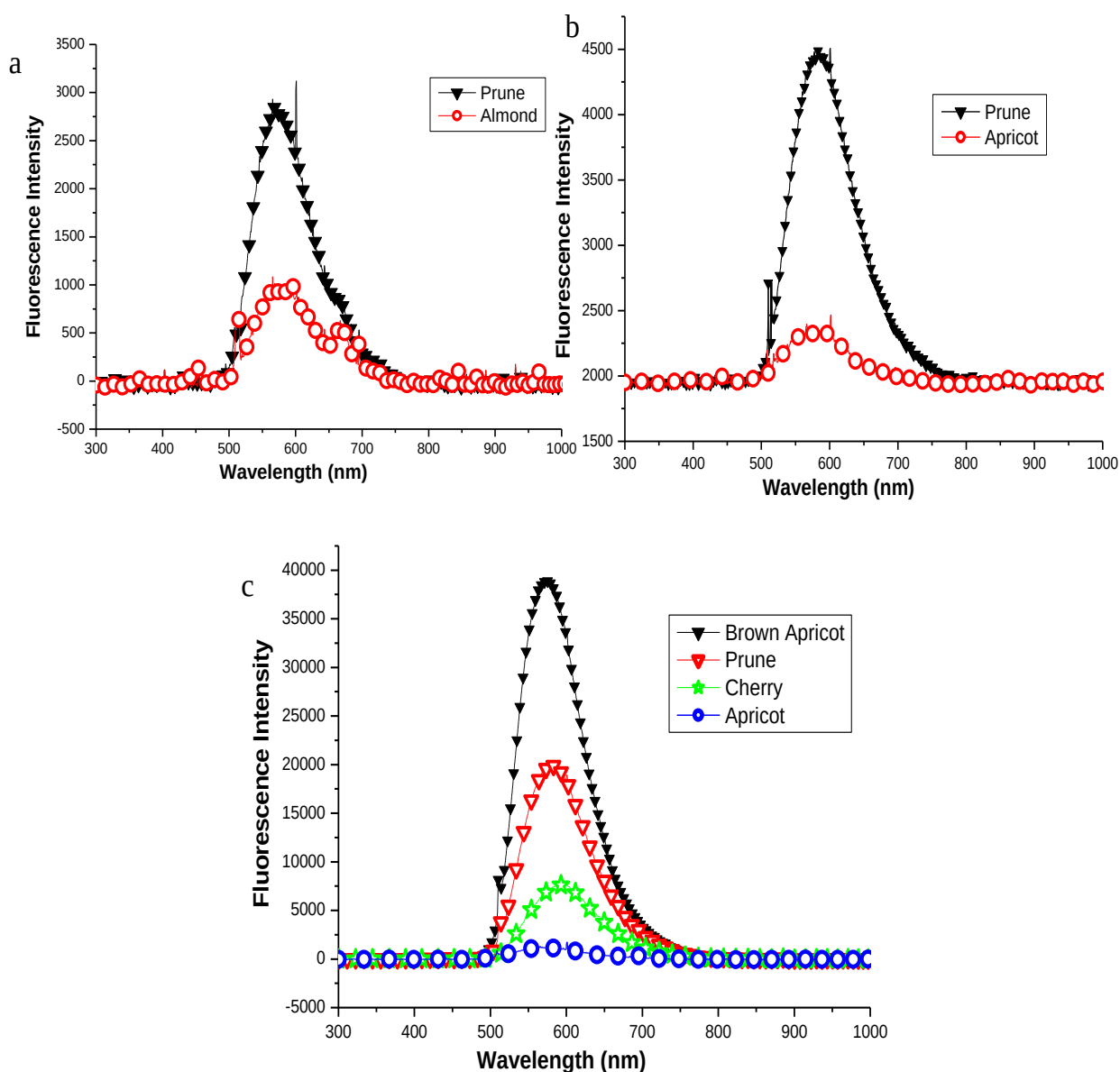


Figure (71): Fluorescence spectra of different prunes extracts a) at 0.1 g/ml concentration using methanol as solvent, b) at 0.6 g/ml concentration using methanol with acid as extracting solvent, and c) at 0.6 g/ml concentration using only methanol as extracting solvent.

4.4.3 Nonlinear Index of Refraction

4.4.3.1 Effect of excitation power level

For sample extracts in methanol and methanol with acid at different concentrations, Figure (72) shows the variation of nonlinear index of refraction as function of excitation power level at $\lambda = 514$ nm. In general, as excitation power increases n_2 value decreases in a nonlinear way. This behaviour is a clear indication of optical limiting process capability. This mechanism for optical limiting might arise from thermal defocusing (Henari and Jasim, 2012, Henari, et al., 2013).

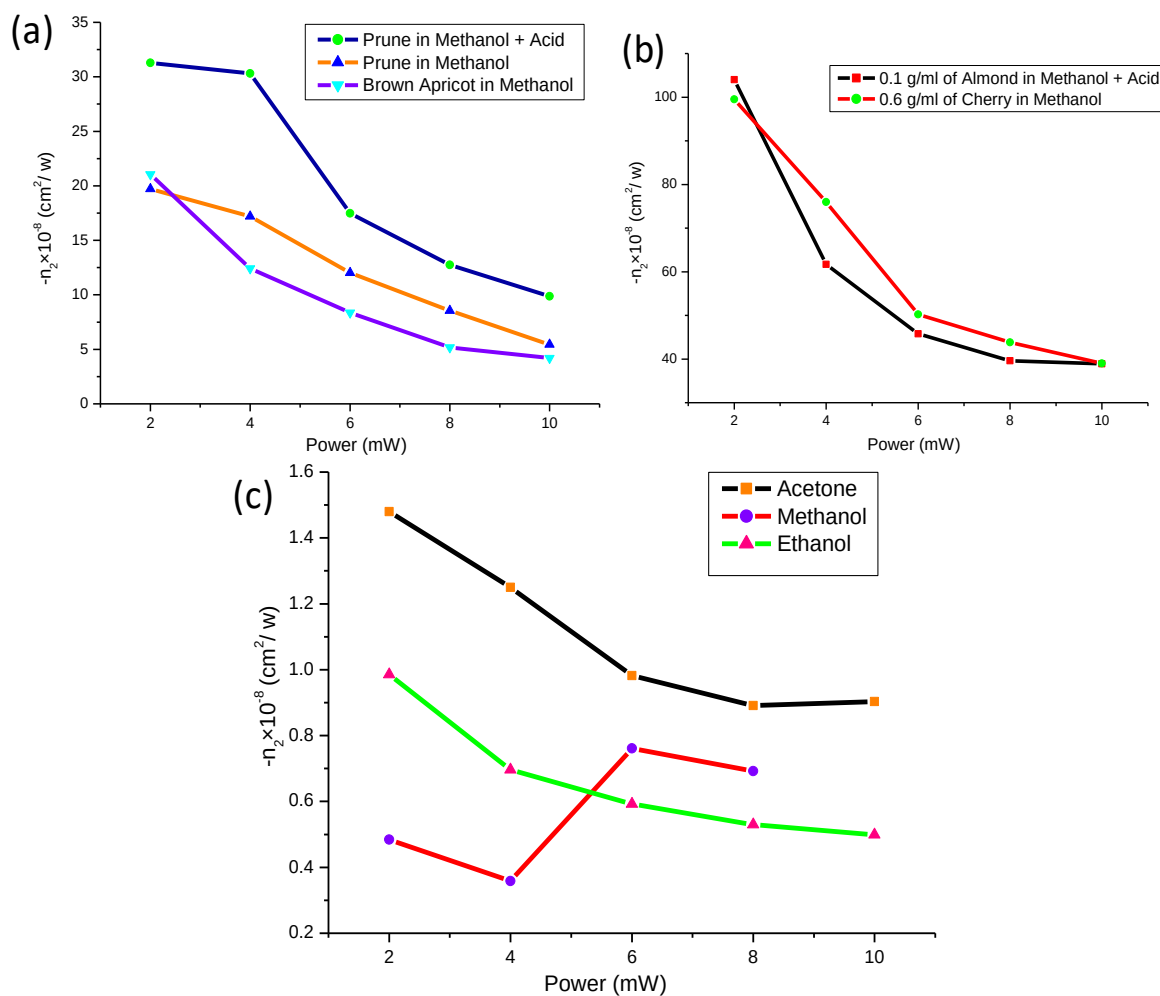


Figure (72): Variation of n_2 as function of excitation power ($\lambda = 514$ nm) for prunes a) at 0.6 g/ml concentration extracted in methanol, b) almond and cheery, and c) Almond with concentration of 0.1 g/ml.

4.4.3.2 Effect of concentration

As it has been found with other groups, higher concentration of the sample results in larger value of n_2 , Figure (73) shows that as sample concentration increases n_2 magnitude increases as well. This is due to the increase in the number of dye molecules.

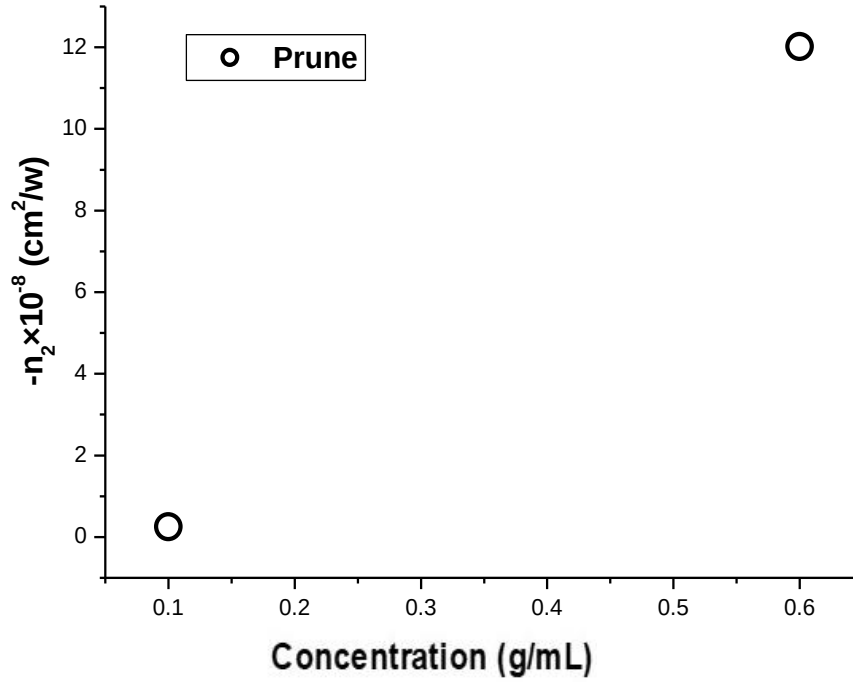


Figure (73): Variation of β as function of concentration ($\lambda = 514 \text{ nm}$, $P = 6 \text{ mW}$) for prune extract.

4.4.3.3 Effect of exciting wavelength

Different excitation wavelengths at beam power of 6 mW have been used to investigate extracts nonlinear index of refraction as shown in Tables (38) to (42). Excitation with 488 nm wavelength resulted in n_2 value greater by one order of magnitude compared to that with excitation wavelength 514 nm regardless the choice of solvent. Also, each wavelength has its own effect regardless the change in concentrations (see for example, Table (41)).

Table (38) shows the higher value of nonlinear refractive index at $\lambda = 488$ nm for almond extracted using methanol with acid. While, at wavelength of 633 nm samples showed no response when ethanol, methanol were used as extracting solvents.

Table (38): Nonlinear parameters for Almond at 0.1 g/ml concentration scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.

Sample	Exciting wavelength nm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m ²	$n_2 \times 10^{-7}$ cm ² /W
Ethanol	488	1.044	3.507	-0.129
	514	1.113	3.081	-0.059
Methanol	488	1.217	2.581	-0.134
	514	1.116	3.065	-0.076
Methanol + 1% HCl	488	0.865	5.111	-6.988
	514	1.354	2.085	-4.577
	633	4.219	0.190	-7.112

Addition of acid to methanol decreases the value of n_2 as listed in Table (39). The higher value of n_2 achieved with excitation at $\lambda = 488$.

Table (39): Nonlinear parameters for apricot at 0.6 g/ml concentration scanned using Ar ion laser at (514 – 488) nm (P = 6mW) for closed aperture configuration.

Solvent	Exciting wavelength nm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m ²	$n_2 \times 10^{-7}$ cm ² /W
Methanol	488	0.918	4.530	-0.477
	514	1.140	2.930	-0.107
Methanol + 1% HCl	488	1.020	3.700	-0.215
	514	1.090	3.240	-0.034

As presented in Table (40), value of n_2 increases as increase the excitation wavelength for brown apricot at 0.6 g/ml concentration extracted in methanol.

