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Study of Native Dyes in Solar Cell Applications*

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Estudio de colorantes naturales en aplicaciones de celdas solares

Étude de colorants natifs dans des applications de cellules solaires

Estudo de corantes nativos em aplicações de células solares

Paula Aschenbrenner [a]
Simon Hertlein [b]
Carlos Villanueva [c]
Tomás Rada [d]

* This article presents some results from the project: "Estudios de Colorantes Nativos en Aplicaciones de Celdas Solares de Bajo Costo." Carried out at Universidad del Norte.

[a] Universität Leipzig, Leipzig, Germany. BSc Physics, Universitat Leipzig, Germany. Internship at Universidad del Norte, 2015. Sponsored by RISE Program from DAAD. <paula.aschenbrenner@gmx.de>.

[b] Ludwig-Maximilians-Universität München, Munich, Germany. Bachelor of Science in Physics, Ludwig-Maximilians-Universität, München, Germany. Internship at Universidad del Norte, 2016. Sponsored by RISE Program from DAAD. <Simon.Hertlein@t-online.de>.

[c] Universidad del Norte, Barranquilla, Colombia. MSc. (c) en Tecnologías Urbanas Sostenibles, Universidad de Buenos Aires, Argentina. Research invited. <carlosvill89@gmail.com>.

[d] Universidad del Norte, Barranquilla, Colombia. Ph.D. in Physics, University of Saint Andrews, United Kingdom, Posdoct in the Helmholtz Zentrum Berlin, Germany. Head of Physics and Geoscience Department, Universidad del Norte. <trada@uninorte.edu.co>.

Abstract. Due to the high solar radiation, constant over the whole year, solar energy is one of the most promising energy sources of the Caribbean for the next decades. But up to now this potential is not used, mainly due to the high costs of solar cells. Solar energy conversion is mainly dominated by expensive cells based on silicon. A promising alternative is the dye sensitized solar cell (DSSC) based on Titanium dioxide (TiO_2), which has generated considerable interest in the last years. Thus, the objective of this study was to analyse and optimize the DSSCs' performance depending on their preparation and lighting condition. Therefore, five different natural dyes were extracted from local Colombian fruits and vegetables, such as Achiote, Agraz, Corozo, Mora and Remolacha. They were characterized using an UV-Spectrophotometer and used as sensitizers to fabricate the DSSCs. To optimize the DSSCs, different conditions and parameters were changed. It was thereby found that beside the fruit that was used, also the thickness of the TiO_2 layer and the preparation procedure of the dye solution have a direct impact on the cell efficiency. The cells fabricated with achiote dye solution were found to have the best efficiency, reaching up to 0,21% under sun and 0,075% under a halogen lamp. The study was executed in the context of internships at the Universidad del Norte in Barranquilla, Colombia, which was enabled by the DAAD through RISE program scholarships.

Keywords: natural dyes; solar cell; TiO_2.

Resumen. La energía solar es una de las más promisorias fuentes de energía en el Caribe en las próximas décadas debido a la alta radiación solar y a que se mantiene muy constante durante la mayor parte del año. Sin embargo, hasta ahora este potencial no se usa debido a los altos costos de las celdas solares, cuya comercialización está principalmente dominada por costosas celdas basadas en silicio. Una alternativa prometedora son las celdas solares sensibilizadas con colorantes (DSSC, por sus siglas en inglés) basadas en dióxido de titanio (TiO_2), las cuales han generado bastante interés en los últimos años. Así, el objetivo del presente estudio fue analizar y optimizar el desempeño de las DSSC dependiendo de su preparación y condiciones de iluminación. Por ello se usaron cinco colorantes naturales diferentes extraídos de frutas y vegetales, tales como: Achiote, Agraz, Corozo, Mora y Remolacha. Estos colorantes fueron caracterizados usando un espectrofotómetro en ultravioleta y visible, y usados como sensibilizadores en la fabricación de las DSSC. En el proceso de optimización se cambiaron varias condiciones y parámetros. En ello se encontró que además de los colorantes usados, los grosores de las capas del TiO_2 y los procedimientos de preparación de la solución colorante tienen un impacto directo en la eficiencia de las celdas. Finalmente, se encontró que las celdas con las mejores eficiencias fueron las de Achiote, cuya eficiencia alcanzó el 0,21% bajo iluminación directa del sol y de 0,075% de eficiencia cuando fue iluminada con una lámpara halógena. Este estudió se desarrolló en el contexto de intercambios académicos en la Universidad del Norte con el apoyo del DAAD a través del programa RISE.

Palabras clave: celdas solares; colorantes naturales; TiO_2.

Résumé. L'énergie solaire est l'une des sources d'énergie les plus prometteuses dans les Caraïbes, pour les décennies à venir, dû au rayonnement solaire élévé qui reste constante pendant la majeure partie de l'année civile. Cependant, jusqu'à présent ce potentiel n'a pas été pleinement exploité, en raison de coût élevé des cellules solaires, dont la commercialisation a été dominée par des cellules de silicium à prix élevé. Une solution prometteuse sont les cellules solaires sensibilisés par un colorant (DSSC, en anglais), à base de dioxyde de titane (TiO_2), qui a suscité des réactions considérables pour ces dernières années. Donc, l'objectif principal de cette étude était d'analyser et d'optimiser la performance de DSSC, en fonction de de ses conditions de préparation et d'illumination. Ainsi, cinq colorants naturels ont été utilisés, de fruits et végétaux extraits, à partir d'Achiote, Agraz, Corozo, Mûr et de Betteraves. Ces colorants ont été caractérisés en utilisant un spectrophotomètre, dans l'ultraviolet et le spectre visible, et utilisés des comme sensibilisants, pour la fabrication des DSSC. Dans le processus d'optimisation des diverses conditions et paramètre ont été changés. En cela il a été établi qu'en plus des colorants utilisés, les épaisseurs de couche du TiO_2 et les processus de préparation de solution colorante ont un impact direct sur la efficacité des cellules. On se retrouva finalement que les cellules avec les meilleures efficacités ont été celles de l'Achiote, dont une efficacité du 0,21% a été atteint, avec un éclairage de la lumière directe du soleil, et une efficacité du 0,075%, lorsqu'elle est éclairée par une lampe halogène. Cette étude a été élaboré dans le contexte d'échanges universitaires dans l'Universidad del Norte appuyée par le service allemand d'échanges universitaires (DAAD), à l'aide du programme RISE.

