Original Research Article
Naturals Dyes FromDetariumMicrocarpumGuill. And Perr. as photosensitizers In DyeSensitized Solar Cells

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ABSTRACT

Dye-sensitized solar cells (DSSC) are promising devices in the photovoltaic industry. In these devices, The dye plays a major role in the performance of the cell. However, the toxicity and cost of synthetic dyes, which are more effective, limit their use. Thus, the use of natural dyes is a promising alternative. In this article, natural dyes extracted from the trunk bark of *DetariumMicrocarpum*Guill. and Perr (DM) were used, for the first time, in DSSC. Aqueous decoction followed by Hydro-acetonic extraction (30/70, V/V) was carried out to obtain the crude extract from the bark ground into a powder. Then a phytochemical screening of the crude extract followed by liquid-liquid separation and assay of the main colored compounds in order to evaluate the amount of total polyphenols, flavonoids and anthocyanins were carried out.The different separated fractions were tested as photosensitizers in DSSC.The extraction of the crude pigment from the bark of the trunk of DetariumMicrocarpum gave a very interesting yield of 20.48%compared to others. The results of the phytochemical tests reveal the presence of the following compounds: catechic tannins, gallic tannins, flavonoids, anthocyanins, leuco anthocyanins, coumarins, quinones and alkaloids with high concentrations.The results of the photovoltaic tests of the different separate extracts show that the n-butanol extract is the most efficient.Cells sensitized with this extract showed a photocurrent (Jcc) of 0.93 mA/cm2, a high open circuit voltage (Voc) of 433 mV and a high conversion efficiency η (%) of 0.38%.This conversion efficiency is higher than that of a recent study which reported a conversion of 0.31%.These results show that *DetariumMicrocarpum* constitutes a potential source of photosensitive dye.

Keywords:Dye-sensitized solar cell, natural organic dye,anthocyaninsDetariummicrocarpum, Niger.

1. INTRODUCTION

With the threat of depletion of fossil fuel reserves, the risk of accidents, nuclear energy waste, air pollution, global warming and climatic hazards, the need for renewable energies is essential. Solar energy is the safest among the possible alternatives. It is in this context that in 1991, Michael Grätzel and O'Regan attempted to develop a dye-sensitized photovoltaic cell called Grätzel cell or Dye Sensitized Solar Cell (DSSC) [1; 4]. This hybrid cell, using inorganic and organic materials, is based on the principle of plant photosynthesis. This cell is less expensive, easy to produce and environmentally friendly, unlike the first- and second-generation cells (silicon-based cells) which dominate the current market (99%) and which are very expensive to produce [1; 4].

A DSSC is composed of a photosensitizer (dye or pigment), a photoelectrode made of a semiconductor, a counter electrode and an electrolyte acting as a redox mediator to regenerate the pigment [1]. Of all these components, the dye plays a key role in the absorption of sunlight and the conversion of solar energy into electrical energy [2;21]. To be effective, the dye must have a wide absorption range in the visible, a good ability to inject electrons into the conduction band of the semiconductor, good adhesion to the semiconductor and good stability.

Many metal complexes and organic dyes have been synthesized and used as sensitizers [3]. Until 2008, the highest yield (11–12%) was obtained with DSSCs sensitized with organometallic compounds containing Ruthenium (Ru) such as Black dye, N3 or N729 [4; 5; 6]. In 2020, a lead-based organometallic perovskite ($CH_3NH_3PbI_3$) gave a yield of 28% [23]. However, organometallic dyes have a drawback. Indeed, the metals used are rare and/or toxic, resulting in expensive production. As for synthetic organic dyes, they often have complicated synthesis methods and low synthesis yield [4]. In this context, the use of natural dyes is a promising alternative[21; 25].Natural dyes are indeed easy to access, easy to extract, non-toxic and totally biodegradable [2; 25].

In recent years, several natural dyes have been used as sensitizers in DSSCs, such as anthocyanins [4; 7], flavonoids [8], carotenoids [9; 10], chlorophylls [11], etc. However, the conversion efficiency of natural dyes often did not exceed the threshold of 2% until 2014 [12]. Thus, the search for natural dye molecules, effective in photovoltaic conversion, is one of the challenges of chemists in the field of dye-sensitized photovoltaic cells. DetariummicrocarpumGuill. et Perr. locally called Taura in Haussa, and Fantou in Zarma which was formerly used as a source of dyes in Nigerien handicrafts [2] could be used as a source of sensitizers in dye-sensitized solar cells.

