International Journal of Engineering and Technical Research (IJETR)
ISSN: 2321-0869 (O) 2454-4698 (P), Volume-6, Issue-2, October 2016

Theoretical investigation of the photoelectrochemical performance of 25 natural dyes used in solar cells

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***Abstract*— Twenty five natural dyes were studied in this work to investigate their potential use in sensitized solar cells (DSSC). HOMO LUMO , open-circuit voltage (Voc) and global electrophilicity were calculated using both DFT/B3LYP-321-G and HF/B3LYP-321-G computational methods which are used as possible methods in describing photovoltaic properties. The results obtained show that Luteolinidin + glucose as natural dye can be chosen as the best photosensitizers for DSSC between all studied pigments when used PCBM as conduction bands.TD-DFT was also used to investigate Uv-Visible spectrum of natural dyes molecules.**

***Index Terms*— natural dyes, solar cells, photoelectrochemical properties, chemical reactivity**

I. INTRODUCTION

Natural dyes are considered as an alternative sources of sensitizers for solar cells because of their low cost, simple separation procedure, their availability and environmentally benefit due to their friendly nature [1].

This interested approach have *started to attract* increasing attention for several researchers to study many kinds of natural pigments extracted from flower, leaves and roots of different plants such as lyciumshawii and olive[2].Some of the studied natural dyes give better performance before drying and others after drying [3].Several types of natural dyes belonging to Anthocyanin goups as natural dyes such as Chlorophyll (Raspberries, Shami-berries, Grapes, Hibiscus, Chlorophyll, and acombination of dyes) have been performed.The prepared dye-sensitized solar cell (DSSC) using a combination of natural dyes (Chlorophyll, Raspberries and Hibiscus) by the ratio (1:1:1) show the better photovoltaic efficiency compared with the single dyes [4].

Computational calculations were used to predict the photovoltaic properties of natural dyes and to determine their potential efficiency in solar cells applications. Density functional theory (DFT) and time dependent (TD-DFT) were used to calculate HOMO and LUMO energy(*highest occupied molecular orbital and lowest unoccupied molecular orbital* respectively), open circuit voltage (Voc) and absorption bands of five kinds of Monascus dyes [5].

As well, chemical reactivity parameters such as hardness, electronegativity, electrophilicity which are very important in designing DSSC were also calculated according toDFT and TD-DFT for five of natural carotenoids group [6].

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II. THEORETICAL CALCULATIONS

density functional theory (DFT) at B3LYP at bases set 3-21G and hartreefock (HF) at B3LYP at the same bases set 3-21G were performed to study 25 natural dyes using Chembio3D ultra program.

Chemical reactivities were derived using HOMO LUMO values obtained from computational calculations. These reactivities have been calculated as follow [7]-[10]:

I (ionization pot.) =- HOMO

A (electron affinity) =- LUMO

X (electronegativity) = (I+A)/2

Global hardness $\eta = (I-A)/2$

Global electrophilicity $\omega=\mu^2/2\eta$

where : $\mu = -X$

III. RESULTS AND DISCUSSION

The structures of the studied natural dyes are shown in fig-1&2 and table-1.There are two groups belonging to these dyes, the first group show that the LUMO energy level is below the conduction band of PCBM(fig-3) which doesn't fit the requirements of efficient photosensitizers materials used for DSSC., while all studied dyes shown in (fig-4) represent the suitable materials*that can be used* for obtaining potential photosensitizers in solar cells due to their LUMO levels which are higher than the LUMO of PCBM.