Mots-clés: cellules solaires; colorants naturels; TiO_2.

Resumo. A energia solar é uma das fontes de energia mais promissores no Caribe, nas próximas décadas, devido à alta radiação solar que se mantém constante durante a maior parte do ano. No entanto, até agora este potencial não é usado por causa do alto custo das células solares, cuja comercialização é dominada principalmente por células de silício de preço elevado. Uma alternativa promissora são as células solares sensibilizadas por corante (DSSC, por sua sigla em Inglês) à base de dióxido de titânio (TiO_2), que geraram um interesse considerável nos últimos anos. Assim, o objetivo deste estudo foi analisar e aperfeiçoar o desempenho de DSSC dependendo de suas condições de preparação e de iluminação. Assim, foram usados cinco diferentes corantes naturais extraídos de frutos e vegetais, tais como: Anato, Agraz, Corozo, Mora e Beterrabas. Estes corantes foram caracterizados usando um espectrofotómetro de ultravioleta e visível, e utilizados como sensibilizadores na fabricação do DSSC. No processo de optimização várias condições e parâmetros foram alterados. Verificou-se que a adição dos corantes utilizados, as espessuras das camadas de TiO_2 e métodos de preparação da solução de corante tem um impacto direto sobre a eficiência das células. Finalmente descobriu-se que as células com as melhores eficiências foram anato, cuja eficiência de 0,21% com iluminação solar direta e eficiência de 0,075% quando foi iluminado com uma lâmpada de halogéneo. Este estudo foi desenvolvido no contexto do intercâmbio acadêmico com a Universidad del Norte e apoiado através do programa RISE.

Palavras chave: células solares; corantes naturais; TiO_2.

Introduction

In sustainable civilisation energy supply sourced in renewable resources is fundamental. Solar energy offers a huge potential to manage this global demand: Being a decentralized and unlimited natural resource, to illustrate this, the amount of energy reaching the surface of the earth in one hour is more than all energy consumed by humans in an entire year (Lewis & Crabtree, 2005). The sun emits light in a broad spectrum of wavelengths, reaching from the ultraviolet to the infrared. As the light is travelling through the atmosphere, varies light sections are absorbed and do not reach earth's surface. In addition to this total absorption, about 15% of the sunlight will be scattered by molecules and particles before coming to earth. This is referred to as diffuse light, whose ratio increases in higher latitudes and covered sky conditions. For high solar-to-electrical energy conversion efficiencies the absorption spectra of solar cells must be adapted to the characteristic sunlight.

The so far dominant and primarily operating solar cells have been Silicon-based, making them complex and costly in production. Dye-Sensitized Solar Cells (DSSC) is amongst the next generation of solar cells: They promise the prospect of low-cost production and show enhanced performance under diffuse light conditions, when compared to other solar cell technologies. Environmentally beneficial DSSCs imply design opportunities in their shape, colour and transparency. This key concept of "diversity", researching thousands of different dyes yields DSSDs' greatest capacity for future improvements. Basic characteristics and conceptual models were developed by O'Regan and Grätzel (1991). The following years the DSSCs' efficiencies have continued to increase, with a confirmed record of nearly 15% (Burschka et al., 2013).

In addition, potential natural fruits can be used with acceptable efficiency in DSSCs. Their advantage is their availability and low cost. That is especially an interesting energy source in emergent countries near to the equator.

Theoretical Aspects

Photovoltaics

Initially reported by Becquerel in 1839, the photovoltaic effect is the mechanism by which all solar cells function. The process of converting sunlight directly into electricity is referred to as photovoltaic effect. Photovoltaic devices are based on the concept of charge separation at an interface of two materials of different conduction mechanism. Observations demonstrated that voltage could be produced by placing two metal electrodes in a redox electrolyte and irradiating with light. To date, this field has been dominated by solid-state junction devices, usually made of silicon, and profiting from the experience and material availability resulting from the semiconductor industry (Graetzel, 2003).

In a simple way, when incident photons hit the electrodes, some electrons break loose from the delocalized metal framework, leaving a hole behind. As electrons and holes move in opposite directions from one another, a small current is established that can drive a load. This effect was further seen in nearly all solid-state materials of the time. It was not until 1954, however, that an efficient silicon cell, a forerunner of today's silicon technology, was produced by Bell Labs (Bell Labs, 1954). Finally, the most important fundamental property of a photovoltaic absorber is its forbidden band gap. The band gap limits the maximum photocurrent and it is the prerequisite for realizing a photovoltage. That means the photocurrent is limited by the difference between the potential energies at which electrons may be extracted from a solar cell and at which electrons may be transferred back after passing an external load (Dittrich, 2015).

Photovoltaic Generations

Martin Green (2006) has grouped various photovoltaic solar cells in three major categories based on the nature of the material, maximum conversion efficiency obtainable and the associated cost of photovoltaic power.

First Generation Photovoltaics use the highest purity materials with least structural defects. First generation cells are based almost solely on silicon technology. The technology is obviously the most mature, with theoretical efficiencies of 33%, but is hampered by the costs of materials processing. It is estimated that materials contribute to 70% of the total cost of first generation photovoltaics with little room for a decrease in production costs (Bruton et al., 1997). Modern commercial mono-crystalline solar cells produce up to 25% conversion efficiency (Green, 2006).

Second Generation Photovoltaics of thin-film solar cell devices are based on low energy, intensive preparation techniques. Regardless of the semiconductor involved, the thin-film technology offers prospects for a large reduction in material costs. But since it is difficult to prepare systems without defects, maximum power conversion is lower, typically efficiencies <15% (Green, 2006).

Third Generation Photovoltaics refers to cell concepts that can potentially overcome the 33% theoretical upper limit of a single junction solar cell as defined by Shockley and Queisser (1961). The Shockley-Quiesser 33% maximum is only valid for single-junction cells with 1.25 to 1.45 eV bandgaps operating at AM1.5 global conditions. The limit increases dramatically with multi-junction concentrator cells which could theoretically utilize the entire photon energy flux from 0.5 to 3.5 eV (as cited in Abrams, 2005). Since solar cells based on dye sensitization have excellent potential to deliver solar electric power at very low costs, they are referred to as third generation photovoltaics (Friedrich, 2011; Kalyanasudaram, 2010).