The main objective of this work is the development and characterization of dye-sensitized solar cells using Detariummicrocarpum trunk bark extracts.In Niger and the sub-region, there is a lack of studies on the use of natural dyes in solar energy. This study constitutes one of the first initiatives to valorize dye plants in Niger in solar energy

2. MATERIAL AND METHODS

2.1. Plant material

The plant material used in the present work consists of trunk bark of DetariummicrocarpumGuill. and Perr. (Caesalpiniaceae).

Figure 1: A sample of the bark of DetariummicrocarpumGuill.and Perr.

The harvested trunk bark of Detariummicrocarpum (DM) was dried in an oven at 50°C before grinding using a manual grinder to obtain a fine powder.The obtained powder was subjected to phytochemical screening in order to detect certain dyes present in this plant material.The compounds targeted are tannoids, flavonoids, anthocyanins, tannins, quinones, leuco-anthocyanins, alkaloids, coumarins, sterols and polyterpenes.These compounds, for the most part, are responsible for the appearance of color in higher plants [2].Chemical detection was carried out by the methods described by [2].

2.2.Dyeextraction

The extraction protocol was carried out according to the method illustrated in Figure 2. Hydrophilic cotton and Wattman papers were used for the filtration of aqueous decoction and water-acetone macerate of the bark powder.

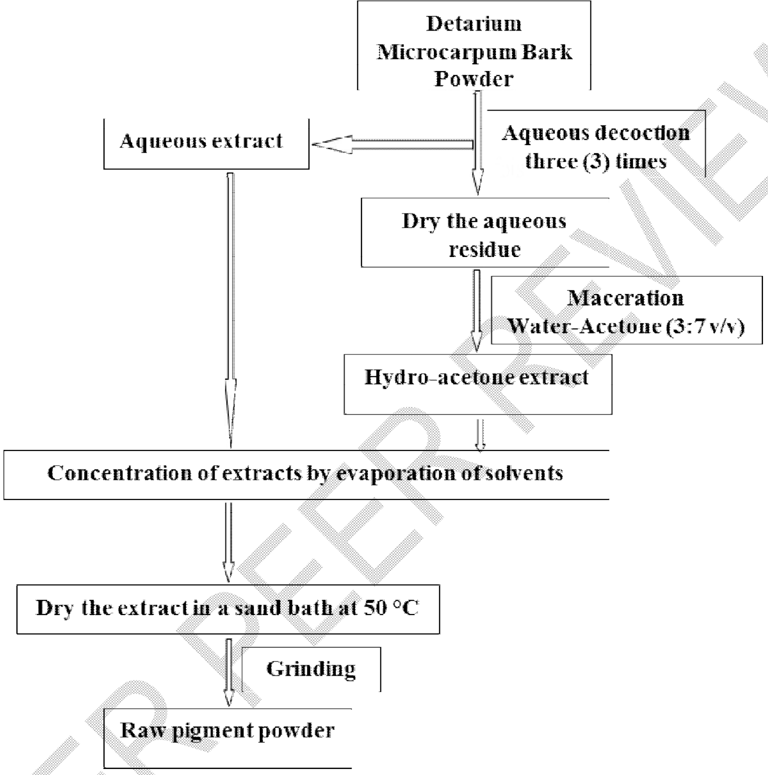

Figure 2: Raw dye extraction process

2.3. Partial purification

Distilled water, petroleum ether, dichloromethane, ethyl acetate, n-butanol, ethanol were used for the preparation of the extracts.All reagents and solvents are of analytical grade.A rota-vapor (R-II Buchi) was usedfor the concentration of the extracts.

A partial separation by liquid-liquid extraction was carried out according to the method of [3] in order to separate polyphenols, notably flavonoids and anthocyanins.The protocol for this method is shown in Figure 3.

