Dye-sensitized solar cells using natural dyes extracted from Barbados cherry fruit, Purple shamrock leaves, and Wild snake root fruit

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1. ABSTRACT

This study focuses on the fabrication and characterization of TiO_2 based dye-sensitized solar cells (DSSCs) using three natural dyes extracted from Barbados cherry (*Malpighia emarginata*) fruit, Purple shamrock (*Oxalis triangularis*) leaves, and Wild Snake root (*Rauvolfia tetraphylla*) fruit. Natural dyes offer several advantages over ruthenium based DSSCs, including ease of extraction, low cost, non-toxicity, eco-friendliness, and local availability. DSSCs using Barbados cherry dye achieved an efficiency of 0.936%, while Purple shamrock dye and Wild snake root dye achieved efficiencies of 0.297% and 0.711%, respectively. The highest efficiency of 1.057% was recorded for the DSSCs fabricated with cocktail dye extracted from Barbados cherry and Purple shamrock. While the combination of Barbados cherry and Wild snake root dyes achieved an efficiency of 0.810%. Three natural dyes were characterized using UV-visible spectroscopy and FTIR spectroscopy. This work emphasizes the feasibility of utilizing natural dyes to develop efficient, affordable, and eco-friendly DSSCs, offering a sustainable alternative to photovoltaic technology.

2. INTRODUCTION

Energy is an essential factor driving economies, societies, and environments toward their goals. An energy crisis occurs when energy demand exceeds the available supply. It has increased due to many factors, such as overpopulation, economic development, technological development, a lack of natural resources, and modern lifestyles.

The global energy landscape heavily depends on fossil fuels such as coal, oil, and natural gas. These resources cause environmental pollution and release greenhouse gases when burned. Moreover, the natural processes that generate fossil fuels take millions of years, far exceeding the rate at which humans extract and consume them. As the supply of fossil fuels is limited and non-renewable, there is an increasing interest in sustainable and renewable energy sources like solar, wind, and hydropower.

Solar energy is a viable and practical alternative for supplying energy demands among all renewable energy sources. It can be used in different technologies known as solar photovoltaics, solar thermal power generators, solar water heating, solar photochemistry purposes, and solar space heating and cooling systems. As a renewable resource, solar energy is naturally replenished and offers a sustainable and environmentally friendly solution. Its utilization significantly reduces greenhouse gas emissions, thereby mitigating climate change and contributing to a cleaner and more sustainable energy future.

Alexandre Edmond Becquerel discovered the photovoltaic effect, which emphasizes electricity production from sunlight in 1839 [1]. Photovoltaic (PV) cells convert sunlight into electrical energy through the photovoltaic effect. The dye-sensitized solar cell (DSSCs) is classified as a third-generation solar cell [2,3]. Compared to conventional silicon-based solar cells, which are expensive and labor-intensive to manufacture, DSSCs are relatively inexpensive and simple to produce.

Synthetic inorganic and organic dyes, as well as natural dyes, are commonly used in DSSCs as dye sensitizers. Most inorganic dyes consist of metal complexes, such as ruthenium, osmium, and copper. The efficiency of DSSCs based on ruthenium complexes is 12.3%, while the lab-scale power conversion efficiency (PCE) has reached 14.3% [4]. Natural dyes are frequently selected for use in DSSCs because they are renewable, biodegradable, non-toxic, and cost-effective [5,6]. On the contrary, natural dyes offer several advantages in comparison to metal complexes. These benefits include ease of extraction with minimal chemical procedures, large absorption coefficients, low cost, non-toxicity, environmentally friendly nature, easy biodegradability, and wide availability [7]. However, their efficiency and stability can vary significantly depending on the dye and operating conditions. Consequently, natural pigments such as anthocyanins, carotenoids, and chlorophylls have been widely utilized as sensitizers in DSSCs [8-10].