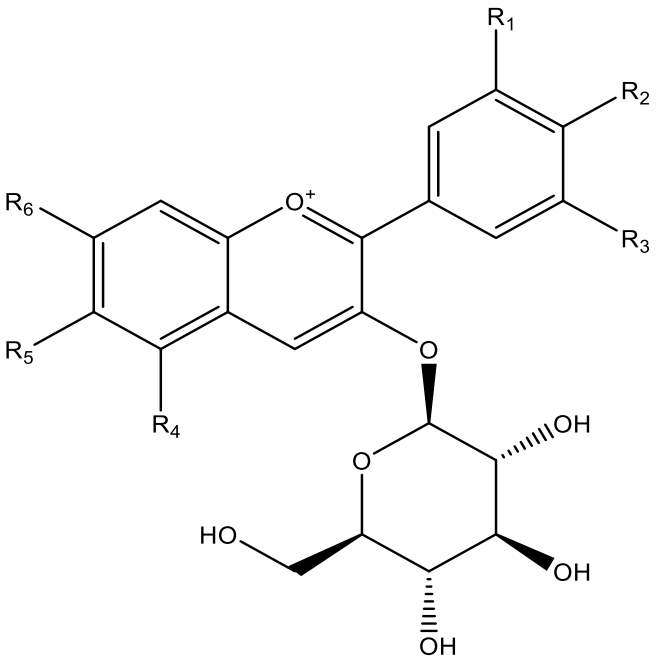
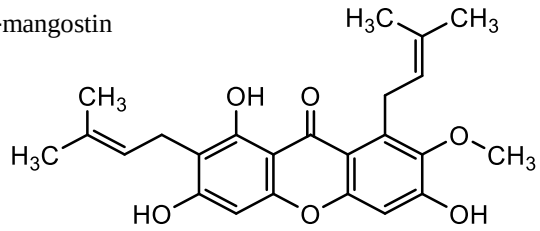


Fig-1: the structure of natural dyes containing Glucose group

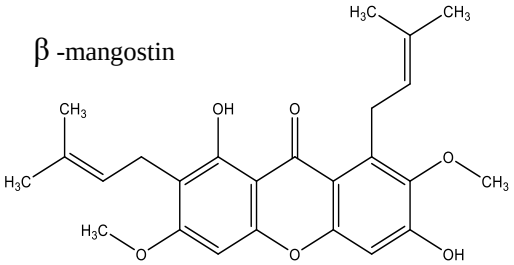
Table-1 : the substitutes available in natural dyes containing Glucose group

	Dyes	R1	R2	R3	R4	R5	R6
1	Delphinidin+glucose	OH	OH	OH	OH	H	OH
2	Aurantinidin+glucose	H	OH	H	OH	OH	OH
3	Hirsutidin+glucose	OCH3	OH	OCH3	OH	H	OCH3
4	Europinidin+glucose	OCH3	OH	OH	OCH3	H	OH
5	Peonidin+glucose	OCH3	OH	H	OH	H	OH
6	Pelargonidin+glucose	H	OH	H	OH	H	OH
7	Malvidin+glucose	OCH3	OH	OCH3	OH	H	OH
8	Triacetidin+glucose	OH	OH	OH	OH	H	OH
9	Petunidin+glucose	OH	OH	OCH3	OH	H	OH
10	Pulchellidin+glucose	OH	OH	OH	OCH3	H	OH
11	Apigeninidin+glucose	H	OH	H	OH	H	OH
12	Capensinidin+glucose	OCH3	OH	OCH3	OCH3	H	OH
13	Rosinidin+glucose	OCH3	OH	H	OH	H	OCH3
14	Cyanidin+glucose	OH	OH	H	OH	H	OH
15	Luteolinidin+glucose	OH	OH	H	OH	H	OH