Table (40): Nonlinear parameters for brown apricot at 0.6 g/ml concentration extracted in methanol scanned using Ar ion laser at (514 and 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.

Exciting wavelength λ nm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ (W/m ²)	$n_2 \times 10^{-7}$ cm ² /W
488	1.240	2.470	-0.669
514	1.250	2.430	-0.836
633	3.370	0.296	-3.921

Table (41): Nonlinear parameters for prune at different concentration scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.

Sample	Excitation wavelength nm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m ²	$n_2 \times 10^{-7}$ cm ² /W
0.1 g/ml in Methanol	488	0.990	3.900	-0.217
	514	0.958	4.160	-0.025
0.6 g/ml in Methanol	488	1.270	2.360	-0.961
	514	1.370	2.050	-1.202
	633	2.860	0.413	-3.255
0.6 g/ml in Methanol + 1% HCl	488	0.936	4.360	-2.726
	514	1.270	2.360	-1.748
	633	3.870	0.225	-6.605

Table (42): n_2 for cherry extracts at 0.6 g/ml concentration in methanol scanned using Ar ion laser at (514 – 488) nm and HeNe laser ($P = 6\text{mW}$) for closed aperture configuration.

Exciting wavelength nm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m ²	$n_2 \times 10^{-7}$ cm ² /W
488	3.620	0.257	-7.190
514	1.160	2.850	-3.901
633	1.460	1.790	-5.022

4.4.4 Nonlinear Absorption Coefficient

4.4.4.1 Effect of excitation power level

As expected excitation power level has clear impact on magnitude of absorption coefficient, this could be concluded from plotted curves shown in Figure (74).

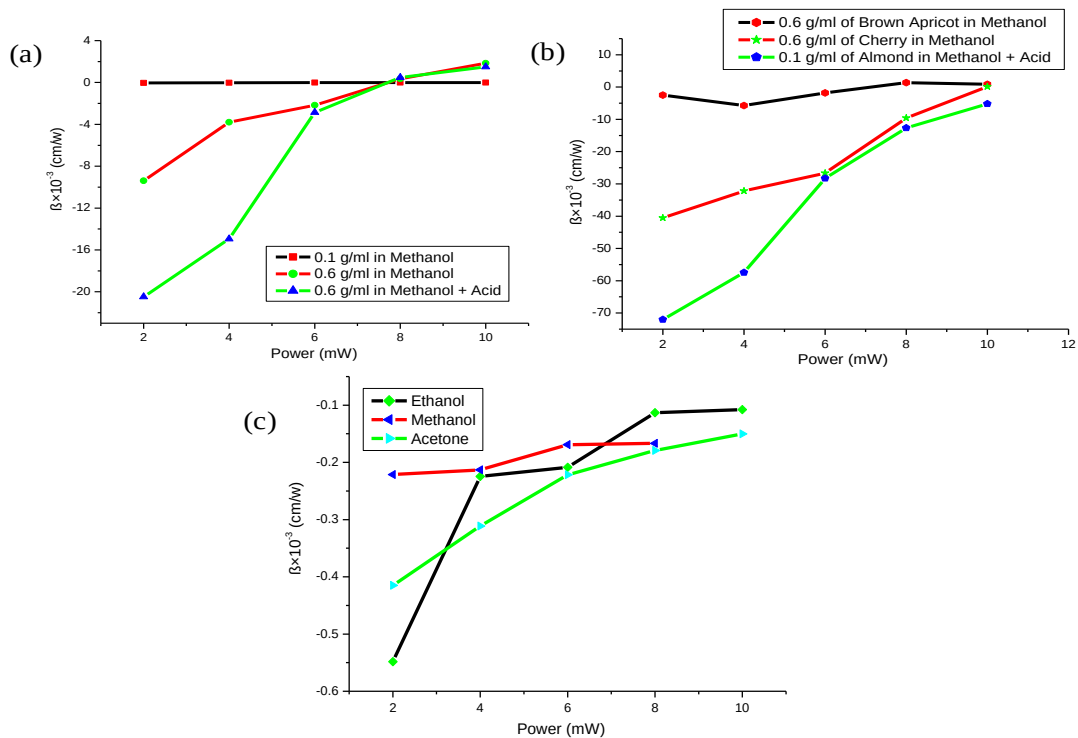


Figure (74): Variation of n_2 as function of excitation power ($\lambda = 514$ nm) for: a) Prune at different concentrations b) Apricot, cherry and almond and c) Almond at 0.1 g/ml concentration using different solvents.

4.2.1.1 Effect of concentration

One example that reflects variation of β value with concentration is shown in Figure (75). It's clear that not only the magnitude of β get change, but also the sign or the saturation type.

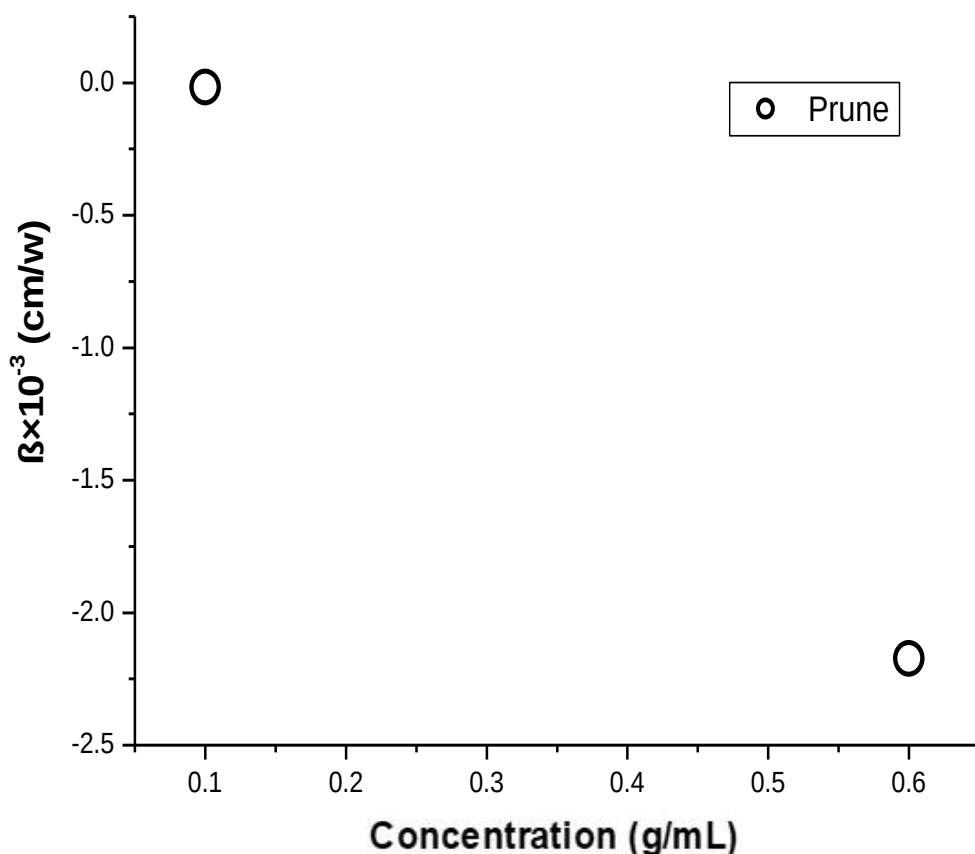


Figure (75): Variation of β as function of concentration ($\lambda = 514$ nm, $P = 6$ mW) for prune.

4.2.1.2 Effect of excitation wavelength

Combination of solvent and excitation wavelength results in remarkable effects on β and $\chi^{(3)}$ magnitudes as detailed in Table (43). For the example shown in Table (43) β for almond not only has larger value at 633 nm, but also its sign has been changed.

Table (43): Nonlinear parameters for almond at different solvent scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) at for closed aperture configuration.

Sample	Excitation wavelength nm	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)}$ $\times 10^{-5}$ esu	$\text{Im } \chi^{(3)}$ $\times 10^{-6}$ esu	$\chi^{(3)}$ $\times 10^{-6}$ esu
Ethanol	488	- 0.022	- 0.061	- 0.040	0.614
	514	- 0.021	- 0.028	- 0.040	0.283
Methanol	488	- 0.010	- 0.061	- 0.018	0.606
	514	- 0.017	- 0.034	- 0.031	0.346
Methanol + 1% HCl	488	- 7.664	- 3.376	- 14.380	36.700
	514	- 2.826	- 2.211	- 5.591	22.810
	633	1.519	- 3.436	3.696	34.560

For the other cases shown in Table (43) when ethanol and methanol being used as solvent values of β are distinguishable even though having the same sign. Moreover, both the real and imaginary parts of $\chi^{(3)}$ have the same sign, but $\text{Re } (\chi^{(3)})$ is one order of magnitude larger than the $\text{Im } (\chi^{(3)})$. Such behaviour observed in the previously investigated group.

Table (44): Nonlinear parameters for apricot at 0.6 g/ml concentration extracted using different solvent and scanned using Ar ion laser at (514 – 488) nm (P = 6mW) for closed aperture configuration.

Solvent	Excitation wavelength nm	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)}$ $\times 10^{-5}$ esu	$\text{Im } \chi^{(3)}$ $\times 10^{-6}$ esu	$\chi^{(3)}$ $\times 10^{-6}$ esu
Methanol	488	- 0.277	- 0.230	- 0.518	2.358
	514	- 0.024	- 0.051	- 0.047	0.517
Methanol + 1% HCl	488	- 0.086	- 0.107	- 0.166	1.081
	514	- 1.957	- 0.017	- 0.398	0.171

It's interesting to note that one of the cases that shows some trend between wavelength and magnitude of β is presented in Table (45).

Table (45): Nonlinear parameters for brown apricot at 0.6 g/ml concentration extracted in methanol and scanned using Ar laser at (514 – 488) nm and HeNe laser (P = 6mW) at for closed aperture configuration.

Excitation wavelength (nm)	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)} \times 10^{-5}$ esu	$\text{Im } \chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
488	- 0.126	- 0.323	- 0.235	3.237
514	- 0.180	- 0.403	- 0.356	4.048
633	- 0.860	- 1.891	- 2.089	19.030

Table (46) shows prune acts as SA at both $\lambda = 488$ and $\lambda = 514$ and RSA at 633. Also, increasing concentration of the extract of the same solvent (Methanol) resulted in enhancement of β value. Addition of acid to methanol as solvent increased the β value many folded.

Table (46): Nonlinear parameters for prune extracted with different solvents and concentrations scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) at for closed aperture configuration.

Sample	Excitation wavelength nm	$\beta \times 10^{-4}$ cm/W	$\text{Re } \chi^{(3)} \times 10^{-5}$ esu	$\text{Im } \chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
0.1 g/ml in Methanol	488	- 7.688	- 0.099	- 1.361	0.999
	514	- 1.610	- 0.011	- 0.301	0.117
0.6 g/ml in Methanol	488	- 21.430	- 0.461	- 3.990	4.625
	514	- 21.730	- 0.576	- 4.267	5.779
	633	0.005	- 1.560	0.001	15.600
0.6 g/ml in Methanol + 1% HCl	488	- 323.00	- 1.307	- 60.130	14.390
	514	- 28.560	- 0.838	- 5.608	8.399
	633	98.120	- 3.167	23.700	31.750

Table (47) shows cherry acts as SA at different wavelength, but and the higher value of β occurred at $\lambda = 514$ nm.

Table (47): Nonlinear parameters for cherry at 0.6 g/ml extracted in methanol scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) at for closed aperture configuration.

Excitation wavelength (nm)	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)} \times 10^{-5}$ esu	$\text{Im } \chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
488	- 0.518	- 3.498	- 1.269	35.00
514	- 3.021	- 1.898	- 5.707	19.82
633	- 2.668	- 2.443	- 5.317	25.00

4.5 Group 5: Tropical

In group 5, 5 materials have been studied using different solvents, concentrations, excitation power level, and excitation wavelengths. These materials are dry kiwi, dry mangosteen peel, dry avocado peel, dry avocado seed and dry avocado seed peel (Elhadi M Yahia, 2006).

4.5.1 Linear Absorption Spectroscopy

4.5.1.1 Effect of concentration

Linear absorption spectroscopy of avocado peels samples at concentration of 0.1 and 0.6 g/ml are shown in Figure (76-a) at wavelengths beyond 700 nm absorbance is very weak. However, at a wavelength less than 700 nm samples absorbance increases reaching a characteristic peak at wavelength 660 nm. Moreover, increasing sample concentration enhances absorbance peak values.

