DYE SENSITIZED NANOCRYSTALINE TITANIA SOLAR CELL USING LAALI STEM BARK (l*awsonia inermis)*

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Abstract

We have investigated the application of natural dyes extracted from the laali Bark (L*awsonia inermis) in dye sensitized solar cells.(DSSC). This was extracted using* Soxhlet extractor with ethanol as the solvent (A) and cold ethanol extraction (B). Solar cells sensitized by extracts **A** achieved up to *Isc 0.49* mAcm–^{2}, *Voc* 0.18V, FF 0.81 and η 0.74% while for extract **B** sensitized cells, the values determined were *Isc 0.94*mAcm–^{2}, *Voc* 0.66V, FF 0.64 and η 0.76%,. The effect of extracting solvent shows that the efficiency of Laali Bark extract sensitized DSSC was improved from 0.74 % to 0.76% when the extract was prepares using (B) instead of (A). The adjustment of pH shows increase in efficiency as pH decreases. A phytochemical screening was performed for the presence of flavonoids and anthraquinones , we notice less anthraquinones and no flavonoids when using method (B), but the presence of flavonoids and less anthraquinone with method (A). This might be responsible for the loss of photoelectric conversion efficiency in the Laali Bark (lawsonia inermis). XRD diffraction pattern of the TiO_2 thin film covered substrate obtained from (A) and (B) exhibited strong diffraction peaks at 25^{o}indicating □ TiO_2 in the Anatase phase.

Keywords: Dye sensitized solar cells, Nanocrystalline TiO_2, Laali Bark (Lawsonia inermis), Natural Dye

Introduction

The use of solar cells, as a viable source of energy, has been studied for possible future integration in a number of different applications for over three decades [1]. An important new class of solar cell that can significantly lower energy requirements in comparison to other conventional solar cells, and which may greatly reduce costs, is the Dye-sensitized solar cell. Dye-sensitized solar cells are electrochemical devices comprising of a light-absorbing molecule anchored to semiconducting nanoparticles, converting sunlight to generate electricity. Light harvesting dyes absorb solar radiation incident on them and this results in excitation of these molecules, which pass the energy obtained by means of transferring electrons onto a nanocrystalline TiO_2 substrate onto which they are adsorbed. The electrons, now in the conduction band of titanium dioxide, conduct around the circuit. The performance of the cell depends on a dye used as sensitizer, the absorption spectrum of the dye and the anchorage of the dye to the surface of TiO_2, which are important parameters for determining the efficiency of the cell [3]. Generally, transition metal coordination compounds are used as the effective sensitizer, and alternatively, natural dye can be used for the same purpose because of their availability and low cost with an acceptable efficiency [4-6]

In this paper, Dye-sensitized solar cells (DSSC) were prepared using natural dyes extracted from Laali Stem Bark (Lawsonia inermis). Lawsonia inermis (Family: Lythraceae) is a shrub that is semicultivated in the savannah region of West Africa [7]. It is abundant in Nigeria, locally called “laali or lali” in Yoruba, "laale" in Hausa and "Uhie" in Igbo. [8] The Bark is grayish brown, unarmed when young but branches of older trees are spine tipped. [9-11], the stem bark is used in traditional medicine to treat a variety of ailments, such as jaundice, enlargement of the spleen, calculus, as an alternative in leprosy and obstinate skin affections, rheumatoid arthritis, headache, ulcers, diarrheoa, fever, leucorrhoea, diabetes, gonorrhoea and herpes infection cardiac disease, hepatoprotective and colouring agent. [12-14]. The phytochemical found in Laali stem Bark (***L. inermi***) is Isoplumbagin and the structure is shown in (Fig 1).

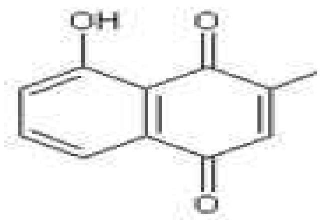

Fig.1 Structure of Isoplumbagin

2. Experimental

2.1 Preparation of Natural Dye Sensitizers

The methods used to extract the filtrate are Soxhlet extractor with ethanol as the solvent (A) and cold ethanol extraction (B). The extractions were obtained according to the following step: Fresh laali stem Barks were collected from farmlands in Badagry, at Badagry local government area of Lagos State. The Fresh laali stem Barks were seasoned by drying them at room temperature in the laboratory for two-weeks, until they became invariant in weight; laboratory ceramic made pistle and mortal are then used to crush each dry specimen into tiny bits.