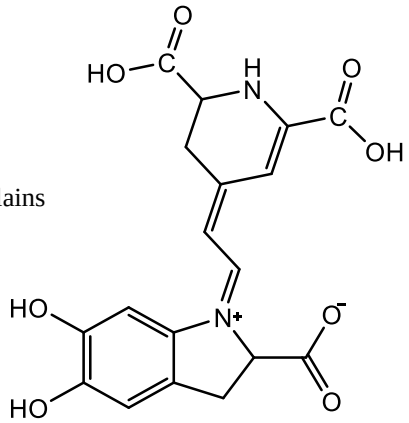
α-mangostin



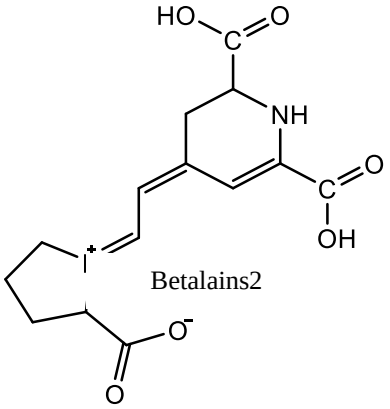
β -mangostin



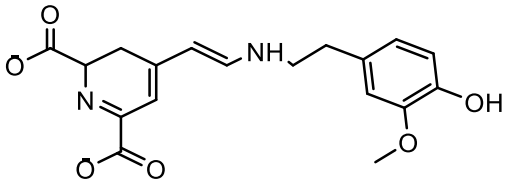
Betalains



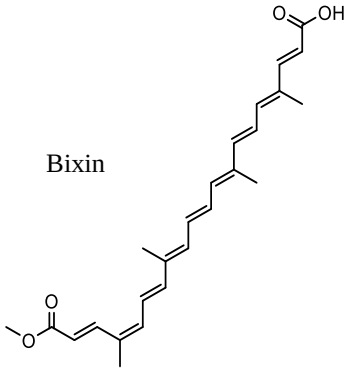
Betalains2



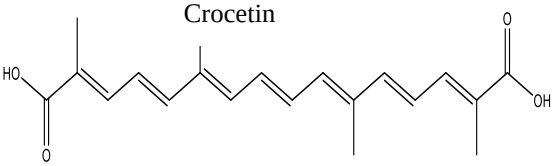
Betaxanthin



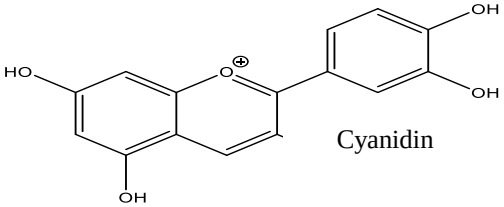
Bixin



Crocetin



Cyanidin



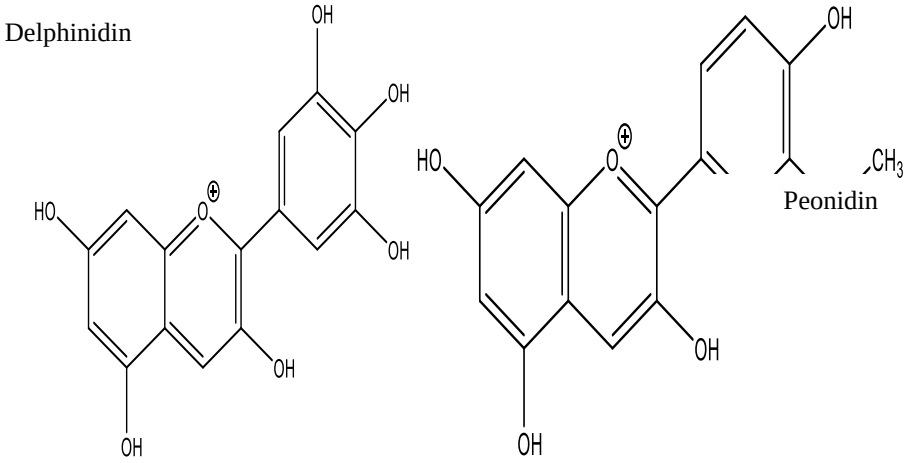


Fig-2: the structure of natural dyes without Glucose group

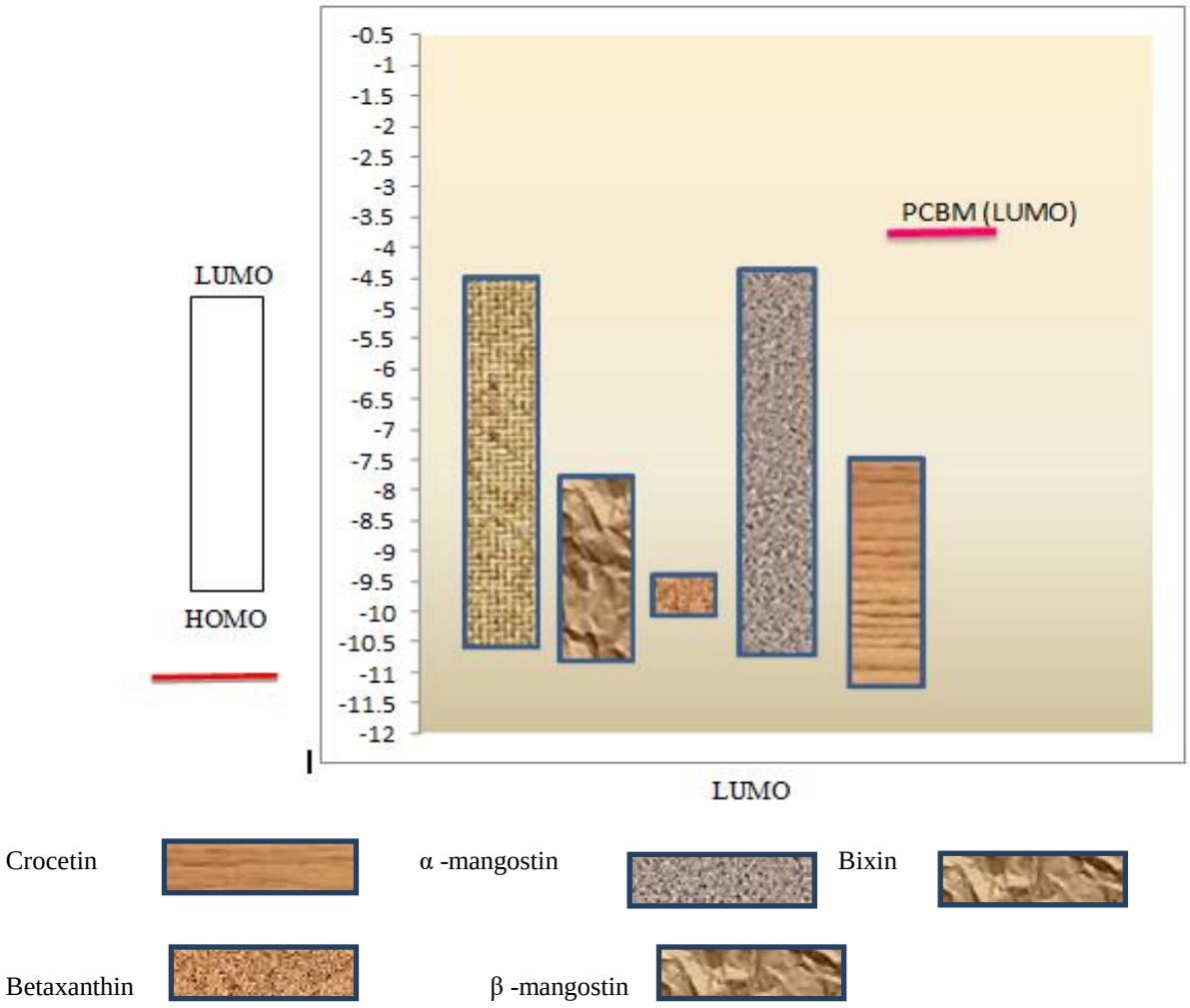


Fig-3: Orbital energy diagram for several species, for non-efficient sensitizers group of dyes

In table-2, the results reveal the relationship between HOMO LUMO and open circuit voltage (Voc) calculated by two methods, DFT/B3LYP-3-21G and HF/B3LYP-3-21G. The obtained values of Voc of the pigments between the numbers 1-18 are sufficient for a possible efficient electron injection which requires Voc values less than 2 (ev) [11], so all the mentioned molecules can be used as sensitizers due to their ability of the electron injection process from the excited dyes to the conduction band (CB) of PCBM. All the rest pigments (19-25) *doesn't match the requirements of* Voc role.

*Comparison of the degree of efficiency*of all 18 molecules can be achieved through the global electrophilicity index. It can be concluded that the shaded values in the table-3 calculated by two methodsrepresent the best three molecules used to achieve the goal of this study due the lowest values of electrophilicity "the smaller the global electrophilicity, the larger the efficiency of the solar cell" [6].