3. METHODOLOGY

3.1 Preparation of natural dye sensitizers

Figure 1: The photographs of a) Barbados cherry fruits, b) Wild Snake Root fruits and c) Purple shamrock leaves

Barbados cherry (*Malpighia emarginata*) fruit, Purple shamrock (*Oxalis triangularis*) leaves, and Wild snake root fruit (*Rauvolfia tetraphilla*) were used to extract three natural dyes. To eliminate any contaminants, the fruits and leaves were thoroughly washed, and dried. The seeds were removed from the Barbados cherry and Wild snake root fruits before they were measured and ground. Purple shamrock leaves were also measured and cut into small pieces before grinding. Then, 40 mL of distilled water was added to 7 g of each ground material at room temperature. A series of mixed dyes was also prepared with varying ratios of Barbados cherry dye. The mixtures were then sonicated for 30 minutes using an ultrasonic bath sonicator.

3.2 Preparation of TiO_2 electrode (photoanode) and counter electrode

The FTO glass substrates were subjected to a thorough cleaning process to remove any organic or inorganic contaminants from their surfaces. They were boiled in an isopropyl alcohol solution at 80 ℃ to eliminate residual organic contaminants. The cleaned glass slides were then dried and prepared for deposition. The TiO_2 paste was prepared by grinding 0.5 g of Degussa P25 TiO_2 powder with 1 ml of 0.1 M HNO_3 in a porcelain mortar for 5 minutes. The resulting mixture underwent a further 45-minutes processing period, during which 1 ml of 0.1 M HNO_3, two drops of Triton-X-100, and two drops of PEG-4000 were added. Then the glass stand was heated using a hot plate to a temperature of 40 ℃ before FTO glass slides were carefully positioned on it. Then, prepared paste was applied on the FTO glass using the doctor blade method. Whereas, an adhesive tape layer was placed over the two edges of the FTO glass plate to mask the electrical contact strips and regulate the film thickness. The coated FTO glass slides were sintered in a furnace at 450 ℃ for 45 minutes to ensure proper adhesion and stabilization of the TiO_2 layer.

3.3 Preparation of the Electrolyte

A 10 ml volumetric flask was filled with 0.83 g of Potassium iodide (KI) and 0.127 g of iodine (I_2). Then it was added with a solution that contained acetonitrile (CH_3CN) and ethylene carbonate ($(CH_2O)_2CO$) in an 8:2 ratio. After that, the magnetic stirrer was used to thoroughly mix the solution for 5 hours until all the solid components had completely dissolved for 5 hours [11].

3.4 Dye adsorbance to Photoanode

For each dye 2.5 ml was pipetted into separate test tubes. A set of TiO_2 thin films on FTO glass substrates was immersed in dye samples prepared from Barbados cherry, Purple shamrock, and Wild snake root for a soaking duration of 3 hours. Cocktail dye samples were made by mixing different volumes of Barbados cherry and Purple shamrock dye (dye X) as well as Barbados cherry and Wild snake root dye (dye Y). Each solution was subjected to ultrasonication for 5 minutes before the dipping process. Then the photoanodes were dipped in the dye solutions for the dye adsorbance process for 3 hours.

3.5 Assemble of the cell

In the current study, platinum (Pt) nanoparticle sputtered FTO glass was used as the counter electrode. During the DSSCs assembling process, the cell was connected by placing the dye-adsorbed photoanode on the counter electrode, which was slightly offset to make space for the crocodile clips. Finally, the electrolyte was carefully filled between the two electrodes using a micropipette to develop complete DSSC.

3.6 Characterization and measurements

Extracted natural dye samples were optically characterized using a UV-Vis spectrometer and FTIR spectroscopy. Photovoltaic measurements of the fabricated DSSCs were performed under an irradiance of 1000 W/m² (AM 1.5) using a white LED light source, a PV power analyzer, and VK-PA-100 software.

4. RESULTS AND DISCUSSION

4.1 Natural dye characterization

4.1.1 Absorbance Spectra for Natural Dyes

Figure 2 shows the UV-Vis spectra of the three extracted dyes, recorded within the wavelength range of 370-1100 nm. Maximum absorption peaks were observed at 500 nm for Barbados cherry (BC) fruit, 450 nm for purple shamrock (PS) leaves, and 520 nm for wild snake root (WSR) fruit. A typical UV-visible spectrum of anthocyanin exhibits two characteristic absorbance regions: one at 260–280 nm in the UV region and another at 490 nm–550 nm in the visible region [12]. The absorbance peaks for purple shamrock and Barbados cherry can be attributed to the presence of anthocyanins. S.P. Vinay et al. reported that alkaloids exhibit maximum absorbance at approximately 535 nm [13]. Therefore, the observed peak for wild snake root dye evident due to the presence of alkaloids, anthocyanins, or both. However, the pigments of wild snake root fruit have not been extensively studied in the literature. Further investigations are recommended to understand the nature of the pigments in this species.