Dye-Sensitized Solar Cells. Operational Principles

The organic Dye Sensitized Solar Cell uses vegetables or fruits as sensitizer. The photocurrent generation is based on the same basic principle as plant photosynthesis. Each plant leaf is a photo-chemical cell that converts solar energy into biological material. The chlorophyll in green leaves generate electrons using the photon energy, which triggers the subsequent reactions to complete the photosynthesis process (Khan, 2013).

The conversion of photons to solar energy is based on sensitization of wide bandgap semiconductor, dyes and electrolyte (Graetzel, 2005; O'Regan & Grätzel, 1991). The DSSCs are based on a transparent conducting glass electrode, which is coated with a nanocrystalline semiconductor TiO_2. Dye molecules are attached to semiconductor's surface and an electrolyte containing a reduction-oxidation couple is injected into the DSSCs, as shown in figure 1. At the illumination, the cell produces voltage over and current through an external load connected to the electrodes. The optimization of each of the components is of great importance in order to improve the overall efficiency. All these components have received thorough investigation during the last decades, see for instance (Karlsson, 2011; Khan, 2013).

Parameters of the DSSC

A DSSC is characterized by a variety of experimental parameters, such as the photocurrent *I* and photopotentials *V* which are measured under different conditions, in open and closed circuit (index oc and sc): I_{oc}, V_{oc}, I_{sc}, and V_{sc} (Kalyanasudaram, 2010).

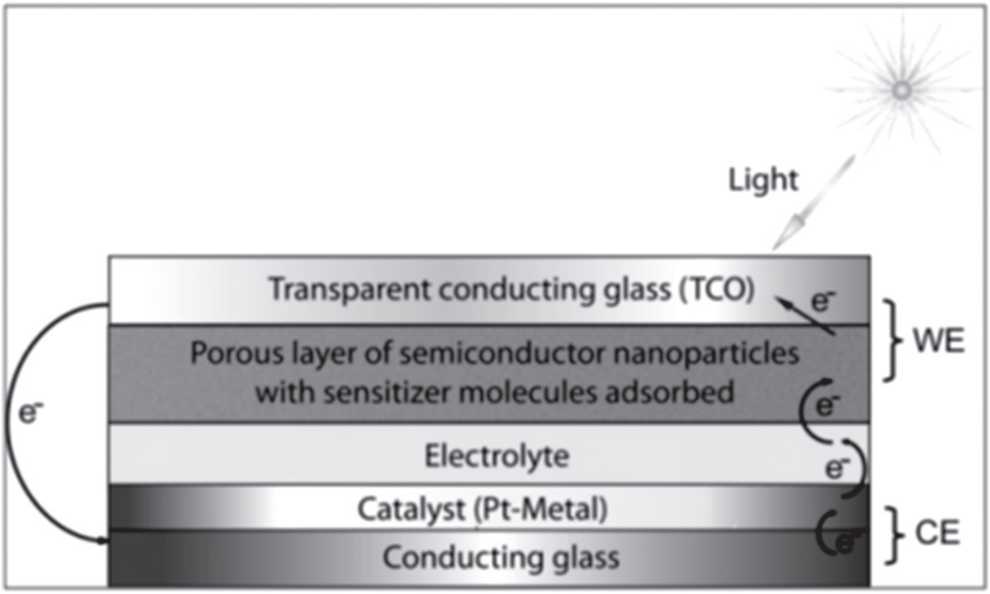

Figure 1. Structure and components of a DSSC.
Source: prepared by the authors.

Open circuit voltage (V_{oc}) and Short circuit current (I_{sc})

The open circuit voltage, V_{oc}, is the difference in potential between the cell's terminals under light illumination when the circuit is open. It is dependent on the gap between the Fermi level of the semiconductor and the redox potential of the electrolyte.

The short circuit current, I_{sc}, is the photocurrent, measured when the illuminated cell is short circuited. Light intensity, light absorption, injection efficiency and the regeneration of the oxidized dye are all factors determining I_{sc}. There is no electric power at short- and open-circuit operation of a solar cell, as either voltage or current vanishes at these points.

For the sake of completeness, open circuit current I_{oc} and short-circuit voltage V_{sc} are enlisted. In following analysis, they are rather circumstantial, as they do not influence other parameters (Karlsson, 2011).

Current-Voltage (I-V) characteristics

The Current-Voltage (I-V) characteristics of a solar cell under illumination are used to determine the Efficiency η. The I-V curves can be obtained by applying a potential scan, from zero voltage (short-circuit conditions) to the open-circuit potential, under constant illumination. They are plots of all possible working points in the considered range. Due to their high capacity, dye-sensitized solar cells have a relatively slow electrical response. For this reason, the voltage scan should be performed sufficiently slowly. From the I-V curve, I_{sc} is determined at the zero voltage measurement point, while V_{oc} is found at the zero current measurement point. The maximum output power of a solar cell is obtained when the product of $|V*I|$ reaches a maximum. At this characteristic point the slope of the I-V curve is highlighted in the following chart, figure 2.