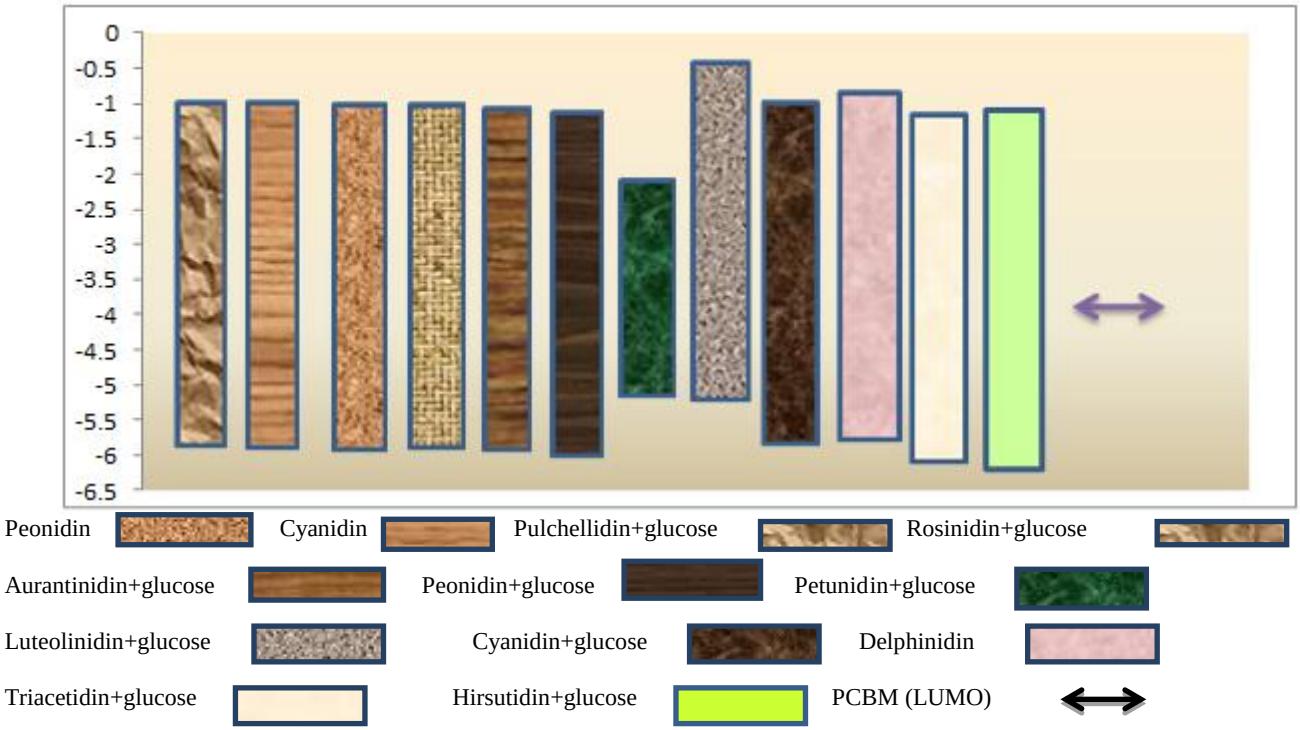


Fig-4 : Orbital energy diagram for several species for efficient sensitizersgroup of dyes

To confirm the highly *Efficient* of Luteolinidin+glucose compared with bixin molecule which is one of the non efficient molecule among all the studied molecules, wide absorption rangesis one of the important requirements for the efficientsensitizers, Fig-5&6 which are investigated by TD-DFT clearly show the absorption range for both molecules and the difference between them.

Table-2: physical parameters calculated by two methods

	Type of Dyes	DFT/B3LYP-3-21G			HF/B3LYP-3-21G		
		HOMO (eV)	LUMO (eV)	Voc/ PCBM (eV)	HOMO (eV)	LUMO (eV)	Voc/ PCBM (eV)
1	Delphinidin+glucose	-5.992	-1.043	1.992	-5.407	-0.318	1.407
2	Aurantinidin+glucose	-5.738	-0.901	1.738	-5.475	-0.526	1.475
3	Hirsutidin+glucose	-5.948	-0.965	1.948	-5.465	-0.33	1.465
4	Europinidin+glucose	-5.898	-0.891	1.898	-5.547	-0.48	1.547
5	Peonidin+glucose	-5.955	-1.019	1.955	-5.491	-0.512	1.491
6	Pelargonidin+glucose	-5.575	-0.894	1.575	-5.536	-0.569	1.536
7	Malvidin+glucose	-5.912	-0.979	1.912	-5.493	-0.307	1.493
8	Triacetidin+glucose	-5.272	-0.883	1.772	-5.317	-0.229	1.317
9	Petunidin+glucose	-5.125	-1.897	1.125	-4.556	-1.393	0.556
10	Pulchellidin+glucose	-5.826	-0.904	1.826	-5.446	-0.329	1.446
11	Apigeninidin+glucose	-5.695	-0.916	1.695	-5.351	-0.473	1.351
12	Capensinidin+glucose	-5.807	-0.821	1.807	-5.391	-0.271	1.391
13	Rosinidin+glucose	-5.76	-0.859	1.76	-5.51	-0.446	1.51
14	Cyanidin+glucose	-5.785	-0.933	1.785	-5.539	-0.535	1.539
15	Luteolinidin+glucose	-5.269	-0.379	1.269	-5.025	-0.03	1.025
16	Cyanidin	-5.789	-0.846	1.789	-5.453	-0.517	1.453
17	Peonidin	-5.755	-0.808	1.755	-5.423	-0.48	1.423
18	Delphinidin	-5.76	-0.777	1.76	-5.392	-0.394	1.392
19	Betalains	-9.27	-3.46	5.27	-9.215	-3.064	5.215
20	Betalains2	-9.377	-2.453	5.377	-9.651	-1.769	5.651
21	Crocetin	-11.34	-7.519	7.341	-11.71	-6.808	7.713
22	Bixin	-11.05	-7.833	7.051	-11.47	-6.905	7.475
23	α-mangostin	-10.86	-4.512	6.866	-10.68	-3.928	6.684
24	Betaxanthin	-10.08	-9.458	6.089	-9.92	-8.96	5.92
25	β-mangostin	-10.77	-4.484	6.777	-10.67	-3.90	6.67