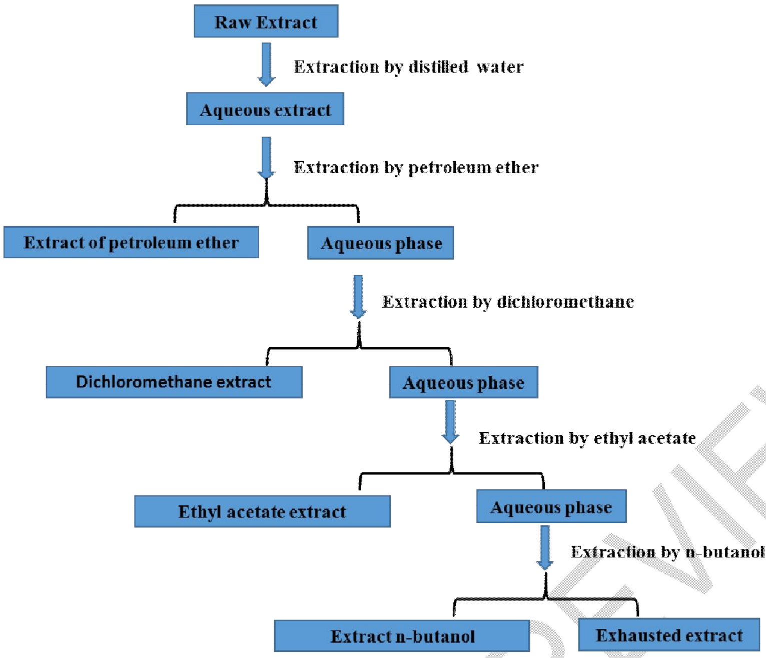

Figure 3: Schematic of the liquid-liquid extraction protocol of crude dye from the trunk bark of Detariummicrocarpum

2.3.UV-visible characterization and dosage of phenolic compounds

Analyzes of the colored DM extracts were carried out using a spectrophotometer (EVOLUTION 300 UV-Visible) in order to identify the absorbances bands of the characteristic groups responsible for the coloring. A determination of total polyphenols, flavonoids and anthocyanins was carried out using a UV visible spectrophotometer.The determination of total polyphenols was carried out according to the method of FolinCiocalteu [15] and the protocol is described in [3;16].The determination of flavonoids was carried out using the aluminum trichloride method and the protocol is described in [3;16;17;18].The determination of anthocyanins was carried out using the sodium bisulfite ($NaHSO_3$) method and the protocol is described in [2;3].

2.4.Dye sensitized solar cells fabrication

Conductive indium tin oxide (ITO) glasses were used as electrodes.A titanium oxide paste (Ti-Nanoxide T/SP,SOLARONIX) was deposited on the conductive faces of the photoanodes in 1 cm2 molds made with 3M tape (Magic Tape, 19 mm x 33 m) according to themethod known as “Doctor Blade” [24].A thin layer of platinum solution (Plastisol T, Solaronix) was deposited on the conductive faces of the cathodes acting as a catalyst.The photoanode was baked at 500°C in a programmable oven for 1 hour with 30 minutes of rise time and at the end of the cooking 18 hours of cooling.The cathode was baked at 450°C for 30 min.After cooling, the electrode with the TiO_2 deposit was immersed in the different colored extracts taken up in ethanol for at least 8 hours [24]. The impregnated electrodes (photoanodes) were gently rinsed with ethanol to remove excess unadsorbed dye and then dried in ambient air.The electrolyte is a mixture of TBAI (tertiobuthylammonium iodide) (0.5M I^- and 0.05M I_2)in an acetonitrile solvent [12;24]. The assembly of the different elements of the cell (figure 4) was carried out according to the protocol described by [24].

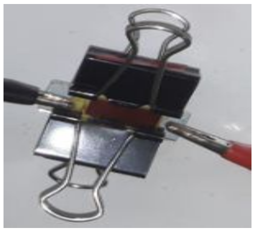

Figure 4: Assembled dye cell

2.5. performance measurement of dye sensitized solar cells

Finally, the characterization of the cells produced was carried out using an assembly consisting of a white light lamp (LED IP66, 50W) as a solar similator, a multimeter (Uni-T, UT30B) as a voltmeter, a multimeter (ALDA, DT-830D) used as amperemeter, a decade box of variable resistors (CENTRAD, DR06; 0Ω to 1111 KΩ) allowing the voltage to be varied, a luxmeter (Ambient weather, TM-206 Solar Power Meter), a thermometer and a stopwatch. The assembly has been illustrated in figure 5.

