10 μg of Mo^{6+}. The leaf powder is stable indefinitely if kept in dry condition at room temperature.

Several other plant extracts were tested qualitatively to record colour reaction with molybdenum, similar to *jambolanum.* Chemical components of leaves are known to vary due to factors like variety, climate, soil, competition, disease, etc. Therefore, the same batch of reagents should be used for preparing the calibration curve and analysis of samples. Table 3 lists other plant extracts that gave similar colour reaction as *S. jambolanum.* Therefore, it may be concluded that compounds responsible for the colour reaction are widely distributed. The *S. jambolanum* extract gave a deep purple colour with ferric iron, lemon yellow colour with titanium and a bluish colour with vanadate ion. A compound like quercetin or tannic acid may be involved in colour development.

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Fruit extract dyes as photosensitizers in solar cells

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Two natural dyes containing anthocyanin are extracted from sour and sweet pomegranate from Iran. Spectrophotometric evaluation of the natural dyes in solution and on a TiO_2 substrate was carried out to assess changes in the status of the natural dyes. The results show that the natural dyes indicate buthochromic shift on the TiO_2 substrates. Dye-sensitized solar cells (DSSCs) are fabricated to determine the photovoltaic behaviour of each dye and the mixture of extracts. Such evaluations demonstrate conversion efficiencies of 0.73%, 1.57% and 0.91% for sour pomegranate, sweet pomegranate and mixed extract respectively. Natural dyes are suitable alternative photosensitizers for DSSCs.

Keywords: Anthocyanin, conversion efficiencies, dye-sensitized solar cells, natural dye.

DYE-SENSITIZED solar cells (DSSCs or Grätzel cells) have become an attractive and low-cost technology for the conversion of solar light into electrical energy[1]. The performance of the solar cells depends on the structure of dye used as photosensitizer[2]. Inorganic complexes have shown good conversion efficiency in DSSCs when

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adsorbed on TiO_2 nanoparticles[3], but this process to synthesize the inorganic complexes is complicated and expensive[2]. However, natural dyes are usually utilized poorly in DSSCs because of low charge transfer absorption in the visible spectrum, but these dyes are low cost and availability, compared to ruthenium polypyridyl complex[4,5]. In nature, the fruits, flowers and leaves of plants display a range of colours from yellow to violet and various natural dyes which can be extracted by simple procedure and utilized as suitable photosensitizers[1,6]. Anthocyanins belong to the major group of natural dyes responsible for cyanic colours ranging from salmon pink through red and violet to dark blue of most flowers, fruits and leaves[7,8]. Sometimes, they are present in other plant tissues such as roots, tubers and stems[9]. Carbonyl and hydroxyl groups present in the anthocyanin molecules can be bonded to the surface of a porous nano anatase TiO_2 substrate. This band makes injection excitation electron from anthocyanin molecule to the conduction band (CB) of TiO_2 (refs 1, 2). Polo *et al.*[10] utilized the natural dyes based on anthocyanin as sensitizer in DSSCs and achieved up to $\eta = 1.5\%$ for jaboticaba extract and $\eta = 0.95\%$ for calafate extract. Nishanta *et al.*[11] fabricated DSSCs with natural dye based on anthocyanin and found $\eta = 0.38\%$ for *Kopsia flavida* fruit.

In the present study, two natural dyes containing anthocyanin have been extracted from sour and sweet pomegranate grown in Iran, as photosensitizers on porous nano anatase TiO_2 substrate. The spectrophotometric properties of the natural dyes in solution and on the nano anatase TiO_2 substrate were examined. The absorption maxima and intensity of the resultant natural dyes were also obtained. Finally, DSSCs were fabricated utilizing these natural dyes and a mixture of extracts and their photovoltaic behaviours were determined.