For the Soxhlet extractor with ethanol as the solvent (A), 25 gramme of each dried/crushed sample were weighed (using OHAUS Electronic weighing Balance Model Brainweight B1500 made in USA) and soaked in 250ml solution of ethanol in the soxhlet, this were heated with the heating mantle for six to eight hours until all the dye has being removed. The Solid residues were filtrated out to obtain clear dye solutions. The ethanol filtrate was placed in hot water bath for vaporization of the ethanol so as to concentrate the extract. The extract was allowed to cool. In the case of cold ethanol extraction (B), 25 gramme of each dried/crushed sample were weighed and soaked into 250ml solution of ethanol, these was left to age at room temperature in a dark place for 12 hours. The residual parts were later removed by filtration. The effect of extracting with (A) and (B) solvent was studied by a comparison of dyes extracted .Then, the phytochemical screening of the plant was done (test on the presence of anthraquinones and flavonoids), and the effect of pH of dye solution was studied by adjusting pH from the original pH using 0.1 M HCI solution to three different pHs (1.0, 2.0 and 3.0). The efficiency of the solar cells related to dye structures is discussed. The pH of the dye solution on the DSSC efficiency and stability were also determined.

2.2 Preparation and construction of the cell

The TiO_2 solution was prepared by the incremental addition of 20 ml of nitric acid solution to 12 g of TiO_2 powder in a crucible. The powder was stirred at each 1ml drop of the nitric acid until an even paste was achieved (Polo et al 2006). For the electrode a glass slide with conductive surface is required. A plane mirror 2x2cm was used with its outer coating removed leaving a sliver (Ag) layer which is conducting. A window is created in the silver conducting film left to allow incident light photon to enter and interact with the Dye Titanium interface. The volt-ohm meter was used to check which side of the glass is conductive.

The titanium paste is poured on the conducting surface of the slide glass. A glass rod is allowed to slide over the titanium dioxide suspension in order to spread evenly and smoothly. (Amao and komori 2004). It was annealed and sintered in an oven at $450^{o}C$ for 30 min. The TiO2-coated conductive glass is allowed to cool to room temperature. After cooling the TiO_2 film is stained with a dye solution and allowed to dry.

A second glass slide 2x2cm with a conducting surface (again plane mirror was used with its outer most coating removed).The conducting side is prepared by carbon coating. The carbon coated slide (counter –electrode) is placed face down on top of the dry stained, titanium dioxide coated side of the other slide (electrode) in such a way that the two slides offset so that all of the TiO_2 is covered by the counter electrode. Two binder clips are used to gently hold the plates together at the edges. The DSCs were constructed by introducing the redox electrolyte containing a mixture of 0.5M potassium iodide and 0.05M iodine. The liquid was drawn into the space between the electrodes by capillary action. The XRD (X-ray Diffraction, MAC Science) was used to analyze the structure of the fabricated TiO_2 nanoparticle.

2.3 Measurement of photoelectric conversion efficiency of DSSC

The absorption spectra of dye solutions and dyes adsorbed on TiO_2 surface were recorded using a VIS Spectrophotometer (Spectrumlab 23A GHM Great Medical England). Solar energy conversion efficiency (the photocurrent voltage (*I-V)* curve) was measured by using digital multimeters under illumination of sunlight. Based on *I-V* curve, the fill factor (FF) is defined as

$$FF = (I_{max} \times V_{max})/(I_{sc} \times V_{oc}), \qquad (1)$$

where I_{max} *and* V_{max} denote the maximum output power current and voltage respectively, and I_{sc} *and* V_{oc} denote the short-circuit current and open-circuit voltage respectively. The total energy conversion efficiency (η) was defined as follows:

$$\eta = (I_{sc} \text{ x } V_{oc} \text{ x FF})/P_{in}, \qquad (2)$$

where P_{in} denote the energy of incident light.