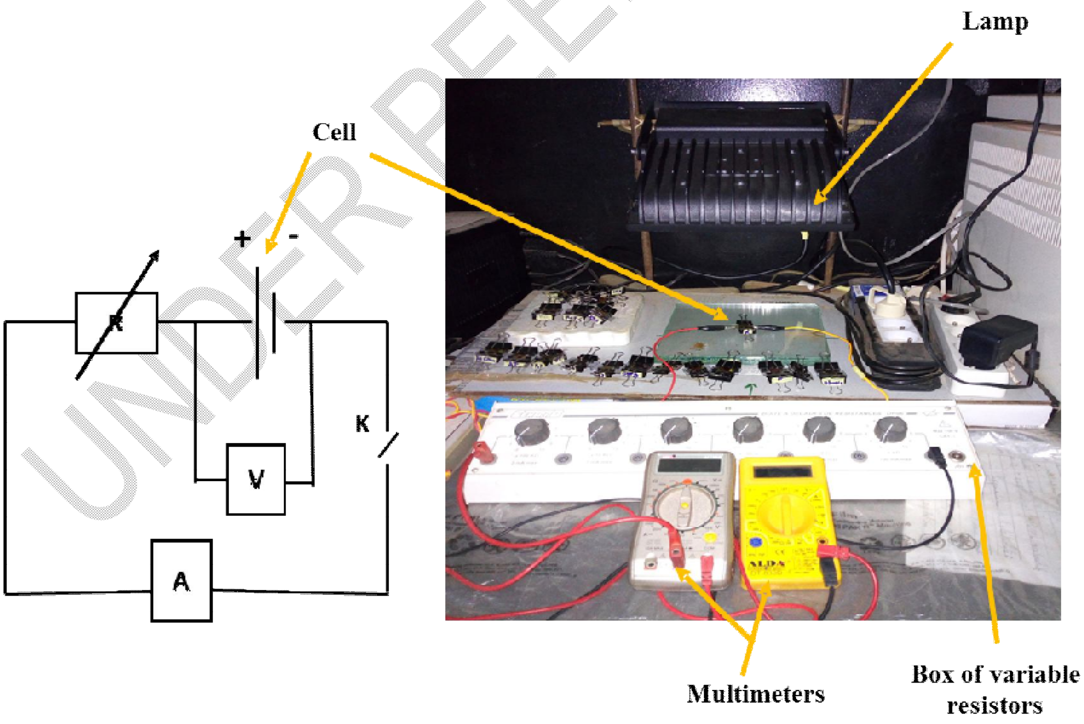

Figure 5: Electrical device of I-V characterization.[24]

The current-voltage (I-V) characteristics are produced by measuring the current generated by the Grätzel cell as a function of the voltage delivered to its terminals.The voltage is varied using a decade of variable resistors.

The **Icc** and **Voc** were obtained by directly connecting an ammeter and a voltmeter respectively to the cell.

The form factor FF was obtained using the following relationship:

$$FF = \frac{V_{max} \times I_{max}}{V_{oc} \times I_{cc}} \quad (1)$$

Where I_{max} and V_{max} represent the intensity-voltage couple for which the power delivered by the cell is maximum.

The power conversion efficiency η is defined by the ratio between the maximum power delivered by the cell Pmax and the incident light power Pin:

$$\eta = \frac{FF \times V_{oc} \times I_{CC}}{P_{in}} \times 100 \quad (2)$$

The most commonly used standard illumination corresponds to the AM1.5 standard, i.e. an incident power of 1000 W/m^2 [1 and 24].

3. RESULTS AND DISCUSSION

3.1. Results

3.1.1.Extraction yield

The extraction of the raw pigment from the bark of the trunk of Detarium Microcarpum gave a result of 10.24 g of extract for 50 g of sample: a yield of 20.48%.

3.1.2.Results of phytochemical screening

The results of phytochemical tests carried out on the bark extract of the trunk of Detarium Microcarpum reveal the presence of the following compounds: catechic tannins, gallic tannins, flavonoids, anthocyanins, leuco anthocyanins, coumarins, quinones andalkaloids (table 1).On the other hand, we observe the absence of steroids and polyterpenes in the aqueous phase but its present in the petroleum ether extract.As for quinones, their presence is significantly observed in petroleum ether extract.