Linear absorption spectroscopy of mangosteen peels samples at concentration of (0.1, 0.3 and 0.6) g/ml have similar absorbance spectrum as shown in Figure (76-b), but absorption edge is red shifted as sample concentration increased. Materials show different absorption level, but the behaviour is almost the same where above 700 nm its very weak. At the visible range it has broad absorption peak and good level of absorbance. Figure (76-c) indicates that avocado seeds extracts have different absorbance than its peels extracts. Figure (76-d) shows

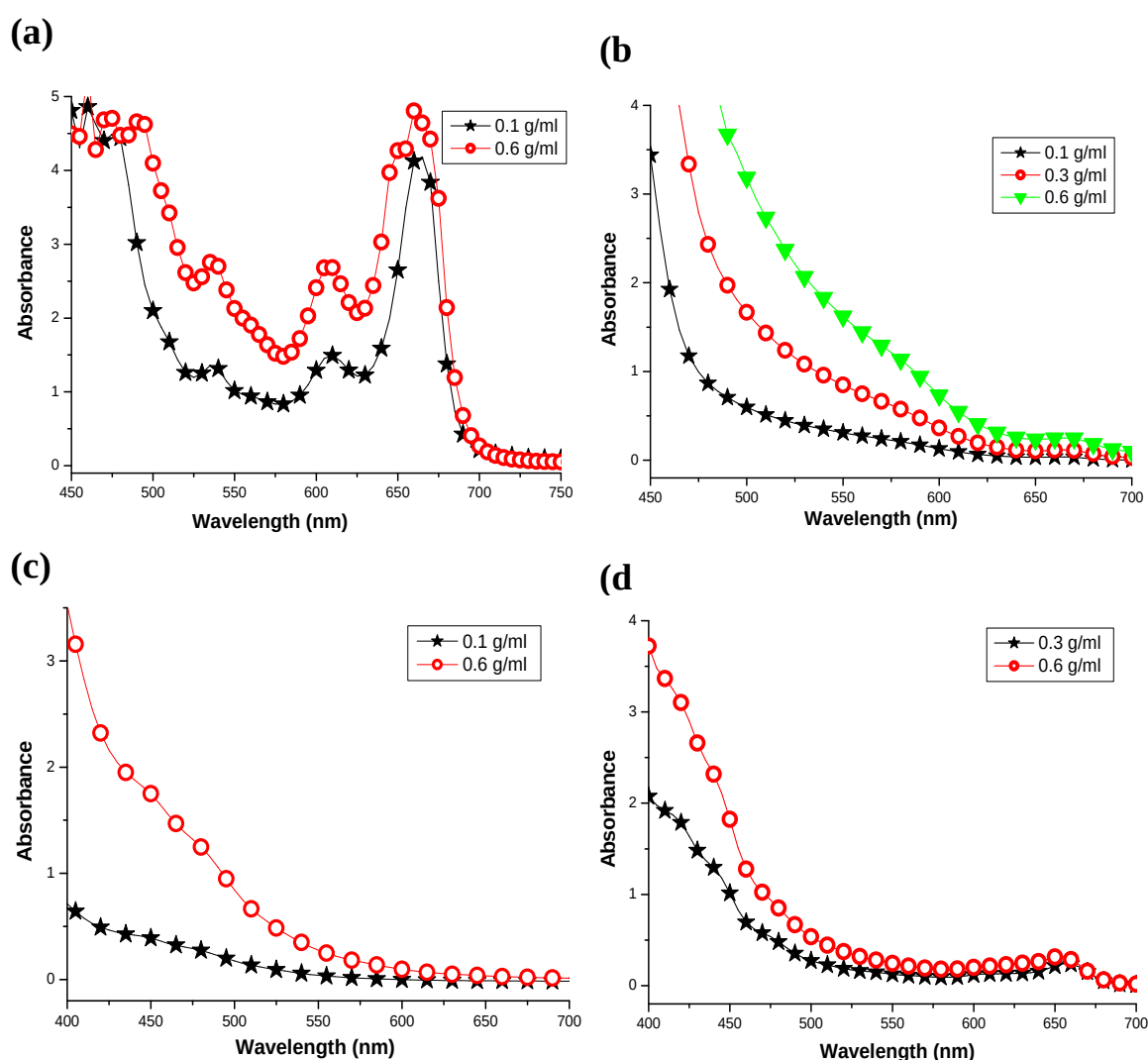


Figure (76): Linear absorption spectra for a) avocado peels extracted in methanol at different concentrations b) mangosteen peels extracted in methanol. at different concentrations c) Avocado seeds d) Kiwi extracted in methanol at different concentrations.

4.5.1.2 Effect of solvent

Figure (77) shows the effect of solvent on absorbance of kiwi at concentration of 0.6 g/ml. Addition of HCl acid to methanol showed no noticeable change in absorbance of the extract such that characteristic absorption peak at 655 nm is overwhelmed. Also, the addition of HCl to methanol for mangosteen showed no change in absorption peak of the sample and the slight change start at $\lambda = 650$ nm as shown in Figure (77).

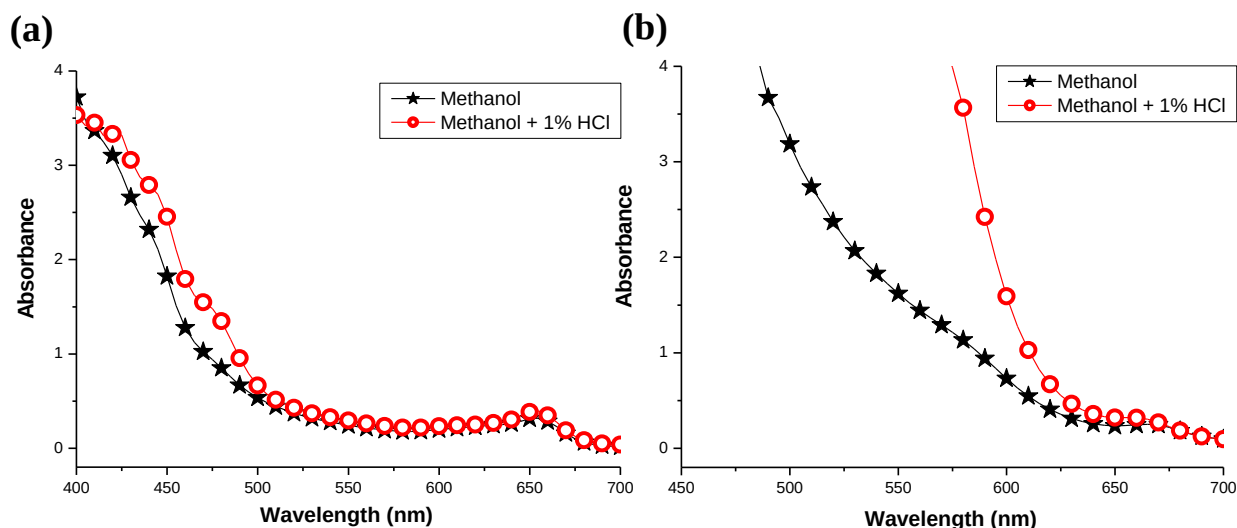


Figure (77): Linear absorption spectra for a) kiwi b) mangosteen with concentration of 0.6 g/ml extracted in different solvent.

4.2.1.3 Effect of Materials

Effect of extract material at same concentration using the same solvent is presented in Figure (78). Figure (78-a) shows avocado seeds and avocado seed peels in methanol at 0.1 g/ml have similar absorbance spectrum. Whereas the mangosteen absorbance spectrum differs from avocado seed in the beginning of absorption increasing. While the avocado peel have characteristic peak at 660 nm.

Figure (78-b) shows mangosteen and kiwi in acid at 0.6 g/ml of concentration have similar absorptance spectrum above 650. The mangosteen start absorption at 650 nm wheal the kiwi start absorption at 500 nm. The avocado peel have characteristic peak at 655 nm and 610 nm.

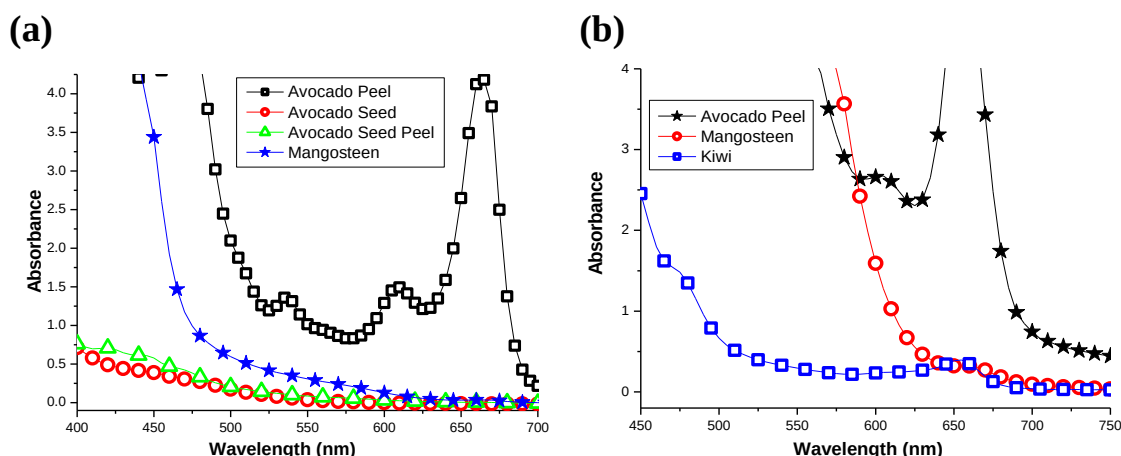


Figure (78): Linear absorption spectra for different materials at a) 0.1 g/ml concentrations extracted in methanol b) 0.6 g/ml concentration extracted in methanol with 1% HCl at different concentrations.

4.5.2 Fluorescence Spectroscopy

4.5.2.1 Effect of concentration

Figure (79-a) shows the fluorescence spectra for avocado seeds extracted in methanol. The sample demonstrated remarkable fluorescence behaviour with characteristic peak wavelength at 548 nm. As the concentration increases fluorescence intensity increases.

Figure (79-b) shows the fluorescence spectra for avocado peels extracted in methanol at different concentrations. The samples showed remarkable fluorescence behaviour with emission peaks at wavelengths of 685 nm and 569 nm. Moreover, as the concentration increases fluorescence intensity increases

Figure (79-c) shows the fluorescence spectra for mangosteen peels extracted in methanol at different concentrations. Samples showed remarkable fluorescence behaviour with emission peaks at wavelengths of 560 nm and 673 nm. Moreover, as the concentration increases fluorescence intensity increases.

Figure (79-d) shows the fluorescence spectra for kiwi extracted in methanol at different concentrations. Samples showed remarkable fluorescence behaviour with emission peaks at wavelengths of 575 nm and 667nm.