3.0 Results and Discussion

Fig.2-3 shows the XRD diffraction pattern of the TiO_2 thin film covered substrate obtained from the Soxhlet extractor with ethanol as the solvent (A) and cold ethanol extraction (B). One notice that the XRD patterns exhibited strong diffraction peaks at 25^{o}indicating TiO_2 in the Anatase phase not in amorphous phase,since it was annealed and sintered in an oven at 450^{o}C.. Amorphous revealed broad pattern with low intensity. [2]

Fig.4 shows the acquired absorption spectra of Laali Stem Bark (Lawsonia inemis) extract using (A) and (B), the two methods of extraction after UV illumination. As seen from the graph, the maximum absorption peak value for the stem is at 400nm.Within this wavelength range the Laali Stem Bark (Lawsonia inemis) using (A) has higher absorption intensity, narrow absorption range than Laali Stem Bark (Lawsonia inemis) using (B).The difference in absorption intensity is due to difference in absorption properties of pigmentsn and colors of extract and chemical structure of these pigments ,which will reflect the absorption spectrum . [15]

Fig.5 compares the absorption spectrum of Laali Stem Bark (Lawsonia inemis) extract with the Laali Stem Bark (Lawsonia inemis) extract mixed with TiO_2 nanoparticles using the two methods of extraction. As observed from the figure, after TiO_2 nanoparticles was added to the Laali stem Bark (lawsonia inemis) extract, its absorption intensity obviously decreases with (A) method. There is increase in the absorption intensity for the (B) method with two wavelength ranges, increases from 400nm to 600nm and 700nm to 800nm.The Difference in the absorption characteristics is due to the chemical constituents of the Laali Stem Bark (Lawsonia inemis) extract using the methods.[16,17].

Fig.6 shows the I-V curve of the prepared DSSC sensitized with Laali Stem Bark (lawsonia inermis) using the soxhlet extractor (A) and cold ethanol extraction (B). The Laali Stem Bark extracts using the the soxhlet extractor (A) method results shows non-ideal I-V characteristics even though it possesses 100% light harvesting efficiency in the UV and in the visible parts of the electromagnetic spectrum. In Fig.7-8 , the absorption spectrum of the irradiated TiO_2 nanoparticles adsorbed Laali Stem Bark (Lawsonia inermis) soxhlet extract is rather flat showing no light absorbtion compares to other method.This makes the DSC prepared not to function after a short period of operating.

Table 1 shows the comparison of different parameters of DSSC's using the natural dye extract. The photoelectric conversion efficiency of Laali Stem Bark (Lawsonia inermis) using (B) method is higher than the photoelectric conversion efficiency of Laali Stem Bark (lawsonia *inermis*) using the (A) method. This is because extract adsorbed on the surface of TiO_2 nanoparticles has broad absorption wavelength range and high absorption intensity .The effect of pH values was also investigated in this paper. Table 2-3 shows that as pH value decreases from 3.0 to 1.0, the performance of DSSCs rises clearly, the photoelectric conversion efficiency of DSSCs is enhanced and it increases. The phytochemical screening of the plant was done (test on the presence of anthraquinones and flavonoids), Anthraquinone is an aromatic organic compound that occurs naturally in plants and contributes to the coloring pigment of such plants, the compound is used commercially to manufacture dyes Flavonoids are widely disbursed throughout plants and are what give the flowers and fruits of many plants their vibrant colors. We observed the presence of less anthraquinones and no flavonoids when using method (B), but the presence of flavonoids and less anthraquinone with method (A). This might be the reason for the loss of photoelectric conversion efficiency.

Conclusion

The XRD diffraction pattern of the TiO_2 thin film covered Laali Stem Bark (Lawsonia inermis) substrate obtained from the extraction solvents exhibited strong diffraction peaks at 25^oindicating□ TiO2 in the Anatase phase.

The absorption spectra of Laali Stem Bark (Lawsonia inemis) extract mixed with TiO_2, nanoparticles using the two methods shows decrease in absorption intensity for the method (A) and vice versa for (B). This gives better absorption property since there is increase in charge transfer ability under normal sunlight for the DSSCs and the maximum acquired after UV illumination is 400nm.

Comparison shows difference in the absorption spectrum using (A) and (B) method, these characteristics is due to the chemical constituents of the extract. The I-V curve of the prepared DSSC sensitized extracts using the the soxhlet extractor (A) shows non-ideal I-V characteristics and there is increase in efficiency as pH decreases.