Table-3: global electrophilicity for all dyes

	Type of Dyes	Global electrophilicity	
		DFT/B3LYP-3-21G	DFT/B3LYP-3-21G
1	Delphinidin+glucose	2.499	1.609
2	Aurantinidin+glucose	2.276	1.818
3	Hirsutidin+glucose	2.396	1.634
4	Europinidin+glucose	2.299	1.791
5	Peonidin+glucose	2.463	1.807
6	Pelargonidin+glucose	2.234	1.875
7	Malvidin+glucose	2.406	1.621
8	Triacetidin+glucose	2.157	1.511
9	Petunidin+glucose	3.818	2.796
10	Pulchellidin+glucose	2.3	1.629
11	Apigeninidin+glucose	2.286	1.738
12	Capensinidin+glucose	2.202	1.565
13	Rosinidin+glucose	2.234	1.751
14	Cyanidin+glucose	2.325	1.843
15	Luteolinidin+glucose	1.63	1.278
16	Cyanidin	2.225	1.805
17	Peonidin	2.176	1.761
18	Delphinidin	2.143	1.674
19	Betalains	6.972	6.132
20	Betalains2	5.053	4.136
21	Crocetin	23.266	17.481
22	Bixin	27.703	18.48
23	α-mangostin	9.304	7.9
24	Betaxanthin	151.365	92.366
25	β-mangostin	9.252	7.847

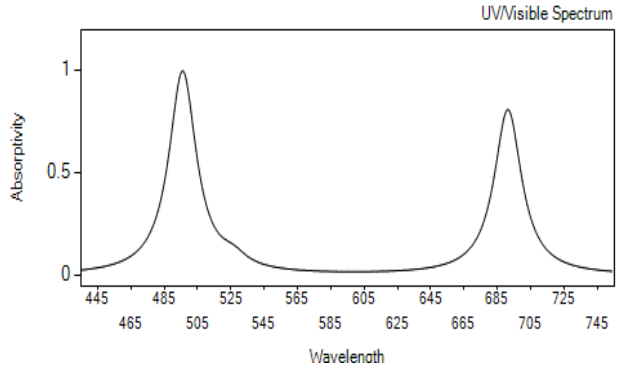


Fig-5: absorption spectrum of Luteolinidin+glucose

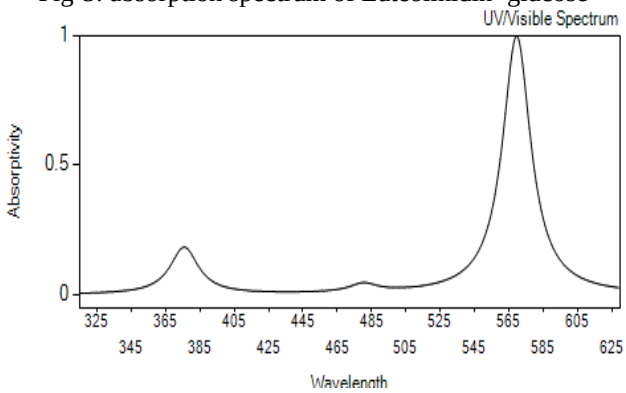


Fig-6: absorption spectrum of Bixin

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