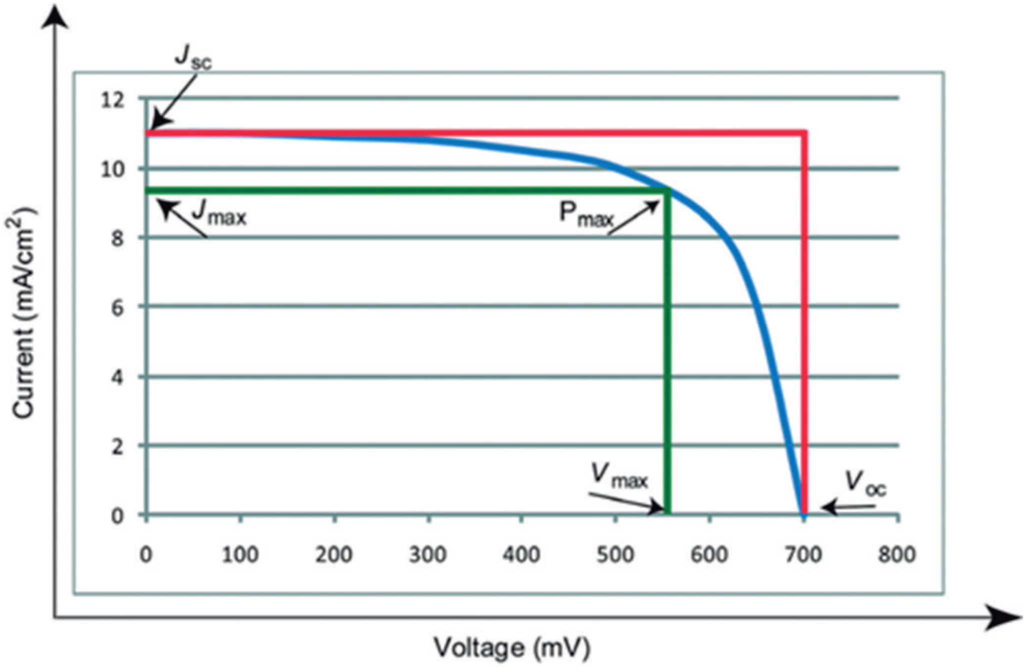

Figure 2. Current-voltage characteristics for solar cells. *Blue line:* measured current-voltage curve. *Red line:* area of $V_{oc} * I_{sc}$. *Green line:* area of $V_{max} * I_{max}$.
Source: Karlsson (2011).

The overall sunlight to electric power conversion efficiency η of DSSC is given by:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{|V * I|_{max}}{P_{in}} = \frac{V_{oc} * I_{sc} * FF}{P_{in}}$$

Whereas refers to the solar power input and FF is defined as the fill factor:

$$FF = \frac{V_{max} * I_{max}}{V_{oc} * I_{sc}}$$

The fill factor is a value between zero and less than one and describes the shape of the I-V curve. A high value indicates a more preferable rectangular shape. A low value indicates high electrical and electrochemical losses of the solar cell, so that the fill factor measures the ideality of the device. In summary, I_{sc}, V_{oc}, FF and η are the key performance parameters of the solar cell (Dittrich, 2015).

Materials

Transparent and Conductive Oxide Substrate (TCO)

The building process of the DSSCs starts with the substrate, which forms the basis of the cell. We used a transparent and conductive oxide substrate (TCO), from Solaronix. This has a resistivity of 8 ohm/sq and is made out of sodalime glass with one-side coated with fluorine-doped (FTO) tin oxide, forming the conductive layer. The Coating ensures optimal adhesion of the TiO_2, an important requirement for the electrode fabrication (Solaronix, 2013).

Half of the glass panes were set apart for the anode, whereas the other half were appropriated for the cathode. For the later injection of the electrolyte into the cell, two holes running through the cathode substrate were required. Hence the glass planes underwent an ample cleaning process including an Ultrasonic bath.

TiO_2

As explained above, the photo-anode consisted of mesoporous layers of titanium dioxide nano-particles on top of the cut and cleaned substrates described above. All layers were stained with Ti-Nanoxide D/SP from Solaronix. It is a diffusing active layer obtained from a mixed titania particle paste. The mixing of large and small nano-particles ensured both very high surface area and light diffusion. TiO_2 was deposited at two different superficial contents: 0.5cm x 0.5cm and 1.0 cm x 1.0 cm. The application process for all samples is called slot-coating or doctor blade.

Once the TiO_2 printing is completed, the samples need to be sintered at a temperature of 450 °C. In prior studies at the laboratory, three layers were found out to be optimal. Once the first layer had been sintered, the second and third prints were applied in identical manners as described above. Samples were labelled with numbers. Each number was scratched onto the anode's non-conductive surface at one the corner of the cell, so that the light transmission wouldn't be hindered.

The Natural Dyes

The last step in the preparation of the anode is the subsidence of the TiO_2 layer into the natural dyes. The photo sensitizer dye is the heart of the operation of the DSSC. The photo sensitizer dye for the cells was extracted from fruits and vegetables that are available in Colombia. All in all, more than 100 cells out of 5 different dyes were built. Different procedures to get the dye solution were used according to the fruit or vegetables. These are: *Bixa orellana* (Achiote), *Vaccinium meridionale* (Agraz), *Bactris guineensis* (Corozo), Blackberry (Mora) and Beet Root (Remolacha) (figure 3). In the following they will be referred to by their native Colombian names, marked in parentheses. Examples of glasses coated with TiO_2 and dyes are shown in figure 4.

Figure 3. Achiote Seeds, Corozo and Agraz Grapes.
Source: prepared by the authors.

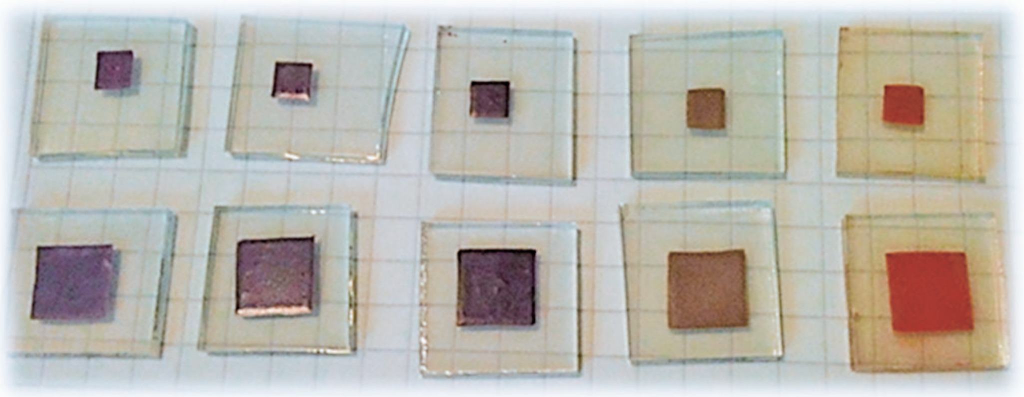

Figure 4. DSSCs soaked into (from left to right) Mora, Corozo, Agraz, Remolacha, Achiote.
Source: prepared by the authors.

Achiote

Achiote is a shrub native to tropical areas of America and mainly known for being the source of the Annatto seeds, containing the carotenoid Bixin. Carotenoids are organic pigments naturally occurring in photosynthetic organisms and are in charge of the blue light absorption in those plants and vegetables (Medina et al., 2016).

Agraz

It is a promising fruit of the family *Ericacease* growing in the Andean highland forests of Colombia. It is known for its high content of anti-oxidant properties and anthocyanin. Anthocyanins are water-soluble pigments, absorbing blue-green and ultraviolet light and thereby naturally protecting the fruit tissues from photo damage (Hernandez, Lobo, Medina, & Cartagena, 2012).