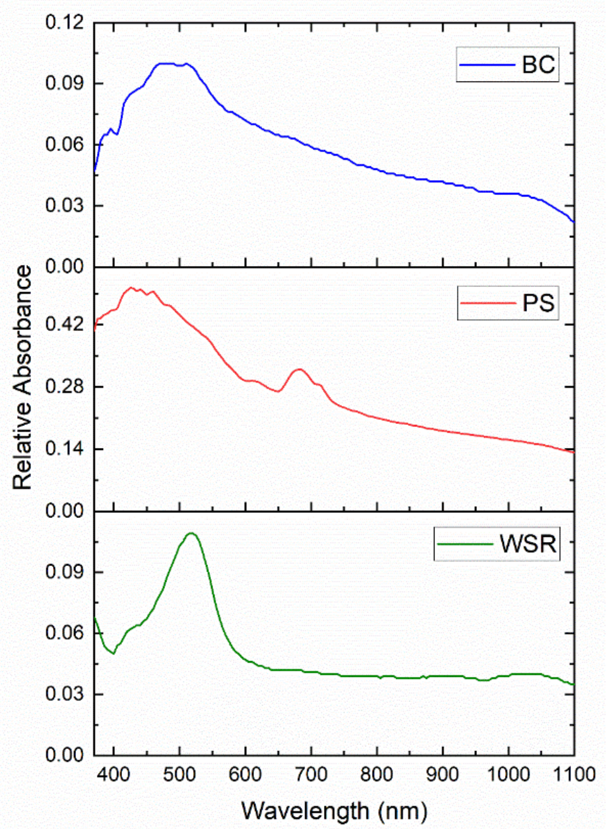

Figure 2: The UV-visible spectra for the natural dyes of Barbados cherry (BC) fruit, purple shamrock (PS) leaves, and Wild Snake Root (WSR) fruit.

4.1.2 Tauc Plots

The bandgap energies for the three natural dyes were determined from Tauc plots obtained from UV-Vis spectral data, as shown in Figure 3.

$$(\propto \mathrm{hv})^{\mathrm{n}} = \mathrm{A}(\mathrm{hv} - \mathrm{E_g})$$

$$\propto = \frac{4\pi\mathrm{k}}{\lambda}$$

Where A= Constant, hv is the photon energy, $\propto$ is an absorption coefficient, k is the absorbance, and Eg is the band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the dye molecules. The bandgap energy corresponds to the minimum photon energy necessary for the excitation of an electron from the HOMO to the LUMO, resulting in the generation of an electron-hole pair within the dye molecules. Corresponding n values are n = 2 and n =1/2 for direct band gap and indirect band gap. Since dyes have a direct band gap, n was taken to be equal to 2, and the band gap energy was determined using the Tauc plot drawn $(\propto \mathrm{hv})^2$ vs $A\mathrm{hv}$. The calculated bandgap energy values for Barbados cherry, Purple shamrock, and Wild snake root dye were 2.01 eV, 1.93 eV, and 2.14 eV, respectively. Various factors, including solvent effects, molecular structure, and the presence of impurities can influence these bandgap energy values.