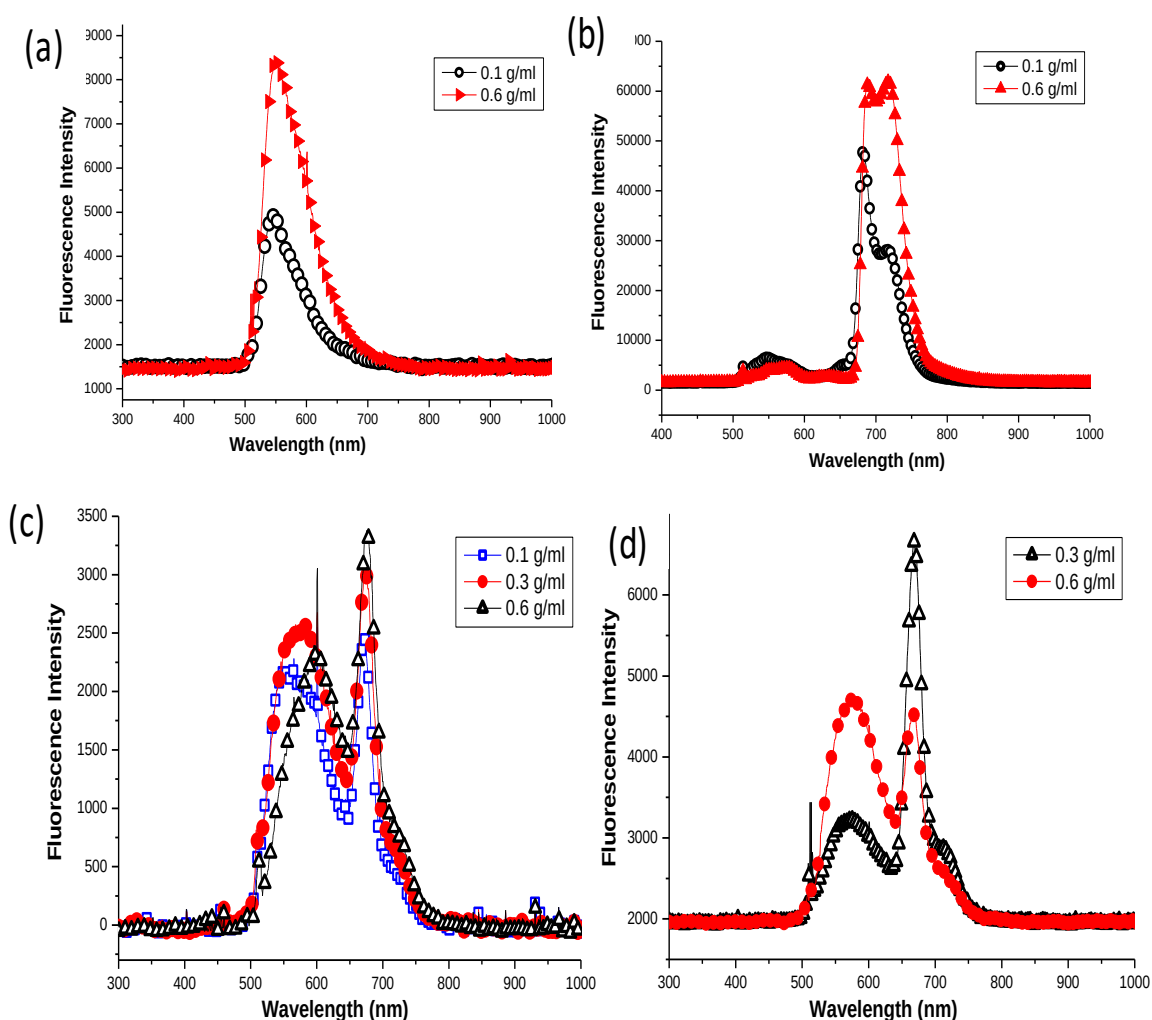


Figure (79): Fluorescence spectra at excitation wavelength 514 nm of a) Avocado seeds extract b) Avocado peels extract c) Mangosteen extract d) Kiwi extract at different concentrations in methanol

4.5.2.2 Effect of solvent

Figure (80) shows the effect of solvent on fluorescence behaviour of the sample. Addition of acid to methanol as solvent for cases kiwi and mangosteen at 0.6 g/ml concentration decrease the fluorescent intensity.

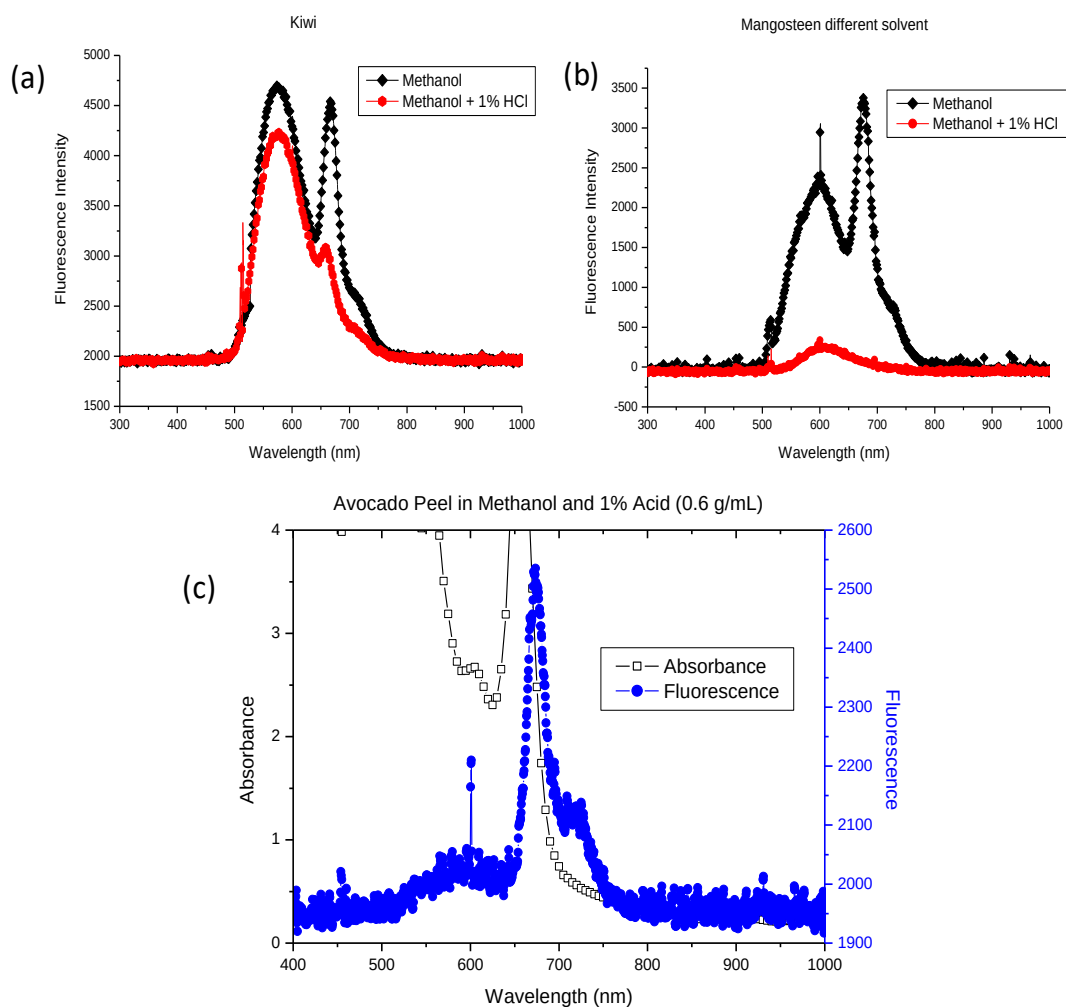


Figure (80): Fluorescence spectra of a) kiwi b) mangosteen at 0.6 g/ml concentration c) Fluorescence and absorbance of avocado peels extracted in methanol with 1% HCl at 0.6 g/ml concentration.

It can be deduced from Figure (80-c) that most of the fluorescence intensity is absorbed by the extract itself.

4.5.2.3 Effect of materials

Figure (81) illustrates the effect of material on fluorescence behaviour of the sample. Figure (81-a) shows different materials extracted in methanol at 0.1 g/ml concentration. Avocado peels extract has higher fluorescence intensity. While the other samples have almost the same fluorescence intensity. Figure (81-b) shows different materials in methanol with 1% HCl acid at 0.6 g/ml concentration. Kiwi extracts have higher fluorescence intensity.

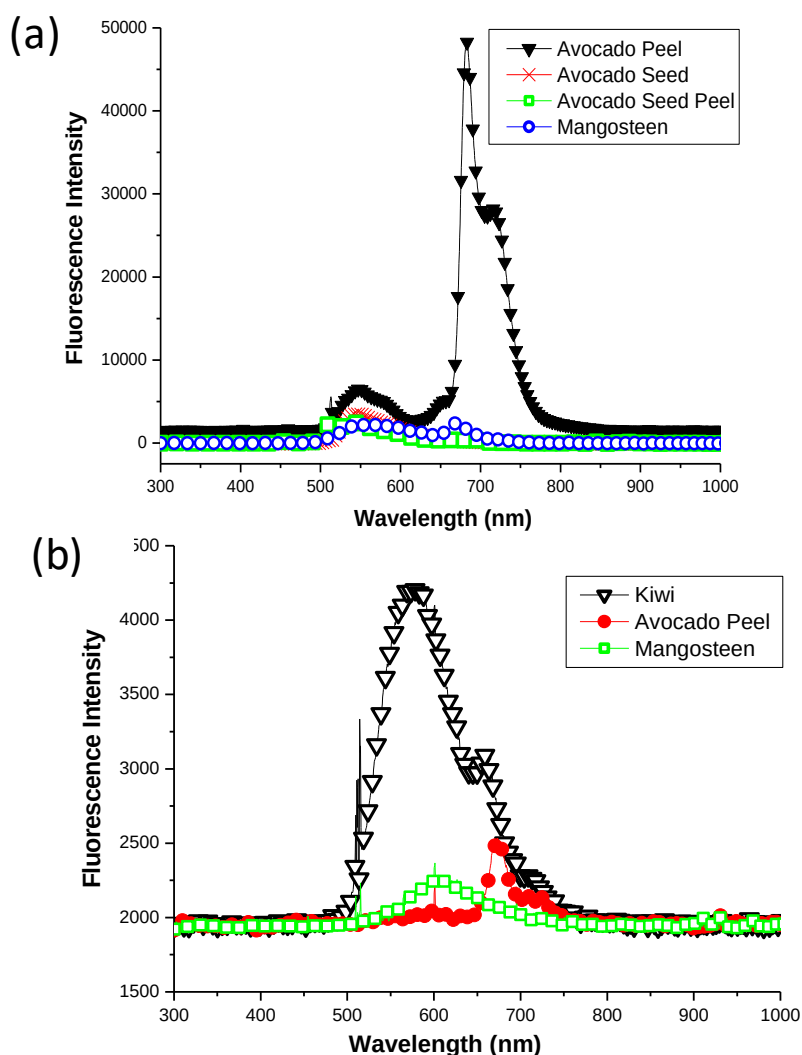


**Figure (81): Fluorescence spectra of tropical group extracted with a) Methanol
b) Methanol with 1% HCl.**

4.5.3 Nonlinear Index of Refraction

4.5.3.1 Effect of excitation power level

For samples extracted in methanol and methanol with 1% HCl acid at concentrations of 0.1, 0.3 and 0.6 g/ml, Figure (82) shows the variation of nonlinear index of refraction versus excitation power level at excitation wavelength $\lambda = 514$ nm. As excitation power level increases, n_2 value decreases in a nonlinear way.

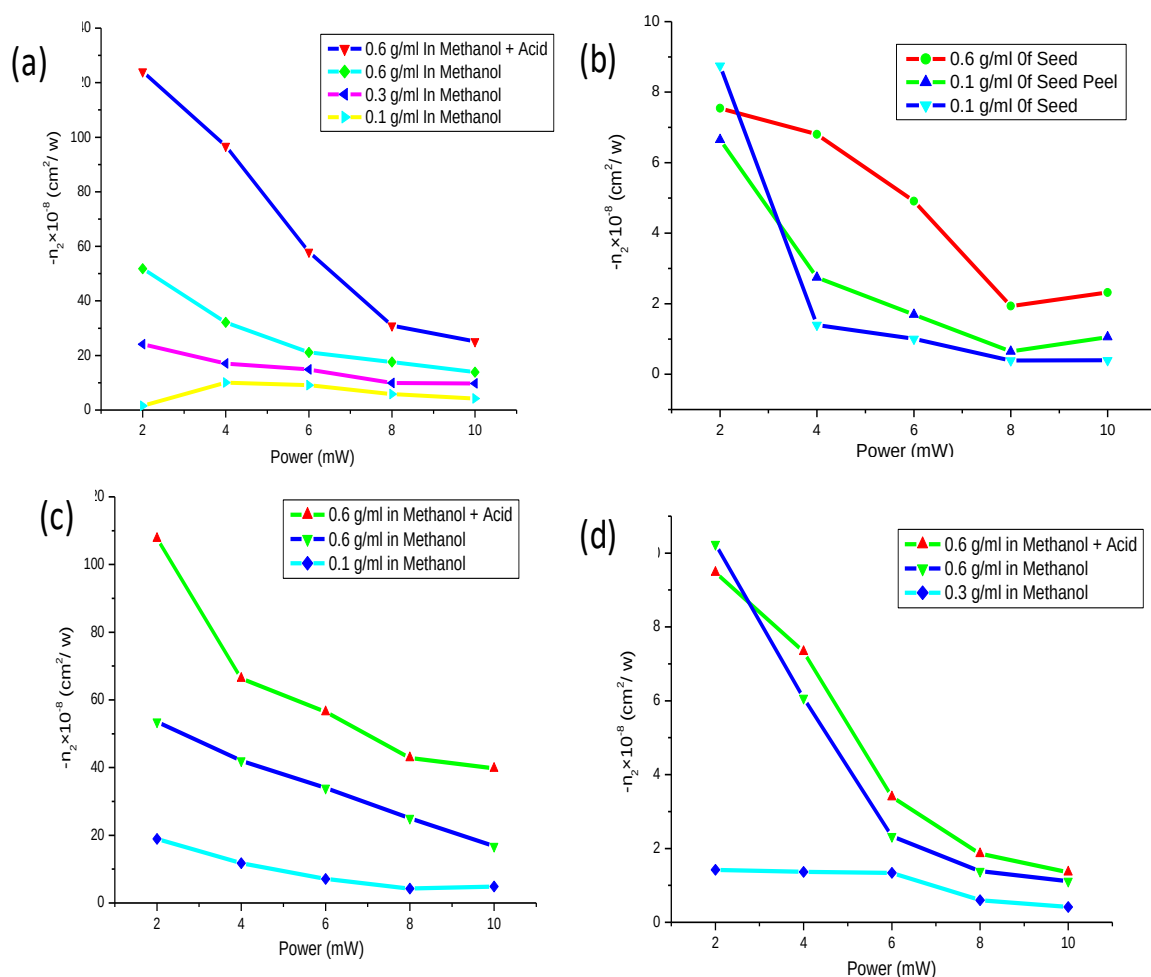


Figure (82): Variation of n_2 as function of excitation power level ($\lambda = 514$ nm) at 0.1 g/ml concentration for a) mangosteen b) avocado seeds c) avocado peels d) kiwi extracts.