Corozo

Corozo is a wild tropical fruit, promising a source of natural pigments due to its high content of anthocyanins. Anthocyanin, characterized above, was extracted by boiling the fruit in water (Osorio, Carriazo, & Almanza, 2011).

Mora

Mora or Blackberries contain a strongly light-absorbing dye molecule called anthocyanin, which occurs in many types of fruits and berries. It's the compound that gives Mora their colour. Anthocyanin is characterized above (Young, 2013).

Remolacha

The red color of beet roots comes from betalain pigments. Betalains are a class of red and yellow indole-derived pigments found in plants, where they replace anthocyanin pigments (Zhang et al., 2008).

Measurement

The method of choice for determining the efficiency η and the fill factor FF of a cell was running a current-voltage characteristic: In following, the solar cell performance was measured under a halogen lamp and in the sun. Under both conditions a measurement pin was attached to each conducting surface of anode and cathode. Between those pins a Keithley 2400 SourceMeter applied an external voltage onto the cell. The input source was set to voltage and the current safety limit to 10mA. No sample ever exceeded this limit when tested. A solar power meter VOLTCRAFT PL-110SM was used to determine the light input.

To encounter the maximum power the cell's performance has to be analysed within its working interval. For this purpose, a voltage sweep was carried out from – 40mV to 600mV. A linear staircase increase with a power-measurement delay of 0.5s and a step width of 5mV was configured and the resulting cell currents stored for later analysis. The delay between applied voltage and measured current prevented inductive or inertial effects from adulterating the performance analysis. This ensured independent measurement points. The short circuit current could be read out at the zero-voltage-point whereas the open-circuit voltage was retained once the current hit zero Ampere. A Solar Power Meter from Ambient Weather measured the incoming luminance in W/m^2 and the received data was recorded in the lab book. This represented the standard sequence for analysing the cell's performance. They recorded data was entered and analysed in Microsoft Excel using the equations addressed in the theoretic part.

As some samples comprised preparation defects, a full current-voltage scan was not carried out and the performance only characterized through their I_{sc} and V_{oc} values, obtained through a multimeter. I_{sc} and V_{oc} both implied a limit to the maximum power and were efficiently measurable.

To measure the photocurrent spectrum of the individual dye solutions, a UV visible spectrophotometer (Shimadzu UV-2600) was used. It was measured in the range of 250nm-700nm.

Results and Discussion

In following, the cell's performance was analysed depending on the different dyes and TiO_2 surfaces, dye preparation, light sources and power input. Optimizations were developed as well as the DSSCs' longevity was tested.

Different Dyes

The objective in varying the dye type in cell preparation was to find out which dyes yielded the greatest efficiencies when assembled identically. The results of this study can be used to optimize the usage of each dye by developing more individually adapted techniques later on. The cells were first measured under the halogen lamp with an incoming power of 1250 W/m^2. In the curse of the investigation a power input of around 500 W/m^2 was found out to be more like to the sun's input and secondly achieving higher efficiencies as well. Certainly, comparisons could only be reasoned amongst identical power inputs.

The subsequently (figure 5) presented cells were the peak performers of each dye and therefore represented the dyes' potential under best possible preparation procedures.

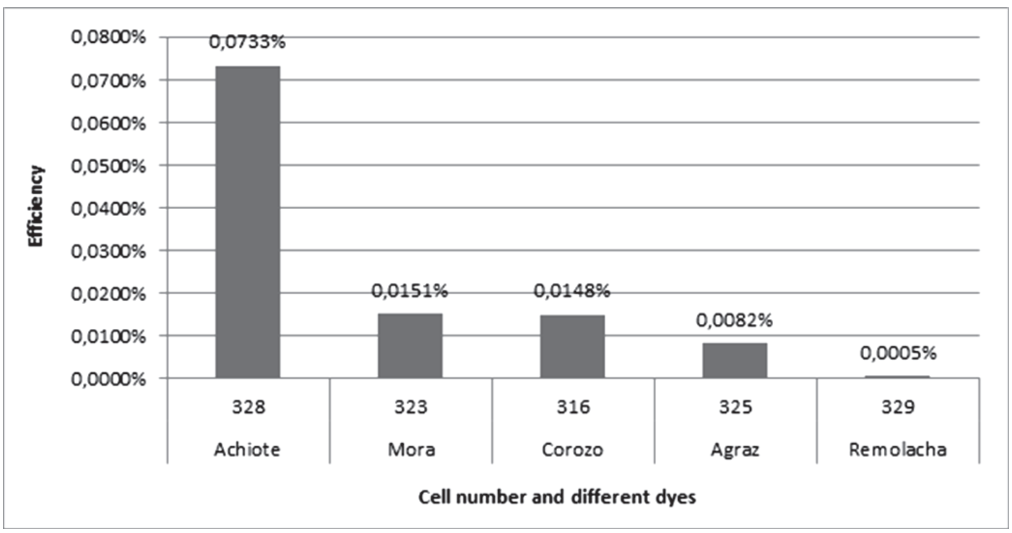

Figure 5. Efficiency of different dyes under halogen light.
Source: prepared by the authors.

The highest performing cell was made from Achiote. Its efficiency of 0.0733% was leading ahead. Almost all DSSCs made from Achiote offered efficiencies that topped the ones of other dyes. Achiote was thus found out to a very powerful dye.

A mid-group, consisting of Mora, Corozo and Agraz, followed the peak performer Achiote. Their efficiencies ranging around 0.01% showed capacity for further usage nevertheless need to be enhanced through better, more explicit or combined manufacturing. Samples from Mora and Corozo broadly yielded very similar results. Their top performers were almost identical: Mora, 0.0151%, leading ahead with a plus of 0.003% when compared to Corozo. The base collective of those two dyes could not be distinguished by their efficiencies. A real power difference yet needs to be worked out. A fusion of Mora and Corozo in future cells would be an interesting part to be investigating in.

Concluding the group of three was Agraz. It only achieved 0.0082% and therefore about half the output of Mora or Corozo. A promising upside of this dye was its potential for improvement in its preparation.

The dye extracted from Remolacha placed last. An efficiency of 0.0005% was far too low, compared to the others cells from this group, however some improvements have been done increasing a bit its performance but still far from Achiote. It was fairly easy to distinguish DSSCs from Remolacha to others as the TiO_2 appeared by far as the brightest after soaking in dye. Of course, as the dye did not soak into TiO_2 properly, the resulting concentration was by far lower than for example using Mora.