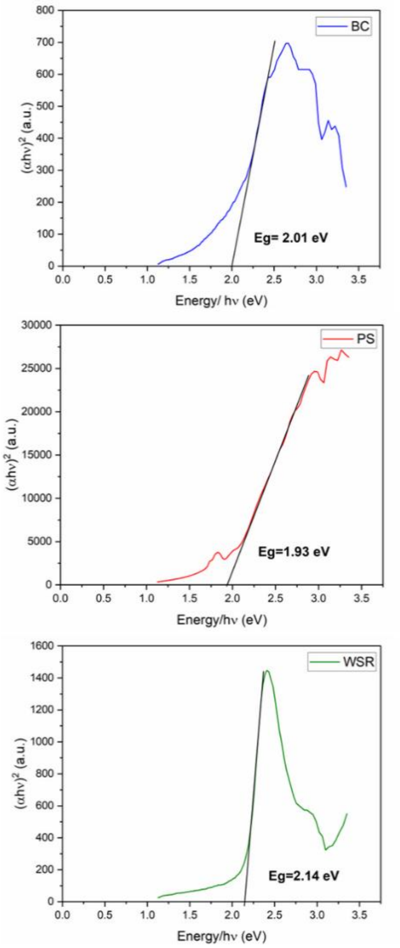

Figure 3: The Tauc plot for the band gap energy of Barbados cherry (BC) fruit dye, Purple shamrock (PS) leaves and Wild Snake Root (WSR) fruit dye.

4.1.3 FTIR spectra

Figure 4 shows the FTIR transmittance spectra for the three dyes The FTIR spectra were recorded in the range of 400 to 4000 cm^{-1} to characterize the functional groups in the natural pigments. For the Barbados cherry dye, a prominent band at 3296 cm^{-1} is attributed to O-H (hydroxyl) stretching vibrations, while a broad absorption band between 3570 and 3200 cm^{-1} indicates the presence of various hydrogen bonding interactions. The band at 1369 cm^{-1} corresponds to C-H (alkyl) bending vibrations, and the peak at 1612 cm^{-1} is characteristic of C=O (carbonyl) stretching vibrations.

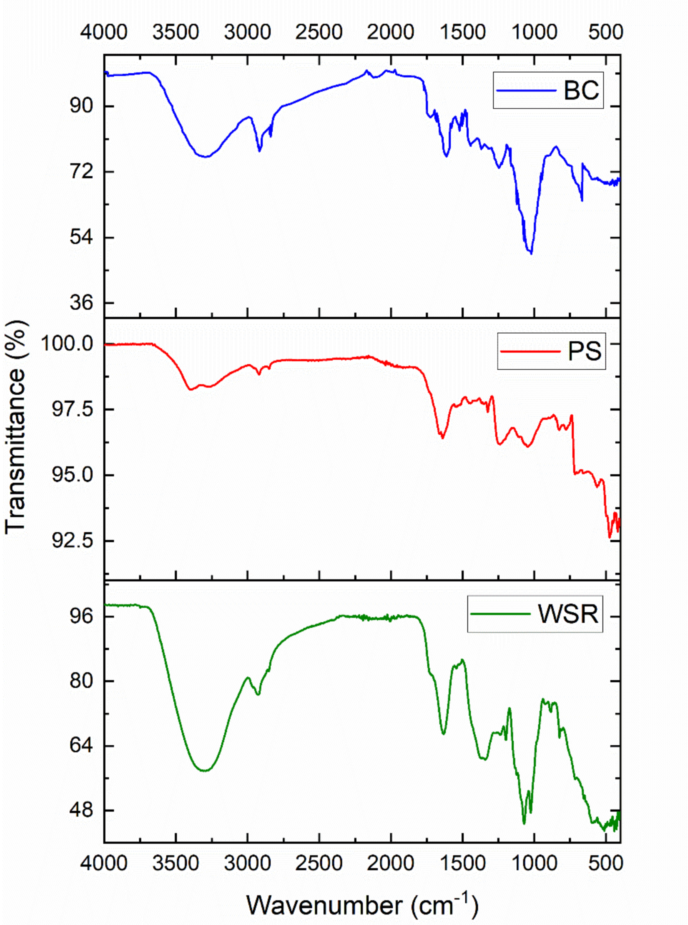

Figure 4: The FTIR transmittance spectra of the three natural dyes extracted from Barbados cherry (BC) fruit, purple shamrock (PS) leaves, and Wild Snake Root (WSR) fruit, recorded in the range of 400–4000 cm^{-1} to identify functional groups in the pigments. Key functional groups include O-H (hydroxyl), C=C (alkene functional group), C-H (alkyl), C-O-C (ether functional group), which contribute to the dye's interaction with the TiO_2 surface in DSSCs