Table 1: Results of photochemical screening

Plant material	Major groups of chemical compounds highlighted												
Species name (part used)	TG	TC	Fl	Lan	Ant	Cou	Quinones		Steroids and polyterpenes		Alkaloids		
											Drg	Myer	Wa
	EA						EA	EEP	EA	EEP	EA		
Detarium microcarpum	+++	+++	++	+++	+++	++	+	++	-	+++	++	+++	+++

Legends: **TG**(gall tannin);**TC**(catechic tannin);**Fl**(flavonoid);**Lan**(leuco anthocyanin;**Ant**(anthocyanin);**Cou**(coumarin); **EA**(aqueous extract);**EEP**(petroleum ether extract);**Drg**(Dragendorff reagent);**Myer**(Mayer reagent);**Wa**(Wagner reagent)

3.1.3 Results of liquid-liquid separation of raw dye

A liquid-liquid separation was carried out by confronting the aqueous crude with four (4) organic solvents of increasing polarity. These are petroleum ether, dichloromethane, ethyl acetate and n-butanol, respectively. At the end of the operation, two colorless fractions were obtained (petroleum ether and dichloromethane) and three other colored fractions (ethyl acetate, n-butanol and the remaining aqueous extract); as shown in Figure 6.

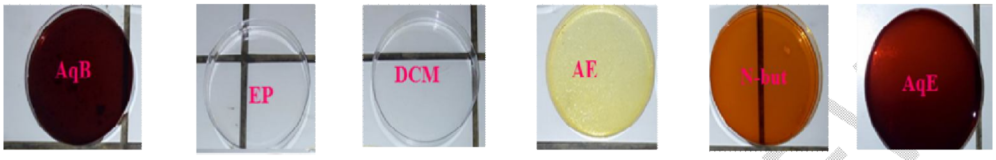

Figure 6: The different extracts of dyes resulting from liquid-liquid separation;Aqueous crude (**AqB**), Petroleum ether (**EP**), Dichloromethane (**DCM**), Ethyl acetate (**AE**), N-butanol (**N-but**) and spent aqueous extract (**AqE**).

3.1.4.Results of Spectrophotochemical Analysis

3.1.4.1.UV-visible spectroscopy of the different extracts

The absorption spectrum of the extracts shows the presence of well-defined peaks around λ = 280 nm and relatively less intense peaks between 400 nm and 600 nm also in all the extracts (figure 7).

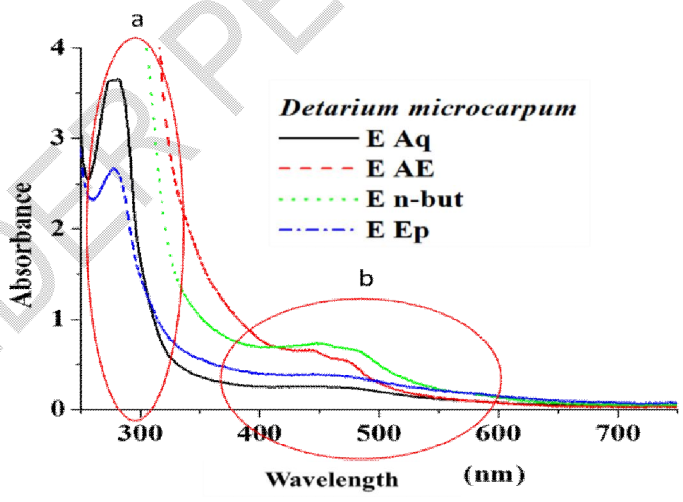

Figure 7: Absorption spectra of the aqueous extract ($\mathbf{E_{aq}}$), ethyl acetate extract ($\mathbf{E_{AE}}$), n-butanol extract ($\mathbf{E_{n\text{-}but}}$), and exhausted extract ($\mathbf{E_{Ep}}$);a) absorption zone of polyphenols, b) absorption zone of anthocyanic polyphenols

3.1.4.2.UV-Visible spectroscopy ofdyesadsorbed into TiO_2

The dyes adsorbed onto semiconductor (TiO2) are tested in order to evaluate their absorption in the visible range (350nm to 750nm), allowing to obtain the spectrogram of Figure 8. All these dyes showed a certain spectrophotometric activity in the visible thus pushing their use in dye-sensitized solar cells as photosensitizers