Addition of acid have increased values of n_2 . Also, n_2 magnitude is increasing as extracts concentration increased. These findings are agreement with the reported resulted (Henari, et al., 2013). Addition of acid resulted in higher values of n_2 for mangosteen, avocado peels and kiwi extracts in methanol at concentration of 0.6 g/ml.

4.5.3.2 Effect of concentration

Figure (83) shows n_2 increasing as the concentration increases. This is mainly due to the increase in the number of dye molecules. These results behaviours are in good agreement with the reported resulted by (Dhinaa and Pallnisamy, 2010; Rashidian, et al., 2008). The optical nonlinearity of tropical dyes is attributed to thermal effect of laser beam (Rekha and Ramalingam, 2009; Yakop & Badran, 2014)

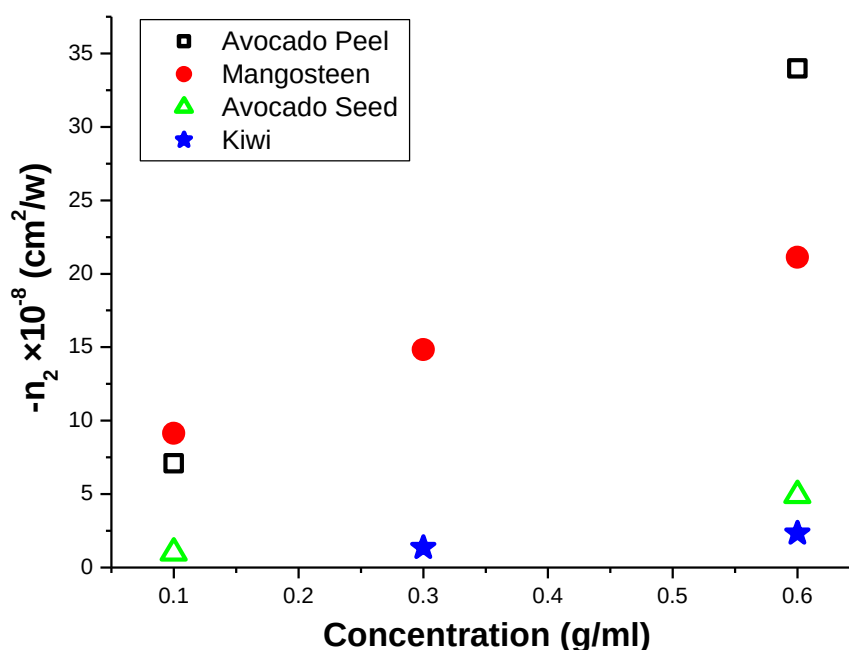


Figure (83): Variation of n_2 as function of concentration ($\lambda = 514 \text{ nm}$) for tropical group.

4.1.1.1 Effect of excitation wavelength

Different excitation wavelengths at beam power of 6 mW have been used to investigate extracts nonlinear index of refraction as shown in Tables (48). No distinct behaviour has been noticed. Therefore, each wavelength has its own effect regardless the change in concentrations. The higher value of nonlinear refractive index for avocado peels extracted in methanol with acid at excitation wavelength of $\lambda = 633$ nm. While the lower value occurred at $\lambda = 514$ nm.

Table (48): Nonlinear parameters for avocado peels extract at different concentrations and scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) at for closed aperture configuration.

Sample	Excitation wavelength nm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m ²	$n_2 \times 10^{-7}$ cm ² /W
0.1 g/ml at methanol	488	1.110	3.090	- 2.814
	514	1.160	2.860	- 0.708
	633	4.080	0.203	- 14.370
0.6 g/ml at methanol	488	1.230	2.540	- 4.052
	514	1.520	1.660	- 3.398
	633	4.580	0.161	- 29.280
0.6 g/ml at methanol + Acid	488	0.881	4.930	- 7.517
	514	1.270	2.360	- 5.647
	633	4.450	0.171	- 48.430

Tables (49), (50), (51), and (52) presents more calculated values of n_2 which show that tested extracts behaved as saturable absorbers at different excitation wavelengths. Each wave length has its own characteristic value of n_2 at the specified concentration after being scanned with 6 mW laser beam.

Table (49): Nonlinear parameters for avocado seeds extracts at different concentrations scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.

sample	Excitation wavelength (nm)	$w_0 \times 10^{-5}$ m	$I \times 10^7$ (W/m ²)	$n_2 \times 10^{-7}$ cm ² /W
0.1 g/ml at methanol	488	1.020	3.660	-0.278
	514	1.190	2.710	-0.100
0.6 g/ml at methanol	488	1.290	2.300	-0.918
	514	1.150	2.900	-0.491
	633	2.000	0.844	-0.355

Table (50): Nonlinear parameters for avocado seeds peels at 0.1 g/ml concentrations scanned using Ar ion laser at (514 – 488) nm (P = 6mW) for closed aperture configuration.

Sample	Excitation wavelength nm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ (W/m ²)	$n_2 \times 10^{-7}$ cm ² /W
0.1 g/ml at methanol	488	1.170	2.780	-0.536
	514	1.110	3.120	-0.169

Table (51): Nonlinear parameters for kiwi extracted at different concentrations scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.

Sample	Excitation wavelength nm	$w_0 \times 10^{-5}$ m	$I \times 10^7$ W/m ²	$n_2 \times 10^{-7}$ cm ² /W
0.3 g/ml at methanol	488	0.943	4.290	-0.277
	514	1.180	2.740	-0.134
	633	3.480	0.279	-3.904
0.6 g/ml at methanol	488	0.968	4.070	-0.457
	514	1.070	3.370	-0.233
	633	4.070	0.203	-7.890
0.6 g/ml at methanol + Acid	488	1.110	3.080	-0.826
	514	1.320	2.190	-0.339
	633	3.760	0.239	-7.020

Table (52): Nonlinear parameters for mangosteen at different concentrations scanned using Ar ion laser at (514 – 488) nm and HeNe laser (P = 6mW) for closed aperture configuration.

Sample	Excitation wavelength nm	w_0 $\times 10^{-5} \text{m}$	$I \times 10^7$ W/m^2	$n_2 \times 10^{-7}$ cm^2/W
0.1 g/ml at methanol	488	1.160	2.840	- 0.863
	514	1.570	1.550	- 0.913
	633	3.900	0.222	- 6.703
0.3 g/ml at methanol	488	1.240	2.480	- 2.067
	514	1.200	2.660	- 1.483
	633	3.990	0.212	- 11.260
0.6 g/ml at methanol	488	1.180	2.730	- 2.882
	514	1.210	2.620	- 2.113
	633	3.670	0.251	- 18.590
0.6 g/ml at methanol + Acid	488	0.914	4.580	- 16.800
	514	1.060	3.390	- 5.802
	633	3.620	0.258	- 11.020

4.1.2 Nonlinear Absorption Coefficient

4.1.2.1 Effect of excitation power level

Figure (84) shows the variation of nonlinear absorption coefficient with excitation power level at fixed $\lambda = 514 \text{ nm}$. The samples have different concentration in which methanol with acid is used to extract mangosteen peels at 0.6 g/ml of concentration, while methanol alone was used to extract mangosteen peels in different concentrations. As excitation power increases β value decreases. This results behaviour are in agreement with the behaviour of the reported results by (Pramodini, et al., 2013). Methanol and methanol with acid have same effect on magnitude of β for mangosteen with concentration of 0.6 g/ml, it possesses SA at all powers levels used as shown in Figure (84-a) and (84-

b). Interestingly, mangosteen peels extract at 0.1 g/ml concentration shows RSA behaviour. Mangosteen peels extract at 0.3 g/ml concentration shows SA at power ranges between (2 -6) mW, but RSA at power ranges between (8–10) mW. Such fluctuation in β sign has been reported by (Srinivas, et al., 2003).

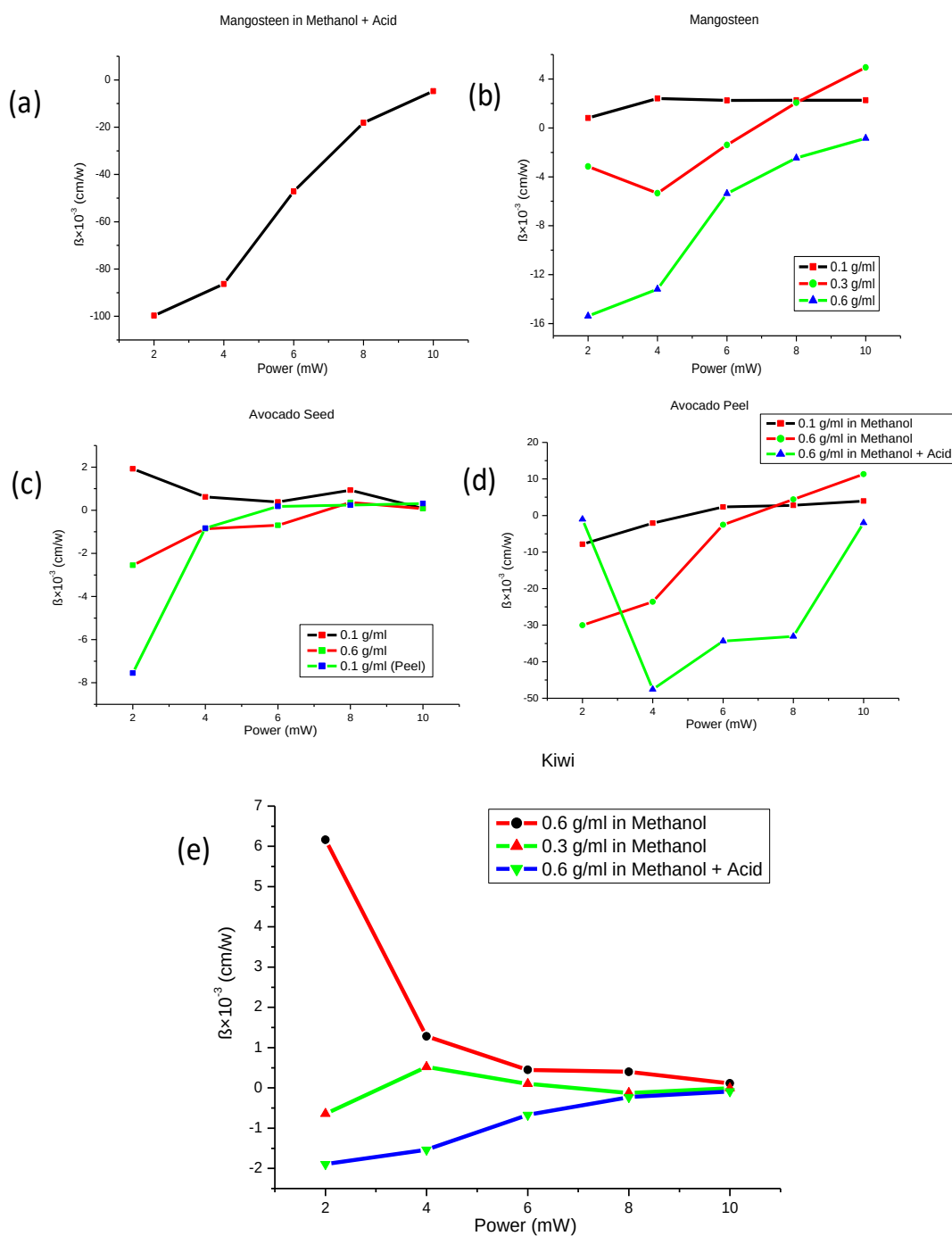


Figure (84): Variation of β as function of excitation power level ($\lambda = 514$ nm).