In the purple shamrock dye, a strong band at 3399 cm^{-1} is observed, which is characteristic of O-H stretching vibrations. The band at 1638 cm^{-1} is assigned to C=C stretching vibrations, while the peaks at 1071 cm^{-1} and 563 cm^{-1} are attributed to C-O-C stretching and C-H bending vibrations, respectively [14]. Based on the spectral features, the wild snake root dye can be classified as anthocyanin. Specifically, the strong band at 3394 cm^{-1} is attributed to O–H stretching, while the band at 2925 cm^{-1} corresponds to C–H stretching. The band at 1632 cm^{-1} is associated with the N–H bond and is likely due to the amide-I bond of proteins present in the extract. Additionally, the band at 1365 cm^{-1} corresponds to O–H bending, and the band at 1071 cm^{-1} is attributed to C–O–C bonds. Previous studies by Vinay et al. on Wild sake root roots have reported peaks in the 1389-1123 cm^{-1} region, which were attributed to N-O symmetric stretching vibrations, characteristic of nitro compounds [13]. However, since this study focuses on fruit extracts, the presence and nature of chemical bonds may differ. The presence of O-

H groups in the pigment molecules of all three dyes suggests a potential role for these groups in anchoring the pigments to the TiO_2 photoanode.

4.2 J-V Characteristic for the solar cell

Table 1 compares different property parameters of DSSCs using various natural dyes, including short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and energy conversion efficiency (η). The current-voltage curves of the DSSCs for three dyes are shown in Figure 5. The highest photovoltaic efficiency of 1.057% was obtained for Barbados cherry and purple shamrock mixture for a 3-hour dipping time. As shown in Table 1, solar cells fabricated using purple shamrock dyes were not shown significant performances. The DSSCs fabricated from Barbados cherry and purple shamrock dyes showed better performance.

Table 1: Photoelectrochemical properties of solar cells with natural extracts including open circuit photovoltage (V_{OC}), short circuit photocurrent density (J_{SC}), Fill factor (FF), and power conversion efficiency (η). The dyes used are Barbados cherry (BC) fruit, purple shamrock (PS) leaves, Wild Snake Root (WSR) fruit, Barbados cherry and Purple shamrock mixed dye (X) as well as Barbados cherry and Wild snake root mixed dye (Y).

Dye	V_{OC} (mV) ± 0.1	J_{SC} (mA cm^{-2}) ± 0.001	FF (%)	η (%) ± 0.001
BC	429.2	4.258	51.2	0.936
PS	355.0	1.532	54.7	0.297
WSR	419.4	3.116	54.4	0.711
X	433.9	4.843	50.3	1.057
Y	407.6	4.877	40.7	0.810

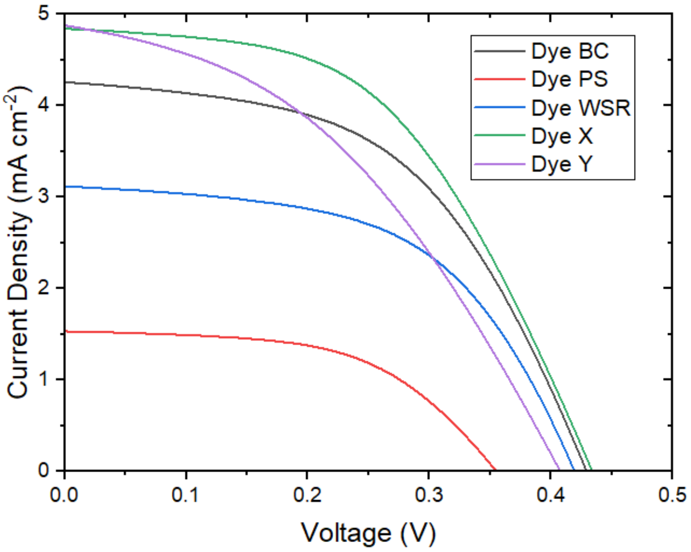

Figure 5: Photoelectrochemical properties of solar cells with natural extracts from Barbados cherry (BC) fruit dye, purple shamrock (PS) leaves, Wild Snake Root (WSR) fruit, Barbados cherry and Purple shamrock mixed dye (X) as well as Barbados cherry and Wild snake root mixed dye (Y).