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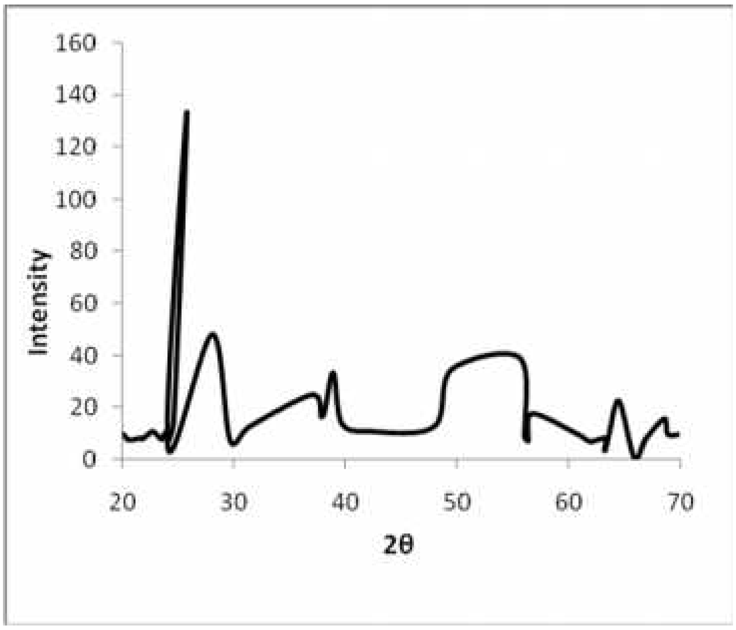


Fig.2 XRD diffraction pattern of the fabricated TiO_2 using the Soxhlet extractor (A)

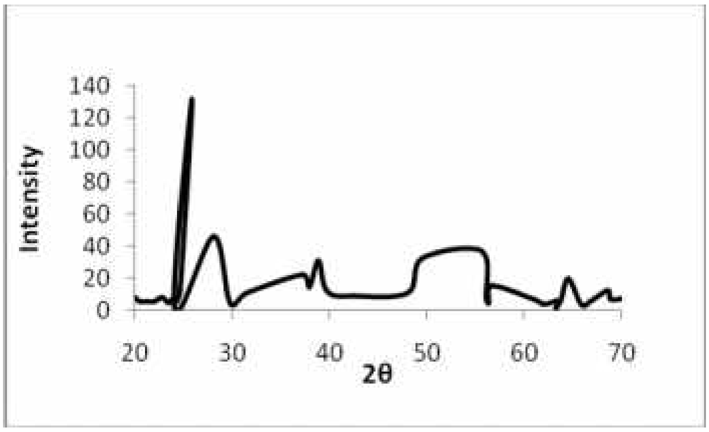


Fig.3 XRD diffraction pattern of the fabricated TiO_2 using the cold ethanol (B).

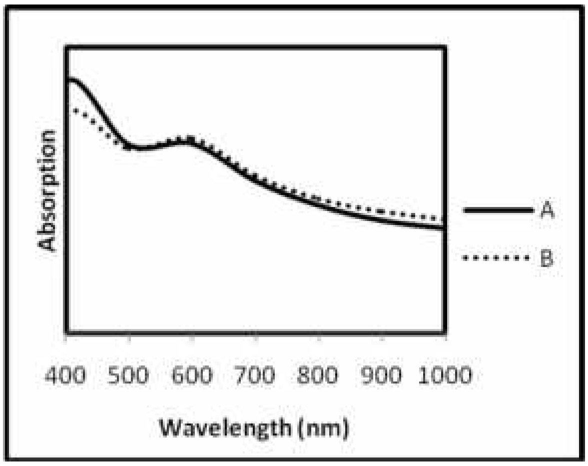


Fig.4 shows the acquired absorption spectra of Laali Stem Bark (Lawsonia inemis) extract using soxhlet ethanol extraction (A) and cold ethanol extraction (B)