The addition of acid to kiwi in methanol at 0.6g/ml concentration change the behaviour of nonlinear absorption from RSA to SA. The RSA in methanol is mainly due to the localization of energy, this behaviour has been reported by (Srinivas, et al., 2003).

4.1.2.2 Effect of concentration

Figure (85) shows each material has different behaviour. β increasing as the concentration increases and RSA for kiwi. While, mangosteen, avocado seeds and avocado peels extracts demonstrated a switching behaviour from RSA at lower concentrations to SA at higher concentrations this might be attributed to aggregation and fast decay times of dimmers. This behaviour are has been reported in (Srinivas, et al., 2003; and Sreekumar, et al., 2009).

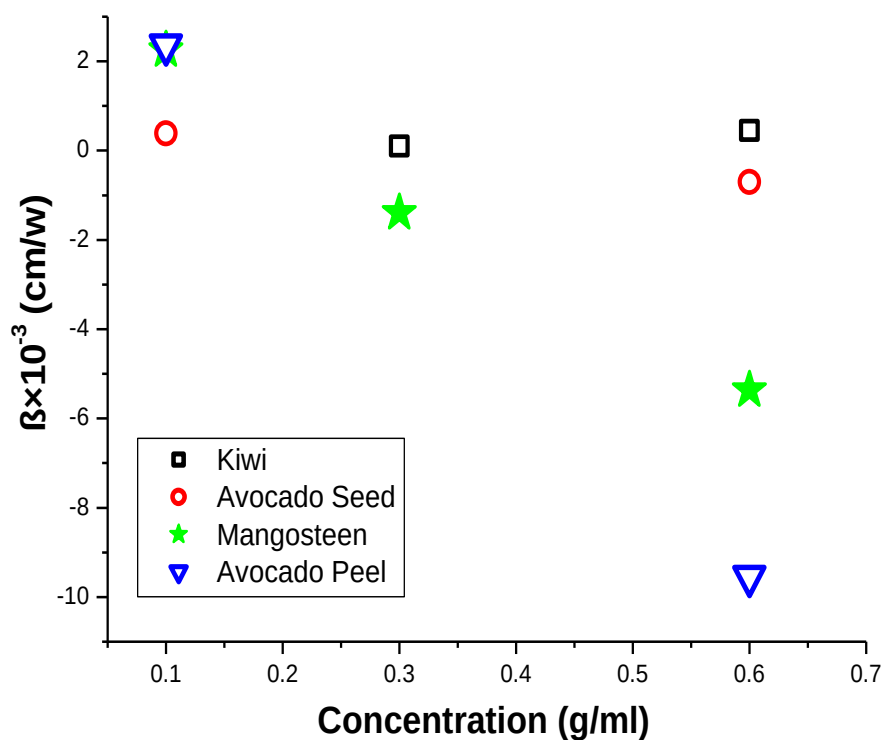


Figure (85): Variation of β as function of concentrations ($\lambda = 514$ nm) for tropical.

Investigation of concentration effect on nonlinear absorption for avocado peels extracted in methanol and methanol with acid as an example is summarized in Table (53). Samples from avocado peels in methanol and methanol with acid at different concentrations behaves as SA at wavelength when excited with laser beam of 6 mW. However, at $\lambda = 514$ nm β have lower value.

Table (53): Nonlinear parameters for avocado peels at different concentrations and scanned using Ar ion laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.

Sample	Excitation wavelength nm	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)} \times 10^{-5}$ esu	$\text{Im } \chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
0.1 g/ml at methanol	488	- 1.955	- 1.270	- 3.420	13.140
	514	0.236	- 0.319	0.435	3.223
	633	4.011	- 6.480	9.110	65.440
0.6 g/ml at methanol	488	- 2.564	- 1.850	- 4.540	19.020
	514	- 0.955	- 1.550	- 1.780	15.590
	633	8.278	-13.300	19.000	134.80
0.6 g/ml at methanol + Acid	488	- 8.476	- 3.500	-15.300	38.200
	514	- 3.435	- 2.630	- 6.550	27.100
	633	- 6.902	- 22.60	-16.200	226.00

4.1.2.3 Effect of excitation wavelength

Table (54) shows nonlinear parameters for avocado seeds extracted at concentration of 0.1 and 0.6 g/ml in methanol excited by different wavelengths. Avocado seed extracts at 0.1 g/ml of concentration acts as SA for $\lambda = 488$ nm, but RSA for $\lambda = 514$ nm. Also, at wavelength of 633 nm samples showed no clear response. On the other hand, at 0.6 g/ml concentration the sample changed its behaviour to SA at $\lambda = 514$ nm and $\lambda = 633$ nm. The higher values of β are found at excitation $\lambda = 488$ nm.

Table (54): Nonlinear parameters for avocado seed at different concentrations in methanol scanned using Ar ion laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.

sample	Excitation wavelength nm	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)} \times 10^{-5}$ esu	$\text{Im } \chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
0.1 g/ml in methanol	488	- 0.274	- 0.125	- 0.480	1.343
	514	0.038	- 0.045	0.070	0.458
0.6 g/ml in methanol	488	- 0.431	- 0.418	- 0.763	4.253
	514	- 0.070	- 0.224	- 0.131	2.241
	633	- 0.099	- 0.162	- 0.228	1.636

Table (55) shows nonlinear parameters for kiwi extract at concentration of 0.3 and 0.6 g/ml in methanol and methanol with acid excited by different wavelengths for closed aperture configuration. Increasing of concentration doesn't effect samples behaviour. However, addition of acid changes the behaviour for the sample at $\lambda = 514$ nm and $\lambda = 633$ nm.

Table (55): Nonlinear parameters for kiwi at different concentrations and solvent scanned using Ar ion laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.

Sample	Excitation wavelength nm	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)} \times 10^{-5}$ esu	$\text{Im } \chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
0.3 g/ml at methanol	488	- 0.298	- 0.124	- 0.519	1.345
	514	0.010	- 0.060	0.018	0.601
	633	0.085	- 1.751	0.191	17.520
0.6 g/ml at methanol	488	- 0.411	- 0.208	- 0.727	2.206
	514	0.045	- 0.106	0.083	1.065
	633	0.018	- 3.593	0.041	35.930
0.6 g/ml at methanol + Acid	488	- 0.723	- 0.387	- 1.317	4.092
	514	- 0.067	- 0.159	- 0.128	1.597
	633	- 0.548	- 3.293	- 1.294	32.960

Table (56) displays the avocado seeds peels extracted in methanol and excited with different wavelengths. The sample demonstrated similar behaviour as avocado seeds peels.

Table (56): Nonlinear parameters for avocado seed peel at different concentrations in methanol scanned using Ar ion laser at (514 – 488) nm for closed aperture configuration.

Sample	Excitation wavelength nm	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)} \times 10^{-5}$ esu	$\text{Im } \chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
0.1 g/ml at methanol	488	- 0.386	- 0.241	- 0.673	2.500
	514	0.018	- 0.076	0.033	0.762

Table (57) displays the effect of excitation wavelength on mangosteen peels extracted with different concentration in methanol and methanol with acid. The sample acted as SA for different concentrations and wavelengths. While, its acts as RSA only at $\lambda = 633\text{nm}$ with acid.

Table (57): Nonlinear parameters for mangosteen peels extracted at different concentrations and solvent scanned using Ar ion laser at (514 – 488) nm and HeNe laser at 633nm for closed aperture configuration.

sample	Excitation wavelength nm	$\beta \times 10^{-2}$ cm/W	$\text{Re } \chi^{(3)} \times 10^{-5}$ esu	$\text{Im } \chi^{(3)} \times 10^{-6}$ esu	$\chi^{(3)} \times 10^{-6}$ esu
0.1 g/ml at methanol	488	-0.341	- 0.392	- 0.600	3.963
	514	0.225	- 0.415	0.419	4.166
	633	-0.351	- 3.040	- 0.802	30.400
0.3 g/ml at methanol	488	-1.178	- 0.961	- 2.127	9.847
	514	-0.139	- 0.690	- 0.265	6.904
	633	-1.810	- 5.235	- 4.240	52.530
0.6 g/ml at methanol	488	-1.991	- 1.375	- 3.690	14.240
	514	-0.537	- 1.009	- 1.049	10.140
	633	-5.066	- 8.873	-12.180	89.560
0.6 g/ml at methanol + Acid	488	-22.38	- 8.286	-42.860	93.290
	514	-4.715	- 2.861	- 9.523	30.150
	633	1.532	- 5.433	3.806	54.460

4.3 Summary of Results Analysis

Below is summary of the findings that have been detailed in this chapter.

1-Effect of excitation power:

- All materials have same behaviour (self-defocusing). the dye exhibited negative nonlinear refractive index
- n_2 decreases as the power increases.
- nonlinear absorption coefficient changes from RSA to SA and vice versa, or the behaviour doesn't change. The justification of the change from RSA to SA is that all electrons become excited and when the electron moves from first excited state to second excited state, the absorption of the excited states larger than that of the ground state, the material shows RSA however.
- Some materials switch over the behaviour from SA to RSA:
 1. Raisin at 0.6 g/ml
 2. Strawberry at 0.3 g/ml
 3. Avocado Peel in methanol at (0.1 – 0.6)g/ml
 4. Avocado Seed in methanol at 0.6 g/ml
 5. Avocado Seed Peel in methanol at 0.1 g/ml
 6. Blueberry in ethanol at (0.1 – 0.3 – 0.6) g/ml
 7. Orange in methanol at 0.6 g/ml
 8. brown apricot in methanol at 0.6 g/ml
 9. Cherry in methanol at 0.6 g/ml
 10. Prune at 0.6 g/ml in (methanol – methanol with 1% HCl)
 11. Mandarin and Raisin at 0.3 g/ml in (methanol – methanol with 1% HCl).
 12. Mangosteen peel extracted in methanol at 0.3 g/ml

13. Indian Pomegranate grains at 0.6 g/ml
14. Pomegranate Peels
 - Indian in methanol Raisin at 0.3 g/ml
 - Egyptian in acetone at 0.1 g/ml
- Some materials switch over the behaviour from RSA to SA:
 1. Kiwi in methanol at 0.3 g/ml
 2. Raisin in methanol at 0.1 g/ml
 3. Indian Pomegranate grains in methanol at 0.1 g/ml
 4. Pomegranate Peels
 - Spanish in (ethanol – methanol)
 - Egyptian in methanol
- Some materials have similar behaviour (SA)
 1. mangosteen in methanol at 0.6 g/ml
 2. Avocado Peel in methanol with 1% HCl at 0.6 g/ml
 3. Kiwi methanol with 1% HCl at 0.6 g/ml
 4. Blueberry in methanol with 1% HCl at 0.6 g/ml
 5. Blueberry in acetone at 0.1 g/ml
 6. Dry Blueberry in methanol at 0.6 g/ml
 7. Cranberry in methanol at (0.1- 0.6) g/ml
 8. Strawberry in methanol at 0.6 g/ml
 9. Almond at 0.1 g/ml in (acetone – ethanol – methanol – methanol with 1% HCl)
 10. Apricot in (methanol – methanol with 1% HCl).
 11. Prune in methanol at 0.1 g/ml
 12. Indian Pomegranate grains in methanol with 1% HCl at 0.6 g/ml
- Some materials have same behaviour RSA
 1. Blueberry in methanol at 0.1 g/ml

2. grapefruit in methanol at 0.3 g/ml
3. Avocado seed at 0.1 g/ml in methanol
4. Kiwi in methanol at 0.6 g/ml
5. mangosteen 0.6 g/ml in (methanol – methanol with 1% HCl).
6. Egyptian Pomegranate peel in ethanol at 0.1 g/ml

2- Effect of concentration on

- **n_2**

1. The tested dyes exhibited self- defocusing when employing different wavelength, concentrations, power and solvent.
2. n_2 increases as the concentration increases except for the blueberry in ethanol at 0.6 g/ml of concentration by using $\lambda=488$ nm. This attributed to the increase in the number of molecular which increases the aggregation and formation of dimer. Formation of dimer decreases the concentration of effective dye molecular for laser.

- **β nonlinear absorption behaviour**

1. SA at $\lambda= 488$ nm (all tested sample).
2. switch over from RSA to SA at $\lambda= 633$ such as:
Blueberry, kiwi, Indian pomegranate peels.
3. switch over from SA to RSA at $\lambda= 633$ nm such as:
Strawberry and Indian pomegranate grains.
4. SA at $\lambda= 514$ nm for raisin, prune
5. RSA at $\lambda= 514$ nm for blueberry Indian pomegranate peels.
6. switch over from RSA to SA at $\lambda= 514$ nm such as:
Avocado (seed – peel), kiwi, mangosteen, strawberry and Indian pomegranate grains.
7. β increases as the concentration increases except the:

strawberry at 0.6 g/ml of concentration by using $\lambda=633\text{nm}$ –
blueberry in ethanol at 0.6 g/ml of concentration by using
 $\lambda=633\text{nm}$ – kiwi in methanol 0.6 g/ml of concentration by
using $\lambda=633\text{nm}$.