5. CONCLUSION

This study highlights the use of natural dyes extracted from Barbados cherry fruit, purple shamrock leaves, and Wild Snake Root fruit as photosensitizers for DSSCs. The DSSCs fabricated using Barbados cherry dye was recorded with an efficiency of 0.936%, while purple shamrock dye and Wild Snake Root dye achieved efficiencies of 0.297% and 0.711%, respectively. The mixture of Barbados cherry and purple shamrock dye achieved an efficiency of 1.057% and the Barbados cherry and Wild Snake Root dye mixture achieved an efficiency of 0.810%. The UV-vis spectra of the dyes exhibited characteristic peaks indicative of anthocyanin presence. FTIR analysis of the natural dye extracts provided strong evidence for the presence of functional groups, including hydroxyl and carboxyl, within the extracted natural pigments. These function groups were directly involved to the strong dye attachment on TiO_2 in DSSCS. These natural dyes offer a compelling alternative for sensitizing DSSCs because of reduced manufacturing costs, enhanced flexibility and transparency and simplified assembly. While the cell efficiencies achieved with these natural dyes are below the requirements for large-scale commercialization, significant potential exists for further optimization and improvement in their performance.

6. REFERENCES

[1] A. E. Becquerel, “Recherches sur les effets de la radiation chimique de la lumiere solaire au moyen des courants electriques,” Comptes Rendus de L’Academie des Sciences, vol. 9, pp. 145–149, 1839.

[2] W. Maiaugree et al., “A dye sensitized solar cell using natural counter electrode and natural dye derived from mangosteen peel waste,” Sci Rep, vol. 5, Oct. 2015.

[3] B. O’Regan and M. Grätzel, “A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films,” Nature, vol. 353, no. 6346, pp. 737–740, 1991.

[4] N. Tomar, A. Agrawal, V. S. Dhaka, and P. K. Surolia, “Ruthenium complexes based dye sensitized solar cells: Fundamentals and research trends,” Sep. 01, 2020.

[5] Bhargava C. and Sharma P., “Use of natural dyes for the fabrication of dye-sensitized solar cell: A review,” 2021, Polska Akademia Nauk.

[6] G. Richhariya, A. Kumar, P. Tekasakul, and B. Gupta, “Natural dyes for dye sensitized solar cell: A review,” 2017.

[7] Sharma K., Sharma V., and Sharma S. S., “Dye-Sensitized Solar Cells: Fundamentals and Current Status,” Nanoscale Res Lett, vol. 13, Dec. 2018,

[8] W. A. Ayalew and D. W. Ayele, “Dye-sensitized solar cells using natural dye as light-harvesting materials extracted from Acanthus sennii chiovenda flower and Euphorbia cotinifolia leaf,” Journal of Science: Advanced Materials and Devices, Dec. 2016.

[9] R. Fernando and G. K. R. Senadeera, “Natural anthocyanins as photosensitizers for dye-sensitized solar devices Developing novel polymer electrolyte and TiO2 and SnO2 based novel photo-anodes View project Preparing an innovative type of TiO2 photoanode consisting of Rice grain shaped TiO2 nano structure View project,” Curr Sci, vol. 95, pp. 663–666, 2008.

[10] F. Gandía-Herrero and F. García-Carmona, “Biosynthesis of betalains: Yellow and violet plant pigments,” Jun. 2013.

[11] Wickramasinghe G. C., Jayathilaka D.L.N., and Perera V.P.S., “Construction of Dye Sensitized Solar Cell Using Natural DyeExtraction from Petals of ErabaduFlower,” OURS, pp. 523–526, 2017.

[12] S. Saha, J. Singh, A. Paul, R. Sarkar, Z. Khan, and K. Banerjee, “Anthocyanin Profiling Using UV-Vis Spectroscopy and Liquid Chromatography Mass Spectrometry.,” J AOAC Int, vol. 103, no. 1, pp. 23–39, Jan. 2019

[13] S. P. Vinay, Udayabhanu, G. Nagarju, C. P. Chandrappa, and N. Chandrasekhar, “Enhanced photocatalysis, photoluminescence, and anti-bacterial activities of nanosize Ag: green synthesized via Rauvolfia tetraphylla (devil pepper),” SN Appl Sci, vol. 1, no. 5, May 2019.

[14] S. Jeyaram and T. Geethakrishnan, “Vibrational spectroscopic, linear and nonlinear optical characteristics of Anthocyanin extracted from blueberry,” Results in Optics, vol. 1, Nov. 2020.