In previous studies at the laboratory, derived from published papers like Zhang et al. (2008), the TiO_2 layer was treated with a mix of ethanol and HCl before soaking it into the dye. The measurements could slightly be improved, however the short-circuit current of the dye dropped significantly during illumination. Neither did the circuit recover properly, once the cells were shaded and put aside from the light input.

Compared to the efficiencies obtained in the stated paper Zhang et al. (2008), Remolacha performed poorly. This could be due to more explicit, expensive and complex procedures in Zhang et al. (2008) – extracting the dye from the roots, yielding higher concentrations of light absorbers. At this point, it was questionable, whether an investigation with Remolacha should be continued.

As showed above, differences in performance could be a result of disparities in dye concentration: Some of the prepared juices might have simplified the dyes' adhesion onto the TiO_2 more than others. The absorption spectra of the dye solutions were measured in order to find an explanation for the different efficiencies. As it can be seen in figure 6, the absorption spectra for the different fruits differ. The following analysis will be referring to those results, in particular to figure 6.

It needs to be mentioned, that higher amplitudes of the measured dyes did not directly imply higher rates of absorption. This might have been due to different concentration levels of the dye.

Achiote held the biggest peak width amongst all dyes, consisting of two closely together located peaks at 432.50nm and 455.50nm of wavelength. The core peak sprawled over a band width of over 100nm. It appeared to be a profuse absorber in this region of wavelength. For wavelengths, smaller than the peaks, the absorption spectra of Achiote did not seem to be dropping significantly.

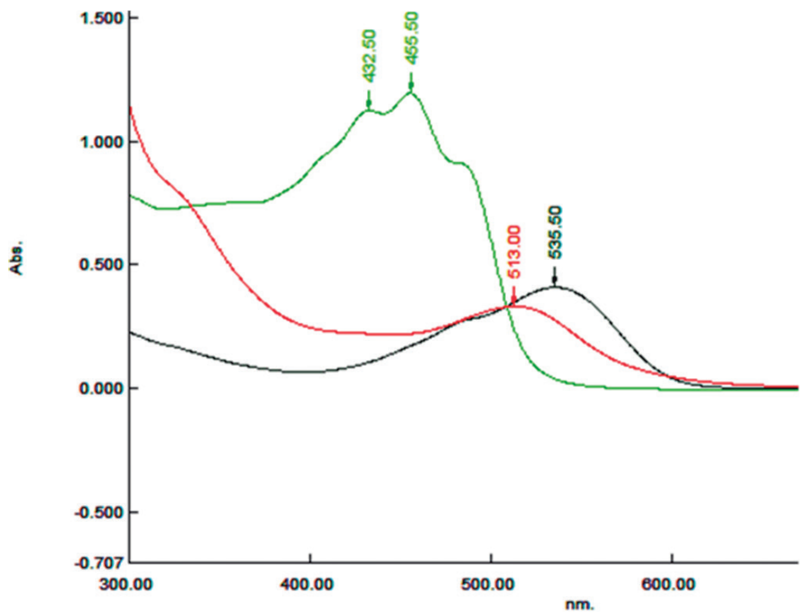

Figure 6. Absorption spectra for Achiote *(green)*, Corozo *(red)* and Remolacha *(black)*.
Source: prepared by the authors.

Corozo showed a smoother absorption curve than Achiote. A low top and gentle peak at 513.00nm of wavelength was followed by a steady increase towards UV. For wavelengths reaching beyond 600.00nm Corozo looked to be absorbing poorly. This low-performance in the infra-red regions could be noticed for Achiote as well.

The absorption curve of Mora was very similar to Corozo. For the purpose of clarity, it was relinquished to demonstrate its trend.

The absorption curve of Remolacha incorporated the most rolling developing. The knoll reached its summit at 535.50 and a steadily declined for both higher and lower wavelengths. It appeared that Remolacha might have been slightly absorbing once again in UV, nevertheless worse than Corozo or Mora.

Relating the absorption spectra to performance of the built solar cells, one might trace Achiote's excellence back to its broad peak. However it needs to be taken into account, that the spectrum of the halogen lamp did not produce much light of a wavelength smaller than 500nm. Therefore the Achiote did not hit the emitter's core spectrum.

In contradiction Mora, Corozo and Remolacha showed far better absorption characteristic above 500nm but worse performances. At this point conclusions might have been drawn too early as broadening and red-shifting was taking place once the dyes had been surfaced onto TiO_2. Further investigations need to be followed into this direction.

As explained above a criterion of losses could be derived from the fill factor. A higher fill factor corresponded to a more ideal power transition. This could be shown in practice (referring to figure 7):

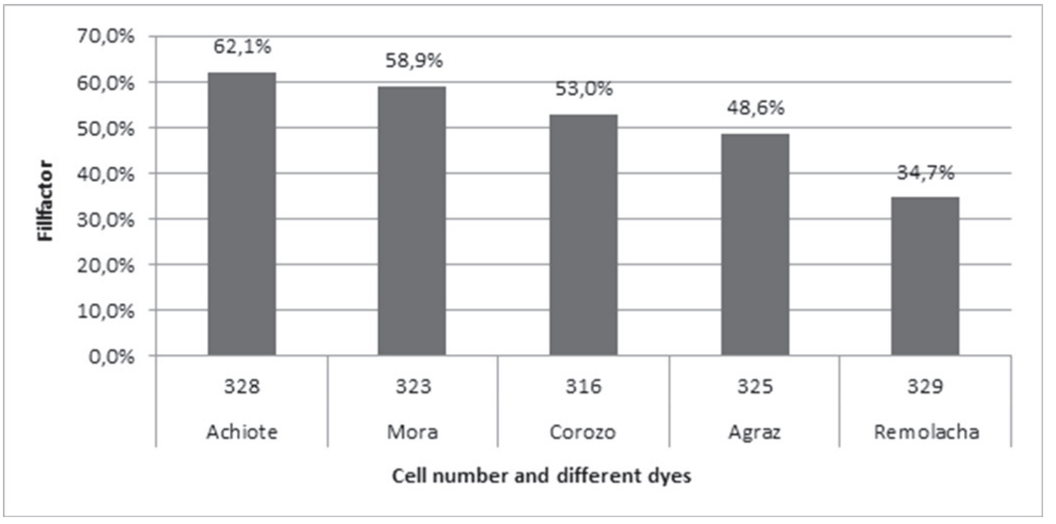

Figure 7. Fill factor of different dyes under halogen light.
Source: prepared by the authors.