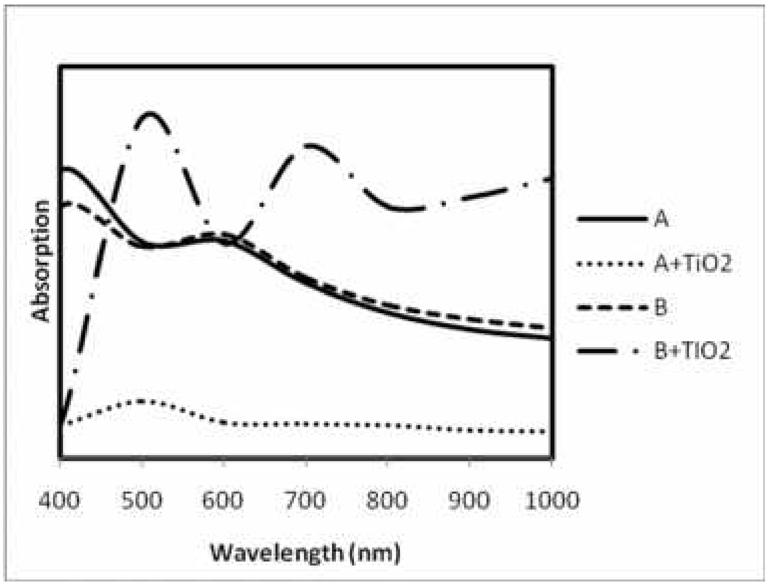
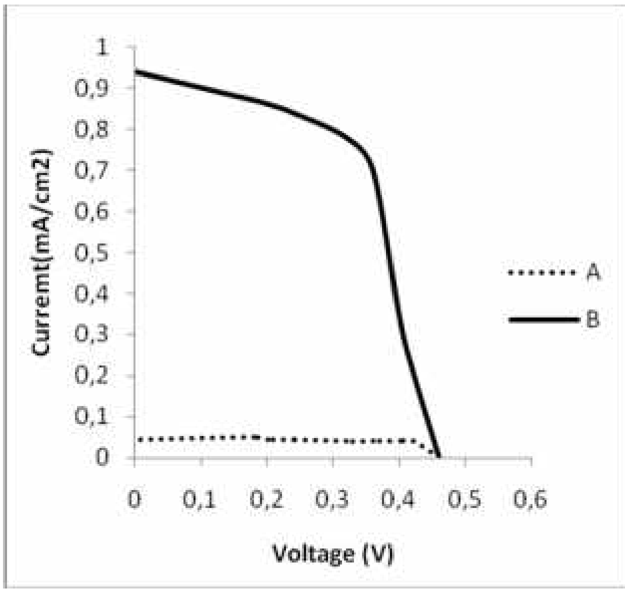


Fig.5 compares the absorption spectrum of (A) Laali Stem Bark (Lawsonia inemis) soxhlet ethanol extraction with Laali Stem Bark (Lawsonia inemis) soxhlet ethanol extraction + TiO_2 (B) Laali Stem Bark (Lawsonia inemis) cold ethanol extraction with Laali Stem Bark (Lawsonia inemis) cold ethanol extraction + TiO_2


Curremt(mA/cm2)
1
0,9
0,8
0,7
0,6
0,5
0,4
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Voltage (V)
A
B

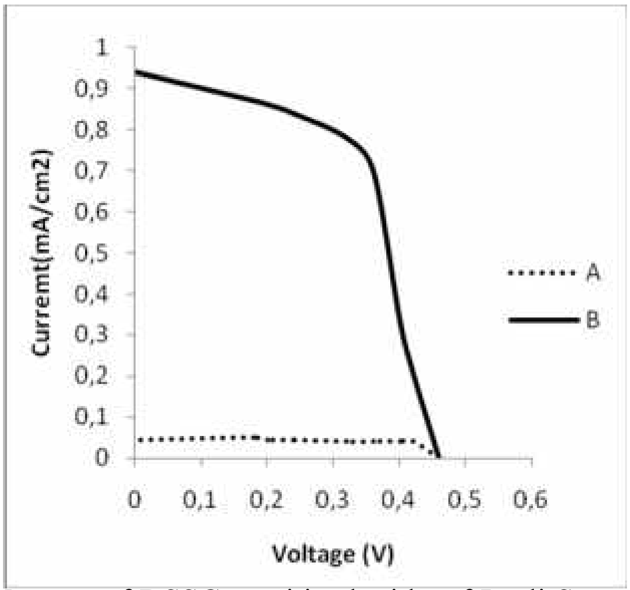

Fig.6 I-V curve of DSSC sensitized with of Laali Stem Bark (Lawsonia inemis) soxhlet extractor (A) and ethanol extraction (B)

Table.1

Extracting solvent	Extract	V_{0c}(V)	Isc(mA/cm^2)	FF	η%
Soxhlet Extractor (A)	lawsonia inermis Bark	0.175	0.49	0.606	82.1
Cold Ethanol (B)	lawsonia inermis Bark	0.066	0.94	0.639	76.1

Table 2

Effect of pH on of Laali Stem Bark (Lawsonia inemis) extract solution (soxhlet ethanol solvent (A)

pH	V_{0c}(V)	Isc(mA/cm^2)	FF	η%
3.4	0.18	0.49	0.606	62
3	0.19	0.50	0.624	62
2	0.20	0.52	0.729	67.8
1	0.23	0.54	0.809	73.8