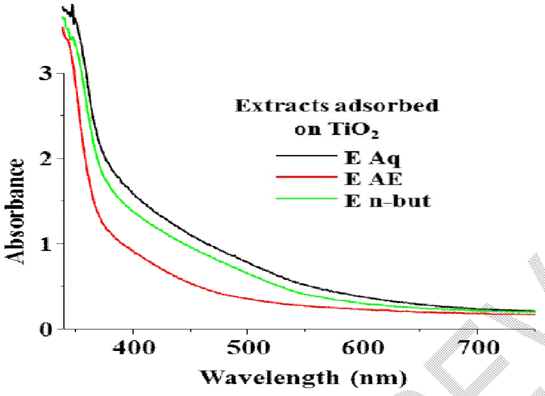

Figure 8: Absorbance spectrograms of the dyes adsorbed on the TiO_2 layer

3.1.4.3.Results of the quantitative dosage of some compounds of photovoltaic interest

Three extracts of dyes from the bark of the trunk of Detarium Microcarpum were subjected to a quantitative dosage of some compounds of photovoltaic interest.These are the aqueous extract, the n-butanol extract and the ethyl acetate extract.This quantitative analysis by spectrophotometry was carried out to determine the proportions of total polyphenols, flavonoids and anthocyanins in these extracts.The different dosages being carried out at least three times, the averages of the results are grouped together in Figure 9.

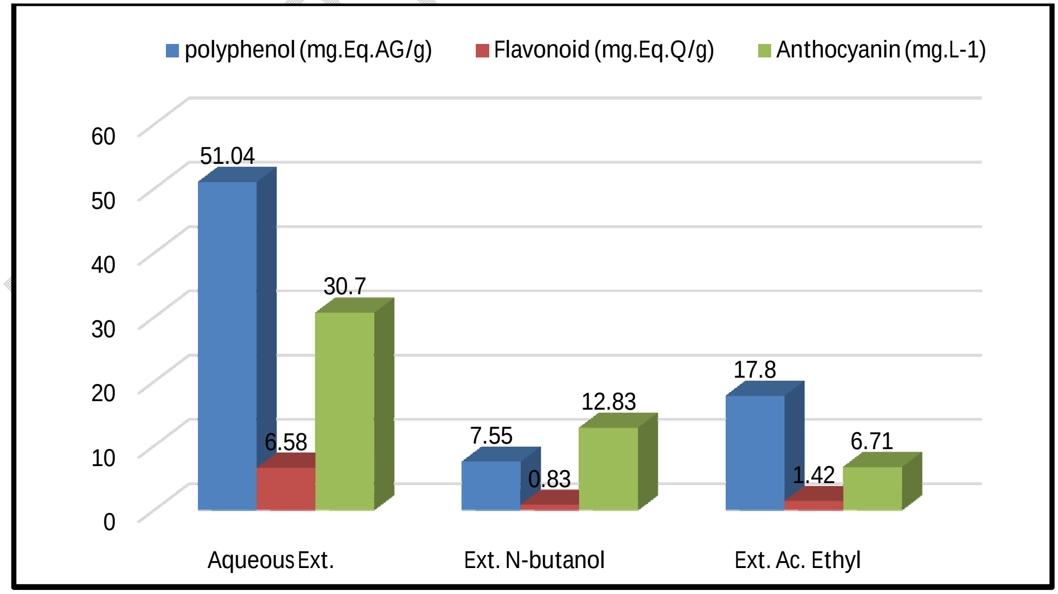

Figure 9: Results of total polyphenol, flavonoid and anthocyanin contents of 3 extracts

These data reveal that the quantity of polyphenols and flavonoids is greater in the aqueous extract then in the acetate extract.ethyl (Ext$_{aq}$> Ext$_{AE}$> Ext.$_{n-\ but}$).On the other hand, the anthocyanin content is higher in the aqueous fraction followed by the n-butanol extract (Ext$_{aq}$> Ext.$_{n-but}$> Ext.$_{AE}$).

3.1.5.Photovoltaic activities

3.1.5.1.Results of the intensity-voltage measurement of cells

Figure 10 (a) shows the measurement curves of the electrical characteristics of four cells in order of decreasing efficiency, that of the n-butanol extract, the aqueous extract, the ethyl acetate extract and the exhausted aqueous extract.Figure 10 (b) shows the curves of the powers delivered by the manufactured solar cells as a function of the voltage of the four previous cells.These curves will allow us to extract the parameters necessary to calculate the conversion efficiencies of the manufactured cells.