3- Effect of solvent.

Addison of 1% HCl to methanol.

- No change in tested dyes behaviour at $\lambda= 488\text{nm}$ if we change the solvent.
- avocado peels (0.6 g/ml):
 1. 633 nm: switch over from RSA to SA
 2. 514 nm: no change
- kiwi extract (0.6 g/ml):
 1. 633nm: switch over from RSA to SA
 2. 514 nm: switch over from RSA to SA
- mangosteen peels (0.6 g/ml):
 1. 633 nm: switch over from SA to RSA
 2. 514 nm: no change
- Mandarin peels (0.3 g/ml)
633 nm: no effect without acid – RAS with acid
514 nm: switch over from RSA to SA
- Indian pomegranate grains (0.6 g/ml)
633 nm : no change
514 nm: no change
- Almond (0.1 g/ml)
633 nm: no effect without acid – SA with acid
514 nm: switch over from SA to RSA
- apricot extract (0.6 g/ml)

633nm: no effect

514 nm: no change

- prune (0.6 g/ml)

633 nm: no change

514 nm: no change

- blueberry (0.1 g/ml)

633 nm: no change

514 nm: switch over from RSA to SA

Change solvent (ethanol to methanol)

- Spanish pomegranate

633 nm: no effect

514 nm: switch over from SA to RSA

Yamani pomegranate

633 nm: no effect

514 nm: switch over from RSA to SA

Egyptian pomegranate

633 nm: no effect

514 nm: no change

- Almond peel extract

633 nm: no effect

514 nm: no change

The effect of adding 1% HCl to methanol:

1. 514 nm:

a) switch over from RSA to SA

kiwi (0.6 g/ml), mandarin (0.3 g/ml) and blueberry (0.1 g/ml)

b) switch over from SA to RSA

Almond 0.1 g/ml

c) no change:

- Indian pomegranate grains (0.6 g/ml), avocado peel (0.6 g/ml), mangosteen peel (0.6 g/ml), apricot (0.6 g/ml), prune (0.6 g/ml)

2. 633 nm

a) switch over from RSA to SA

avocado peel (0.6 g/ml), kiwi (0.6 g/ml),

b) switch over from SA to RSA

mangosteen (0.6 g/ml)

c) no change:

- Indian pomegranate grains (0.6 g/ml), prune (0.6 g/ml), blueberry (0.1 g/ml)

3. 488 nm: No change.

Adding acid to solvent has different effect on the nonlinear optical behaviour of the dyes under study. Whereas some of the materials haven't changed and some have changed from RSA to SA and vice versa. Moreover, some of the materials showed the nonlinear behaviour only after adding the acid by using $\lambda = 633\text{nm}$.

Changing solvent from ethanol to methanol had no impact on the behaviour of the materials when using $\lambda = 488\text{nm}$. as no nonlinear response shown for materials like (Spanish, Yamani, Egyptian) pomegranate and almond by using $\lambda = 633\text{ nm}$.

When using wavelength $\lambda = 514\text{ nm}$:

- 1- some materials like Spanish pomegranate changed from RSA to SA.
- 2- some materials like Yamani pomegranate changed from SA to RSA.
- 3- some materials like Egyptian pomegranate and almond were not affected.

Justification: Each solvent has different impact on dyes.

4- Effect of excitation wavelength.

When different wavelength is used to excite samples at specific power and concentration, their nonlinear absorption behaviour may change from SA (-) to RSA (+) examples are listed below for each group.

Tropical sample	488	514	644	Highest n_2	Highest β
avocado peel (0.1 g/ml)	-	+	+	633	633
avocado peel (0.6 g/ml)	-	-	+	633	633
avocado peel (0.6 g/ml) HCl	-	-	-	633	488
avocado seed (0.1 g/ml)	-	+	No	488	488
avocado seed (0.6 g/ml)	-	-	-	488	488
avocado seed peel (0.1 g/ml)	-	+	No	488	488
Kiwi (0.3 g/ml)	-	+	+	633	488
Kiwi (0.6 g/ml)	-	+	+	633	488
Kiwi (0.6 g/ml) HCl	-	-	-	633	488
Mangosteen (0.1 g/ml)	-	+	-	633	633
Mangosteen (0.3 g/ml)	-	-	-	633	633
Mangosteen (0.6 g/ml)	-	-	-	633	633
Mangosteen (0.6 g/ml) HCl	-	-	+	488	488

Citrus sample	488	514	633	Highest n_2	Highest β
mandarin (0.3g/ml)	-	+	No	488	488
mandarin (0.3g/ml) HCl	-	-	+	633	488
Orange (0.6g/ml)	-	-	No	488	488
Grapefruit (0.3g/ml)	-	+	No	488	488

Note that, citrus group extracted in methanol did not show any nonlinear action when excited with laser beam with $\lambda = 633$ nm may be due to the very low linear absorption of these samples to 633 nm. However, once

1% of HCl has been added, linear absorbance of them become more and hence, nonlinear action has been observed.

Prunus sample	488	514	633	Highest n_2	Highest β
apricot (0.6 g/ml)	-	-	No	488	488
apricot (0.6 g/ml) HCl	-	-	No	488	488
Brown apricot (0.6 g/ml)	-	-	-	633	633
prune (0.1 g/ml)	-	-	No	488	488
prune (0.6 g/ml)	-	-	+	488	488
prune (0.6 g/ml) HCl	-	-	+	633	488
Almond (0.1 g/ml) ethanol	-	-	No	488	488
Almond (0.1 g/ml) methanol	-	-	No	488	514
Almond (0.1 g/ml) methanol+HCl	-	+	-	633	488

Berry sample	488	514	644	Highest n_2	Highest β
Blueberry (0.1 g/ml) ethanol	-	+	+	633	633
Blueberry (0.1 g/ml) ethanol+HCl	-	-	+	514	514
Blueberry (0.1 g/ml) methanol	-	+	No	488	488
Blueberry (0.3 g/ml) ethanol	-	+	-	633	488
Blueberry (0.6 g/ml) ethanol	-	+	-	633	488

Berry sample	488	514	644	Highest n_2	Highest β
Dry Blueberry (0.6 g/ml)	-	-	-	633	633
cranberry (0.6 g/ml)	-	-	+	488	488
cherry (0.6 g/ml)	-	-	-	633	488
Raisin (0.1 g/ml)	-	-	No	488	488
Raisin (0.6 g/ml)	-	-	+	514	488
Strawberry (0.3g/ml)	-	+	-	633	633
Strawberry (0.6 g/ml)	-	-	+	633	633

Pomegranate	488	514	644	Highest n ₂	Highest β
Indian grains (0.1 g/ml)	-	+	-	633	633
Indian grains (0.6 g/ml)	-	-	+	633	633
Indian grains (0.6 g/ml) HCl	-	-	+	633	488
Indian peels (0.1 g/ml)	-	+	+	633	488
Indian peels (0.3 g/ml)	-	+	-	633	488
Egyptian peels ethanol	-	+	No	514	514
Egyptian peels methanol	-	+	No	488	488
Spanish peels ethanol	-	-	No	488	488
Spanish peels methanol	-	+	No	488	488
Yamani peels ethanol	-	+	No	488	488
Yamani peels methanol	-	-	No	488	488

4.4 Study Recommendations

The following are some recommendations:

1. In order to have better extraction of samples we recommend the use of a quite sophisticated extraction system such as Soxhlet extractor.
2. Purifying dye extracts from any contaminations.
3. Measuring the FTIR spectrum for the samples in order to determine its molecular structure. And constructing energy levels diagrams. Hence, get better understanding of both absorption and fluorescence spectra.
4. Excite samples with other wavelength such as those below 400 nm (UV) and those above 800 nm (NIR)
5. Use pulsed laser to avoid unwanted thermal effect that overwhelms electronic based nonlinear actions.

6. Extract dyes at different temperatures below or above room temperature and investigating any change in nonlinear parameters.
7. Extract fruits dyes at different pH solutions and study the impact of this factor on nonlinear parameters of the prepared samples.
8. Incorporation of purified dye extracts in polymer films and investigate their nonlinear properties.
9. The outcome of this study showed that natural dyes extract are exhibiting unique nonlinear optical parameters and hence they have capability of being used as optical limiter. It is suggested to further investigate them as optical limiters.
10. The outcome of this study showed that natural dyes extract are exhibiting unique nonlinear optical parameters and hence they have capacity of being studied as all optical switches.
11. Since nanostructured materials are attracting attention as nonlinear media, we suggest investigating nonlinear optical properties of natural dye extracts after being mixed with nanostructured materials to produce exotic nonlinear optical media.

References

- Abrahart EN (1977). *Dyes and their Intermediates*. New York: Chemical Publishing. pp. 1–12.
- Abrahart, E. (1982). *Dyes and their intermediates* (pp. 1-12). Taipei: Kao Li.
- Alkema, J., & Seager, S. (1982). *The chemical pigments of plants*. Journal of Chemical Education, 59(3), 183. <http://dx.doi.org/10.1021/ed059p183>
- Al-Saidi, I. A., & Abdulkareem, S. A. (2015). *Nonlinear optical properties and optical power limiting of Leishman dye using z-scan technique*. Journal of Materials Science: Materials in Electronics, 26(5), 2713-2718. doi:10.1007/s10854-015-2747-3
- Al-Saidi, I., & Abdulkareem, S. (2015). *Nonlinear optical properties and optical power limiting behavior of Leishman dye in solution and solid polymer film using z-scan*. Optik - International Journal For Light And Electron Optics, 126(23), 4299-4303. <http://dx.doi.org/10.1016/j.ijleo.2015.08.144>
- Bhute, A., & Prabhu, K. (2012). *Plant based natural dyes and mordants: A Review*. J. Nat. Prod. Plant Resour, 2 (6)(2231 – 3184), 649-664. Retrieved from (<http://scholarsresearchlibrary.com/archive.html>)
- Biswajit Das. (2011). *Prunus diversity- early and present development: A review*. International Journal Of Biodiversity And Conservation, 3(14). <http://dx.doi.org/10.5897/ijbcx11.003>

Carmen, Z., & Daniela, S. (2012). *Textile Organic Dyes - Characteristics, Polluting Effects and Separation* (pp. 55-82). INTECH Open Access Publisher.

Chi, S. (2009). *Third-order nonlinear optical properties of conjugated polymers and blends* (Unpublished doctoral dissertation). Georgia Institute of Technology.

Degiorgio, V., & Flytzanis, C. (1995). *Nonlinear optical materials* (p. 512). Amsterdam: IOS Press.

Delgado-Vargas, F., Jiménez, A., & Paredes-López, O. (2000). *Natural Pigments: Carotenoids, Anthocyanins, and Betalains — Characteristics, Biosynthesis, Processing, and Stability*. Critical Reviews In Food Science And Nutrition, 40(3), 173-289. <http://dx.doi.org/10.1080/10408690091189257>

Delgado-Vargas, F., Jiménez, A., & Paredes-López, O. (2000). *Natural Pigments: Carotenoids, Anthocyanins, and Betalains — Characteristics, Biosynthesis, Processing, and Stability*. Critical Reviews In Food Science And Nutrition, 40(3), 173-289. <http://dx.doi.org/10.1080/10408690091189257>

Elhadi M Yahia. (2006). *Modified and controlled atmospheres for tropical fruits*. Stewart Postharvest Review, 2(5), 1-10. <http://dx.doi.org/10.2212/spr.2006.5.6>

Fainman, Y., Ma, J., & Lee, S. (1993). *Non-linear optical materials and applications*. Sciencedirect, 9(2-3), 53-139.