The Achiote cell #328 held a fill factor of 62.1%, which was almost twice the fill factor of the Remolacha cell #329. The fill factors of Mora, Corozo and Agraz were linearly distributed between Achiote and Remolacha. An important deduction could be made: Generally, a higher efficiency posed lower losses and therefore a higher fill factor.

In the course of the study it could be shown that the fill factor was a good tool of loss measurement, but should not be used exclusively in determining the performance of a cell. A slight plus in fill factor did not necessarily lead to a power boost. Such counter-examples will be treated further on.

Now it is time to assess the surface's impact onto the efficiency of the solar cell. Here, evaluating the samples, it could be stated that the bigger surface also scored a higher efficiency. This held true for both dyes, Mora and Achiote (figure 8). It might appear that this trend was particularly in force for Achiote, but one has to keep in mind that at the scale presented relative difference for Mora show up diminished.

In previous studies executed in the laboratory, both the fill factor and the efficiency approximately remained the same regardless of the surface area. In this study this applied to the fill factor. The discrepancy of the efficiency yet has to be worked out.

For further analysis of the correlation between fill factor and efficiency, it was particularly interesting to compare the power output of two cells with similar fill factor but different surface and dye. Looking at the presented samples with 1cm^2 of TiO_2 surface in figure 7, their fill factors differed marginally by less than 5%. On the contrary their resulting efficiencies varied heavily (figure 8). One must take into account as well that the cells are of different dyes. That was why, a comparison of identical dyes would reasonable.

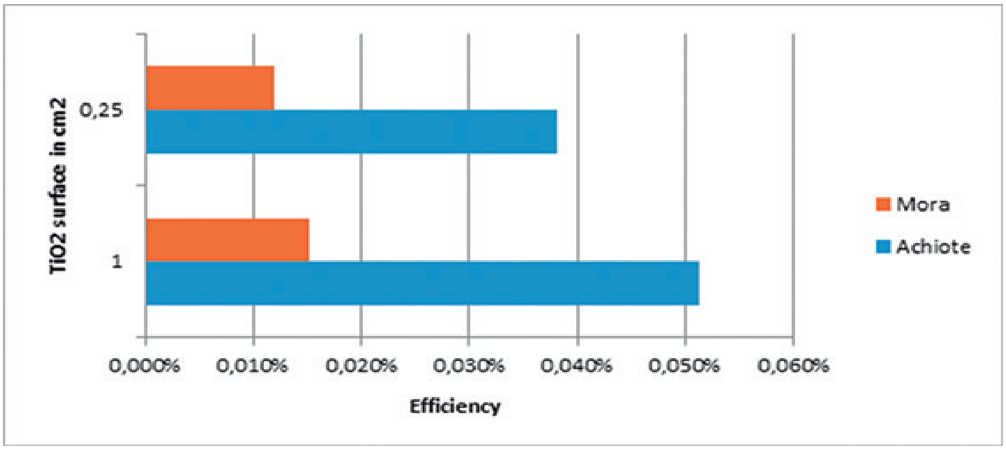

Figure 8. Efficiency changing with TiO_2 surface area and dye.
Source: prepared by the authors.

Power Input

The goal of this experiment was to analyse the working capacity of the DSSCs at several power inputs. Varying the distance between the halogen lamp and the samples regulated the amount of illumination. As the hanger of the lamp was vertically adjustable, the cells' incoming power became a function of height. Nevertheless, in order to achieve greater precision, the luminance was measured at each individual position. The scope of light reached from only diffuse light to high-intensity illumination and therefore all working points could be tested.

In order to obtain the efficiency of a solar cell, one had to execute a current-voltage characteristic. The outcomes are presented in figure 9.

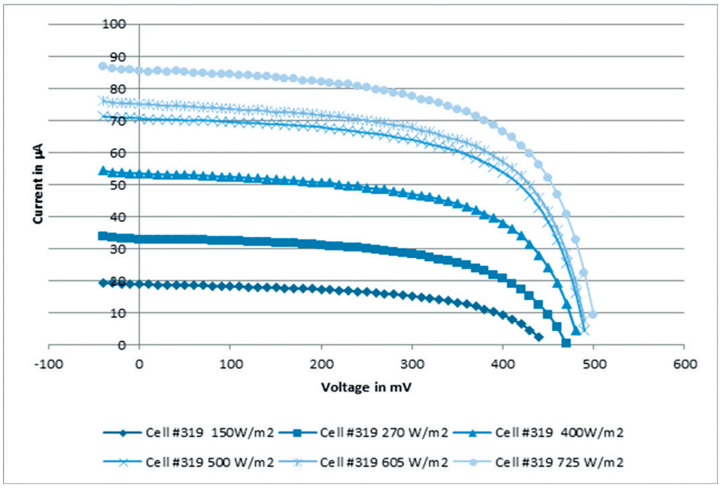

Figure 9. I-V characterization of Achiote #319 for changing power inputs.
Source: prepared by the authors.

The smoothness of some I-V scans appears deformed, as the illustration had been scaled to enfold all power points. Once scaled individually, their shape matched the characteristics of real solar cells with little losses (figure 9).

Subsequently new cells were assembled to carry out a more detailed, peak-oriented power scan. The tested DSSC was #328 and made out of Achiote as well. The sought-after ideal power input should be independent of the individual cell. Of course, dependencies might have been subject to different dyes and were in function of the cell's quality.