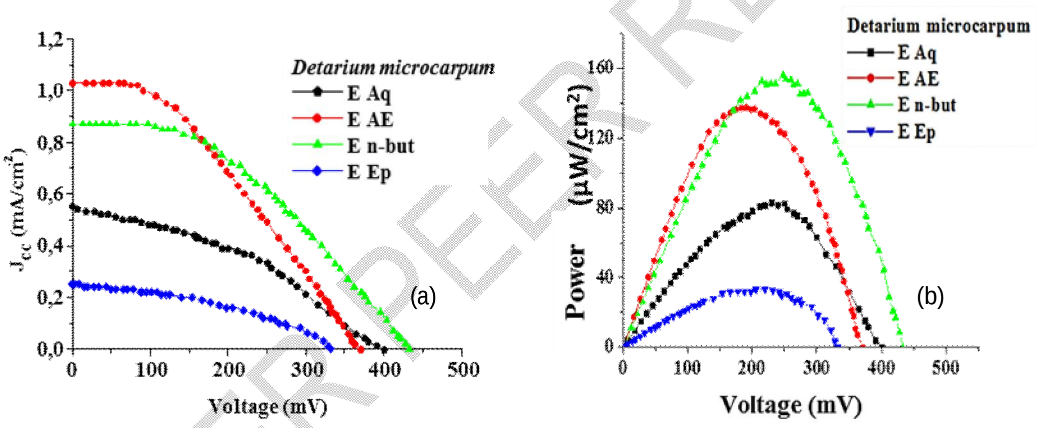

Figure 10: J-V characteristic curves of DSSCs (a) and Curves of the powers delivered as a function of the voltage of the DSSCs (b) sensitized with the aqueous extract (E$_{aq}$), ethyl acetate extract (E$_{AE}$), n-butanol extract (E$_{n-but}$), exhausted extract (E$_{Ep}$)

Table 2

presents the electrical parameters of the four previous cells and those of the cell sensitized with the reference dye (N719).The data in Table 2 reveal that the cell sensitized with the n-butanol extract is the most efficient among the four DM extracts, with an efficiency of 0.38%, a current Icc = 0.93 mA and a voltage Voc = 433 mV.The cells of ethyl acetate, aqueous extract and spent aqueous extract have conversion efficiencies of 0.14%, 0.08% and 0.03%, respectively.The cell sensitized with the reference pigment (N719) gave a current Icc = 8.1 mA, a voltage Voc = 791 mV, a form factor FF = 0.37 and a conversion efficiency η = 2.39%.

Table 2: Photoelectrochemical parameters of the DSSCs produced

Extracts	**V$_{oc}$ (V)**	**J$_{cc}$ (mAcm^{-2})**	**P$_{max}$(µW/cm^{2})**	**FF**	**η (%)**

Aqueous extracts	0,401	0,55	82,80	0,38	0,08
AE	0,371	1,03	137,52	0,36	0,14
n-but	0,433	0,93	156,24	0,41	0,38
E Ep	0,332	0,25	33,00	0,40	0,03
N719	0,791	8,1	2386,3	0,37	2,39

3.2. Discussion

The extraction of raw pigment from the bark of the trunk of Detarium Microcarpum gave a yield of 20.48%. This yield, compared to the extraction yields by aqueous decoction only of natural dyes from the work of [19] ranging from 7% to 14%, shows that the aqueous decoction technique followed by water-acetone maceration would optimize the extraction of the raw dye.

The results of phytochemical tests carried out on the bark extract of the trunk of *Detarium Microcarpum* reveal the presence of the following compounds: catechic tannins, gallic tannins, flavonoids, anthocyanins, leuco anthocyanins, coumarins, quinones andalkaloids.These results are in agreement with those found by [15].