Food-Info.net : *Chlorophyll*. (2017). Food-info.net. Retrieved 1 July 2017

Franken, P. A., Hill, A. E., Peters, C. W., & Weinreich, G. (1961). *Generation of Optical Harmonics. Physical Review Letters*, 7(4), 118-119. doi:10.1103/physrevlett.7.118

Ganeev, R., Ryasnyansky, A., Redkorechev, V., Fostiropoulos, K., Priebe, G., & Usmanov, T. (2003). *Variations of nonlinear optical characteristics of C60 thin films at 532 nm. Optics Communications*, 225(1-3), 131-139. doi:10.1016/j.optcom.2003.07.019

Garmire, E. (2013). *Nonlinear optics in daily life. Optics Express*, 21(25), 30532. doi:10.1364/oe.21.030532

Gómez, S., Cuppo, F., & Figueiredo Neto, A. (2003). *Nonlinear optical properties of liquid crystals probed by Z-scan technique. Brazilian Journal Of Physics*, 33(4), 813-820. <http://dx.doi.org/10.1590/s0103-97332003000400035>

Gürses, A., Açıkyıldız, M., Güneş, K., & Gürses, M. (2016). *Dyes and Pigments: Their Structure and Properties. Springerbriefs In Molecular Science*, 13-29. http://dx.doi.org/10.1007/978-3-319-33892-7_2

Hassan, Q. M., Al-Ahmad, A., Al-Mudhaffer, M. F., & Badran, H. A. (1962-1969). *Third-order optical nonlinearities and optical-limiting properties of phloxine B dye doped PMMA films investigated by Z-scan technique. Romanian Journal of Physics*, 58. Retrieved 2012

Henari F, Cassidy S, Jasim K, Dakhel A. *Nonlinear refractive index measurements of curcumin with cw laser. Journal of Nonlinear Optical Physics & Materials*. 2013;22(02):1350017. doi:10.1142/s0218863513500173.

HRL Laboratories | About | History. *Hrlcom*. 2018. Available at: <http://www.hrl.com/about/history>. Accessed April 11, 2018.

HRL Laboratories | About | The Laser. *Hrlcom*. 2018. Available at: <http://www.hrl.com/about/laser>. Accessed April 11, 2018.

Hua, Z., Yuesheng, D., Ge, X., Menglu, L., Liya, D., & LiJia, A. (2013). *Extraction and Purification of Anthocyanins from the Fruit Residues of Vaccinium uliginosum Linn. Journal Of Chromatography & Separation Techniques*, 04(02). <http://dx.doi.org/10.4172/2157-7064.1000167>

Isah, K., Ahmadu, U., Idris, A., Kimpa, M., Uno, U., Ndamitso, M., & Alu, N. (2014). *Betalain pigments as natural photosensitizers for dye-sensitized solar cells: the effect of dye pH on the photoelectric parameters*. *Materials For Renewable And Sustainable Energy*, 4(1). <http://dx.doi.org/10.1007/s40243-014-0039-0>

Krishnamurthy, R., & alkondan, R. (2010). *Nonlinear Characterization of mercurochrome dye for potential Application in Optical Limiting*. *Optical Application*, 1, 187-196.

Kuzyk, M., & Dirk, C. (1998). *Characterization techniques and tabulations for organic nonlinear optical materials*. New York: Marcel Dekker.

Liu, X., Yang, Z., Wang, D., & Cao, H. (2016). *Molecular Structures and Second-Order Nonlinear Optical Properties of Ionic Organic Crystal Materials*. *Crystals*, 6(12), 158. <http://dx.doi.org/10.3390/cryst6120158>

Neethling, P. (2005). *Determining non-linear optical properties using the Z-scan technique* (Unpublished master's thesis).9

Nesterov, V., Kuleshova, L., & Antipin, M. (2001). *Formation of crystal structure of cyanovinylbenzene derivatives: X-ray structure investigation of ethyl esters of 3,4-dimethoxy-, 3,4,5-trimethoxy-, and 4-fluorobenzylidenecyanoacetic acids*. Crystallography Reports, 46(3), 452-460. <http://dx.doi.org/10.1134/1.1376469>

Papagiannouli, I., Iliopoulos, K., Gindre, D., Sahraoui, B., Krupka, O., Smokal, V., . . . Couris, S. (2012). *Third-order nonlinear optical response of push-pull azobenzene polymers*. Chemical Physics Letters, 554, 107-112. doi:10.1016/j.cplett.2012.10.007

Paul, B. (2004). *Investigations of Nonlinear Optical Properties of Certain Organic Photonic Materials using Z-Scan and DFWM Techniques*. Cochin University of Science & Technology.

Perry, S. W., Burke, R. M., & Brown, E. B. (2012). *Two-Photon and Second Harmonic Microscopy in Clinical and Translational Cancer Research*. Annals of Biomedical Engineering, 40(2), 277-291. doi:10.1007/s10439-012-0512-9

Phar macognosy. (2012). *beta-caroten*. Retrieved from <http://1.bp.blogspot.com/lvZH4RTN6a4/T2NRvJCNcOI/AAAAAAAAAAWw/XpQ7RwrcTBU/s469/47-beta-caroten.jpg>

Phar macognosy. (2012). *xanthophyll*. Retrieved from http://3.bp.blogspot.com/fy_l8KHC9Lw/T2NRovvEo5I/AAAAAAAAAAWg/m0JkiWuzZ9U/s485/46-xanthophyll.jpg

Pramodini S, Poornesh P, Nagaraja K. *Thermally induced nonlinear optical response and optical power limiting of acid blue 40 dye*. Current Applied Physics. 2013;13(7):1175-1182. doi:10.1016/j.cap.2013.03.002.

Pramodini, S. (2015). *third order optical nonlinearity and optical power limiting of organic materials under CW laser illumination* (Ph.D). Manipal.

Rao, S. V., Anusha, P. T., Prashant, T. S., Swain, D., & Tewari, S. P. (2011). *Ultrafast Nonlinear Optical and Optical Limiting Properties of Phthalocyanine Thin Films Studied Using Z-Scan*. *Materials Sciences and Applications*, 02(05), 299-306. doi:10.4236/msa.2011.25039

Rashidian, M., & Dorrnian, D. (2015). *INVESTIGATION OF OPTICAL LIMITING IN NANOMETALS*. *Advanced Study Center*, 40(12), 110-126.

Rashidian, M., Dorrnian, D., Darani, S. A., Saghaei, S., & Ghoranneviss, M. (2009). *Nonlinear responses and optical limiting behavior of Basic Violet 16 dye under CW laser illumination*. *Optik - International Journal for Light and Electron Optics*, 120(18), 1000-1006. doi:10.1016/j.ijleo.2008.05.001

Rekha, R., & Ramalingam, A. (2009). *Non-linear characterization and optical limiting effect of carmine dye*. *Indian Journal of Science and Technology*, 2(0974-6846), 8th ser., 27-31. Retrieved from <http://www.indjst.org>

Rekha, R., & Ramalingam, A. (2009). *Optical Nonlinear Properties and Optical Limiting Effect of Metanil Yellow*. *American Journal of Engineering and Applied Sciences*, 2(2), 285-291. doi:10.3844/ajeassp.2009.285.291

Sharan, A., Hosseini, S. A., Goswami, D. (2002). *Single experimental Setup for High Sensitive Absorption Coefficient and Optical Nonlinearities Measurements*. *Nonlinear Optics: Materials, Fundamentals and Applications*.

Sheik-Bahae, M., Said, A., Wei, T., Hagan, D., Stryland, E. V. (2007). *Sensitive measurement of optical nonlinearities using a single beam*. IEEE Journal of Quantum Electronics IEEE J. Quantum Electron., 26(4), 760-769.

Shirsath, S., Sonawane, S., & Gogate, P. (2012). *Intensification of extraction of natural products using ultrasonic irradiations—A review of current status*. Chemical Engineering And Processing: Process Intensification, 53, 10-23. <http://dx.doi.org/10.1016/j.cep.2012.01.003>

Sreekumar, G., Frobel, P. G., Muneera, C. I., Sathiyamoorthy, K., Vijayan, C., & Mukherjee, C. (2009). *Saturable and reverse saturable absorption and nonlinear refraction in nanoclustered Amido Black dye–polymer films under low power continuous wave He–Ne laser light excitation*. Journal of Optics A: Pure and Applied Optics, 11(12), 125204. doi:10.1088/1464-4258/11/12/125204

Srinivas N, Rao S, Rao D. *Saturable and reverse saturable absorption of Rhodamine B in methanol and water*. Journal of the Optical Society of America B. 2003;20(12):2470. doi:10.1364/josab.20.002470.

Trakoli, A. (2012). *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*. Volume 99: Some Aromatic Amines, Organic Dyes, and Related Exposures. International Agency for Research on Cancer. Occupational Medicine, 62(3), 232-232. <http://dx.doi.org/10.1093/occmed/kqs011>

Ule, E. (2015). *Measurement of The Nonlinear Refractive Index by Z-scan Technique*. Lecture, University of Ljubljana Faculty of Mathematics and Physics.

Vainio, H. (2003). *IARC handbooks of cancer prevention, volume 8, Fruit and vegetables*. Lyon: IARC Press.

Watson, D. J. (2001). *Chemical characterization of wild Maine cranberries (Unpublished master's thesis)*. University of Maine.

Yakop, N. S., & Badran, H. A. (2014). *Single-Beam Z-Scan Measurement of the Third-Order Optical Nonlinearities of Ethidium Bromide*. Journal of Engineering Research and Applications, 4(3), 727-731. Retrieved from www.ijera.com.

Yan, X., Liu, Z., Zhang, X., Zhou, W., & Tian, J. (2009). *Polarization dependence of Z-scan measurement: Theory and experiment*. Optics Express, 17(8), 6397. doi:10.1364/oe.17.006397

Zhao, P. (2016). *Ultrafast mechanisms of nonlinear refraction and two-photon photochromism (Ph.D)*. Central Florida.

Zongo, S. (2012). *nonlinear optical properties of natural dyes based on optical resonance(master)*. Western Cape.

ملخص الدراسة

تجذب المواد غير الخطية اهتماما كبيرا من قبل كثير من الباحثين؛ حيث يقوموا بتقصي خواصها البصرية الخطية وغير الخطية سعيا لتطوير النباض الفوتونية. مواد كهذه يجب أن تتحلّى بخواص بصرية لخطية عالية، امتصاصية منخفضة، زمن استجابة سريع، مدى ديناميكي واسع واستجابة طيفية ذات نطاق ترددي عريض.

ولتحقيق الغاية العلمية ذاتها، ركزت هذه الدراسة على فحص بعض الخواص البصرية الخطية وغير الخطية لأنواع محددة من الصبغيات الطبيعية المستخلصة من بعض الفواكه في درجة حرارة الغرفة وتحت ظروف تحضير مختلفة من حيث التركيز، ونوع المذيب؛ بهدف تطوير أرشيف المواد البصرية غير الخطية المحتمل توافرها في مملكة البحرين.

وقد تم استخلاص اثنين وخمسين عينة من صبغيات الفواكه مختلفة: الفراولة، التوت الطازج، التوت المجفف، الزبيب، التوت البري المجفف، قشور الكريب فروت، قشور البرتقال، قشور اليوسفي، قشور الرمان، حبات الرمان، اللوز، المشمش المجفف، الكرز المجفف، البرقوق المجفف، الأفوكادو، الكيوي وقشور المانغوستين.

هذا وقد تم قياس وتجميع وتحليل أطياف الامتصاص والفلورة لهذه العينات من أجل حساب معامل الامتصاص الخطي (α_0)، كما تم قياس معامل الإنكسار الخطي، وأخيرا تم حساب كل من: معامل الإنكسار غير الخطي (n_2)، معامل الامتصاص غير الخطي (β)، وقابلية التأثير الغير خطية من الدرجة الثالثة ($\chi^{(3)}$).

جميع النتائج البصرية الخطية التي توصل إليها هذا البحث تم القيام بتجميع بياناتها باستخدام تقنية جهاز المسح على المحاور الثالث Z-scan وباستخدام ليزر الأرجون المؤين عند الطول الموجية 488 نانومتر و 514 نانومتر وكذلك ليزر غاز الهليوم نيون عند الطول الموجي 633 نانومتر بشعاع ليزري ذي كثافة طاقة تمتد من 2 ملي وات حتى 10 ملي وات. أسفرت الكميات المقاسة والمحسوبة عن إمكانية استخدام مستخلصات صبغيات الفواكه المدروسة في تحضير ما يعرف بالمخفض الضوئي (optical limiter) وكذلك صلاحية هذه المستخلصات للعمل كمحولات بصرية لخطية (all optical switch).

جامعة البحرين

قسم الفيزياء



كلية العلوم

دراسة الخواص البصرية اللاخطية لمستخلصات صبغيات الفواكه باستخدام تقنية جهاز المسح على المحور الثالث (Z-scan Technique)

أطروحة مقدمة كجزء من متطلبات الحصول على درجة الماجستير
في الفيزياء التطبيقية

إعداد

رجاء إبراهيم العصفور

الرقم الجامعي: 20002250

إشراف

د. خليل إبراهيم جاسم / أستاذ مساعد

جامعة البحرين

مملكة البحرين

مايو 2018