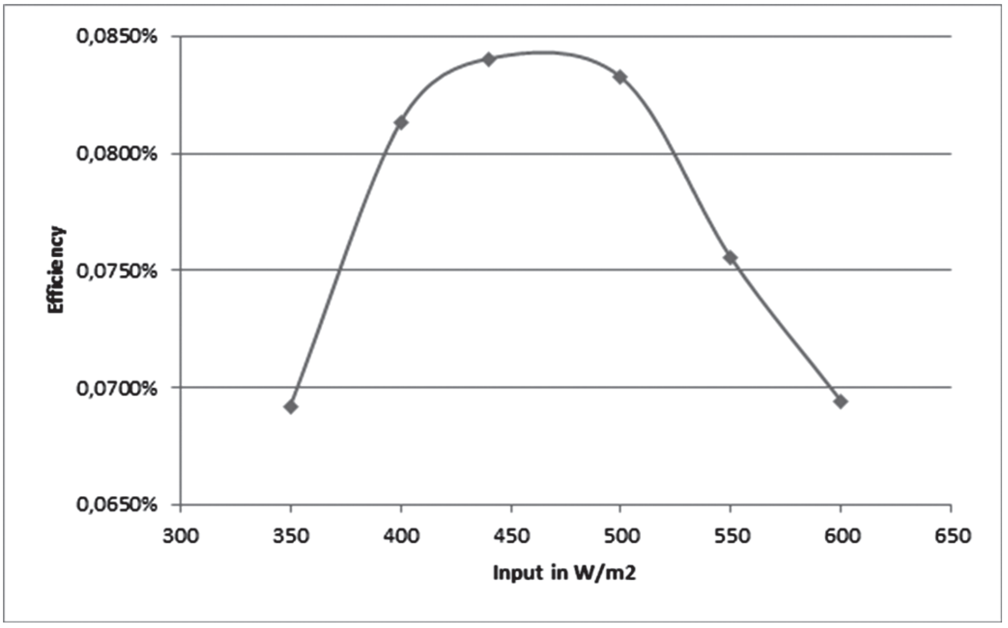

Figure 10. Efficiency of Achiote #328 for changing power inputs.
Source: prepared by the authors.

The power scan of #328, as shown in figure 10, depicted a curve that rather resembled a hood than the before assumed sharp needle peak. To both sides the wide top dropped towards lower levels of efficiencies.

Whereas within a 400 to 500 W/m^2 light input, the efficiency remained at peak performance offering a broad range of excellent application. This fact was very pleasing, as average sun activities alternate around this same scope. It is important to state that the incident solar radiation is highly varying by location and day. For a region, close to the equator, like Barranquilla a daily average solar radiation of 400 W/m^2 could be expected. Which lied within the ideal power input, when measured under the halogen lamp. However, the conditions under sunlight remained different from artificial lighting, which claimed more complex demands.

Measurement under the Sun

Taking the DSSCs out of the laboratory and testing them under the sun performed the ultimate step towards real conditions. The weather at the Caribbean coastline could be very dynamic, making stable illumination a true challenge.

As worked out above, the DSSCs' performances varied with incoming power. Hence the measurements under the sun could only be carried out under blue sky. Clouds would have caused light source altering and in succession falsified the data. Given that longevity and aging up to this point had not been tested sufficiently, the final assembly and the testing of cells had to be performed on the same day.

For those reasons, consistent measurements under the sun posed challenges.

All dyes were conformably to standards analysed by an I-V scan. The sun's power input ranged around 1000 W/m^2 with a deviation of ±10 W/m^2. Once calculating efficiency or fill factors, the altered power value for each DSSC was taken into account. The fluctuation of about 1% in incoming power permitted a comparison of the different dyes. As the halogen lamp posed height adjustable power, all reference measurements were carried out for 1000 W/m^2 light input as well.

Once again, a DSSC made from Achiote scored top efficiency. #339 yielded a 3.4 times higher efficiency when operated under sun than halogen light. Both power inputs were identical, at 1000 W/m^2. Under sunlight the cell topped the I_{sc} of halogen lighting by far. Whereas it was interesting to see that the sun's U_{oc} only increased by merely 5% when compared to halogen measurements.

Measurements shown that the fill factor of sunlight amounted 56.2%, which was mildly lower than 59.1%, for the halogen lamp. This difference in fill factors did not translate to a higher performance under halogen lighting. Quite the contrary, at 400 mV voltage and sunlight measured current for #339 was 0.51 mA. Against it, 410 mV for halogen light only yielded a current of 0.16 mA. These two pairs of values were the maximum power points for sun and halogen light. The sun efficiency of 0.21% for #339 marked the peak value of this study. Under the halogen lamp, the same cell achieved decent but no outstanding 0.062% efficiency.

Conclusions

In the current economic, environmental and social climate, creating a revolutionary low-cost photovoltaic system suitable for large-scale power generation is of utmost urgency. Dye-sensitized solar cells are receiving considerable academic and industrial attention for this purpose, since they promise to convert solar to electrical energy at a fraction of the cost of traditional semiconductor-based photovoltaics.

In the course of this study a variety of different DSSCs were built and tested. The combination of modifying the cells themselves and changing the light input enabled major analysis. The significance and correlation of performance parameters could be monitored under alternant circumstances.

Achiote was found out to be the most promising dye. It achieved maximum efficiencies of all dyes, both under halogen and sunlight. With a halogen efficiency of 0.0733% Achiote lead group of dyes. For these top performers, a higher efficiency came along with a greater fill factor. Taking samples from Mora, Corozo and Agraz into the sun, their efficiencies were more than doubled. Achiote and Remolacha offered even greater improvements: 0.21% efficiency for Achiote and twelve times higher efficiency under sun than halogen light for Remolacha.

The larger 1.00 cm^2 TiO_2 surface area was found out to yield slightly bigger efficiencies than 0.25 cm^2. This trend is likely to dissolve once surfaces are further enlarged. The non-correlation of surface area and efficiency marked a crucial necessity for large-scale application.

Efficiency and fill factor were accounted as the two key parameters. From 40% to 60% fill factors a linear correlation between efficiency and fill factor was discovered. At top performances deviations from this rule of thumb accumulated. Varying the illumination power, the scans showed clearly, that the output was not linear to its input. A halogen lightening between 400 and 500 W/m^2 yielded the greatest efficiencies.

Even though a lot of improvements have been developed, further optimizations still remain to be made. Studying the absorption spectra of the different dyes helped explaining the dyes' output differences. Further spectroscopic analysis of the assembled DSSCs as a whole would be including possible red-shifting effects from TiO_2. Alongside with a solar simulator discrepancies of artificial and outdoor circumstances could be further diminished.

As the dyes' efficiency varied differently with incoming power, a combination of different dyes might be beneficial. It was started in earlier studies and further investigations should be continued. Enlarging the scope of surface area or building a grid of various cells also appears as promising field of studying.

The longevity monitoring revealed a need for better sealing. So far dyes' chemical analysis has not been carried out. It would be beneficial for analysing the decomposing of the dyes over time. New chemical key parameters for longevity testing could be evolved.

Colombia, as any other country, is lacking on a way to produce clean energy. At least it has a high potential of sun energy.

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