The dye is the photoactive element that absorbs incident light and generates charge carriers.The ideal dye must absorb most of the solar spectrum and allow efficient injection of the electron into the conduction band of the semiconductor while exhibiting high photochemical stability. All the cells produced during this work generate significant photocurrents under illumination of 1000 W/m^2 indicating that they carry out photovoltaic conversion.The DM dyes used actually have photovoltaic activity capable of sensitizing a semiconductor such as TiO_2.This activity in the visible can be mainly linked to anthocyanin compounds as shown in Figure 6. The spectra in Figure 7 of the three main extracts all showed appreciable absorbance of anthocyanin molecules in the visible.Better still, the crude aqueous extract adsorbed to the semiconductor absorbs in the visible better than the other two extracts (figure 8).In addition, the aqueous extract contains the highest anthocyanin content (figure 9).However, the cell of the crude aqueous extract is the least efficient of the three (E_{aq}, E_{AE} and $E_{n\text{-}but}$). This low performance of the cell in the aqueous extract could be due to the competition or masking effect of the molecules present[8;9;12]. Indeed, the molecules which would be mainly adsorbed to the semiconductor, although they absorb in the visible, would be incapable of injecting electrons into the conduction band of TiO_2 or would present a low stability of the excited state allowing them to inject electrons[12;14]. Hence the need for partial purification of the aqueous crude extract by liquid-liquid separation. At the end of this partial purification, the first colored extract obtained in order of increasing polarity of the solvents used is the ethyl acetate extract with an orange-yellow hue (the petroleum ether and dichloromethane extracts are colorless). The ethyl acetate extract contains a flavonoid content intermediate between that of the aqueous extract and the n-butanol extract (6.58 mg.Eq.Q/g > 1.42 mg.Eq.Q /g > 0.83 mg.Eq.Q/g). However, the cell of the ethyl acetate extract is less efficient than that of the n-butanol extract but more efficient than that of the aqueous extract ($\eta_{aq} = 0.08\% < \eta_{AE} = 0.14\% < \eta_{n\text{-}but} = 0.38\%$). This would explain on the one hand that liquid-liquid separation would have reduced competition and improved cell performance ($\eta_{aq} = 0.08\% < \eta_{AE} = 0.14\%$). On the other hand, the flavonoids, being predominant in the AE extract, would not be the main responsible for the photovoltaic activity of the DM trunk bark dye ($\eta_{AE} = 0.14\% < \eta_{n\text{-}but} =$

0.38%)[8;12]. The last extract is that of N-butanol which is the most polar solvent of the four solvents used for liquid-liquid separation. The n-butanol extract, red in color and which anthocyanin content is intermediate between that of the aqueous extract and the ethyl acetate extract (30.7 mg.L^{-1} > 12.83 mg.L $^{-1}$ > 6.71 mg.L^{-1}), gave the most efficient cell with a conversion efficiency $\eta_{n\text{-bu}}t = 0.38\% > \eta_{AE} = 0.14 > \eta_{aq} = 0.08\%$ (table 2) . This could be explained by the fact that n-butanol would have essentially extracted the anthocyanin compounds which would be the main responsible for the photovoltaic activity of the dye from the bark of the trunk of Detarium Microcarpum. In previous work, other types of natural products containing anthocyanins such as blood orange and eggplant gave efficiencyof 0.66% and 0.43% respectively [21]. Iman et al., recently reported a conversion efficiency of 0.31% lower than that obtained in this study[25].An anthocyanin dye extracted from black rice gave a DSSC of a voltage V_{oc} of 550 mV and a short-circuit photocurrent Iccof 1.14 mA [11]. Anthocyanin dyes gave DSSCs which retained their yield for a period of 36 weeks [20], which makes these anthocyanin dyes interesting in solar energy production.

4. Conclusion

This study made it possible to produce dye-based solar cells using, for the first time, dyes extracted from Detarium microcarpum, a dye plant from Niger. The extraction yield of 20.48% reveals on the one hand the effectiveness of the extraction procedure of decoction followed water-acetone maceration of the aqueous residue. In another hand it revealed that the Deutarium microcarpum is a plant rich in dyes. Indeed, the phytochemical screening revealed several families of dyes including catechic tannins, gallic tannins, flavonoids, anthocyanins, leuco-anthocyanins, coumarins, quinones, alkaloids, steroids and polyterpenes in the crude extract. Liquid-liquid extraction made it possible to partially separate dyes in the ethyl acetate extract and n-butanol extract which are also colored. The n-butanol fraction essentially contains anthocyanin compounds. Indeed, the characterization of solar cells produced using the four colored fractions showed that the DSSC sensitized by the dye of the n-butanol extract is by far the most efficient with the conversion efficiency $\eta = 0.38\%$. Thus at the end of this study, we can conclude that despite the instability of the elaborated cells which is due among other things to the evaporation of the electrolyte, Detarium Microcarpum could be considered as a potential source of photosensitizing dyes. However, optimization of the photosensitive activity of the dye is possible by carrying out extensive column purification of the n-butanol extract and identification of the active molecule. This would make it possible to consider a possible modification of its structure or co-sensitization with a view to further optimizing its photosensitive activity.

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