Table 3
Effect of pH on of Laali Stem Bark (Lawsonia inemis) extract solution (cold ethanol solvent (B)

pH	V_{0c}(V)	Isc(mA/cm^2)	FF	η%
3.4	0.66	0.94	0.639	76.1
3	0.70	0.96	0.693	73.6
2	0.72	0.99	0.735	74.7
1	0.74	0.99	0.755	75.7

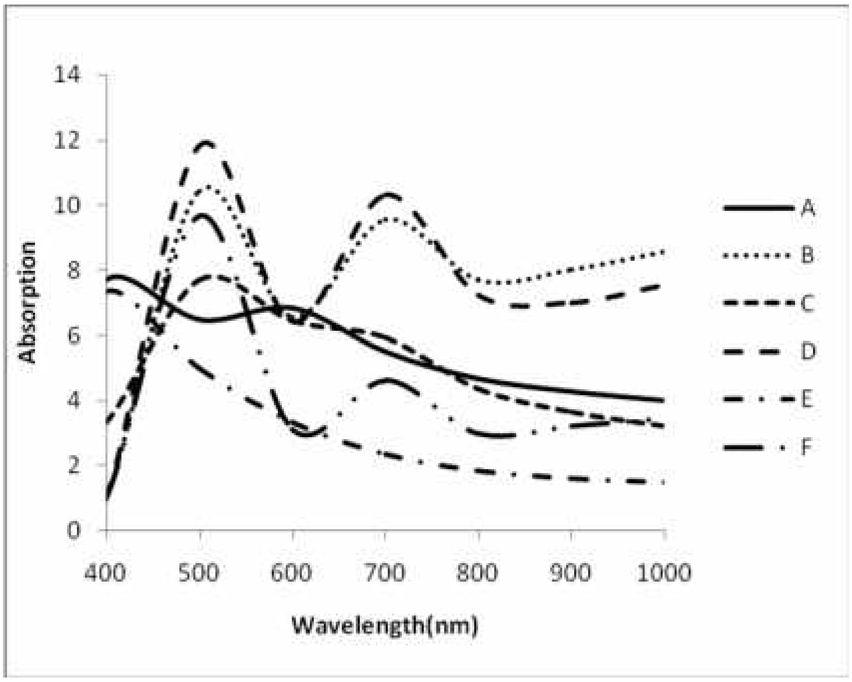

Fig .7 Light Absorption spectra of of Laali Stem Bark (Lawsonia inemis) cold ethanol extract (A) fluid at pH 3.21 (B) adsorbed on TiO_2 at pH3.21 (C) fluid at pH 3.0 (D) adsorbed on TiO_2 at pH3.0 (E) fluid at pH 2.0 (F) adsorbed on TiO_2 at pH 2.0

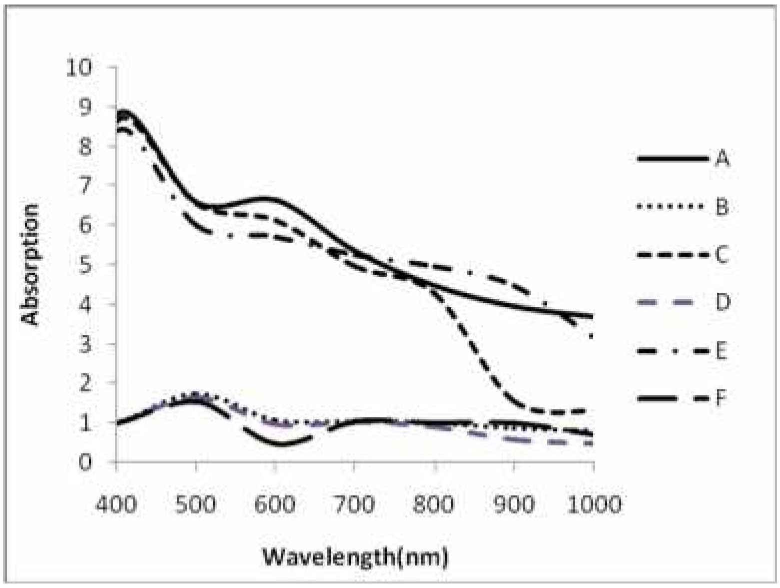

Fig 8 Light Absorption spectra of of Laali Stem Bark (Lawsonia inemis) soxhlet ethanol extract (A) fluid at pH 3.21 (B) adsorbed on TiO_2 at pH3.21 (C) fluid at pH 3.0 (D) adsorbed on TiO_2 at pH3.0 (E) fluid at pH 2.0 (F) adsorbed on TiO_2 at pH 2.0