The samples of pomegranate used in this study were obtained from 7-year-old pomegranate tree grown in Iran. The sour and sweet pomegranate have been grown in Behshahr and Saveh in the north and central Iran respectively. The samples of pomegranate were collected at random from natural source. They were harvested during the 2014 growing seasons. UV–visible spectrophotometry was carried out on a Cecil 9200 double beam transmission spectrophotometer.

Fresh pomegranate weighing 1 g was extracted in 100 ml water at 50°C for 15 min. Solid residues were filtrated out to obtain clear dye solutions. A mixed dye was prepared by mixing sour and sweet pomegranate solutions in the ratio 1 : 1 by volume.

TiO_2 nanoparticles were obtained commercially from Nanomahan Company in Iran. An organic paste containing TiO_2 nanoparticles, a binder and a solvent was printed on conducting glass substrates (FTO glass) by doctor blading, followed by heating in a hot-air stream at 350°C for 30 min. Then, 50 mM aqueous solution of $TiCl_4$ was slowly dropped onto the TiO_2 films and kept at 25°C for 20 h, followed by calcining at 450°C for 30 min in air. The natural dyes were adsorbed by dipping the coated glass for 18 h in aqueous solution of each dye. Finally, the film was washed with an anhydrous ethanol. The iodide electrolyte solution (0.5 M potassium iodide mixed with 0.05 M iodine in water-free ethylene glycol) was used as an electrolyte. The dye-adsorbed TiO_2 electrode, the Pt counter electrode and the electrolyte solution were assembled into a sealed sandwich-type solar cell[12,13].

An action spectrum was measured under monochromatic light with a constant photon number (5×10^{15} photon cm^{-2} s^{-1}). *J–V* characteristics were measured under illumination with AM 1.5 simulated sunlight (100 mW cm^{-2}) through a shading mast (5.0 mm × 4 mm) using a Bunko-Keiki CEP-2000 system.

Anthocyanins are the most abundant of natural dye that adsorb light at the longest wavelength[5]. They often exist in fruits, flowers and leaves of plant[1]. Figure 1 shows the molecular structure of anthocyanin. Carbonyl and hydroxyl groups present in the anthocyanin molecules can be bonded to the surface of a porous nano anatase TiO_2 substrate. This link makes injection excitation electron from anthocyanin molecule to the CB of TiO_2 (ref. 1).

Anthocyanin compounds exhibit a wide band in the UV-visible region of the spectrum due to charge transfer transition[14]. The wavelength of maximum absorption (λ_{max}) and the molar extinction coefficients (ε_{max}) for the two natural dyes in solution are listed in Table 1 and shown in Figure 2, together with λ_{max} of the corresponding dyes adsorbed on TiO_2 films.

Upon dye adsorption onto a TiO_2 surface, the wavelength of maximum absorption is bathochromically shifted by 9 and 7 nm for sour and sweet pomegranate respectively, as compared to the corresponding spectra in solution. Chemical adsorption of these natural dyes is due to alcoholic bound protons which condense with the hydroxyl groups present at the surface of nanostructured TiO_2 film. Their binding can be increased by the chelating effect to the Ti(IV) ions[10]. The attachment to the TiO_2 surface affirms the exited state, and thus the shift toward the lower energy of the absorption maximum[10,15]. The

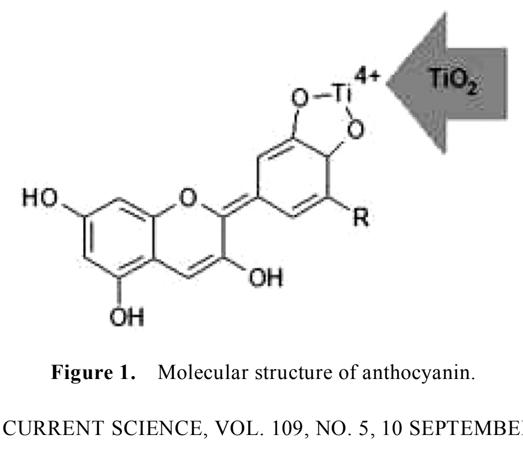


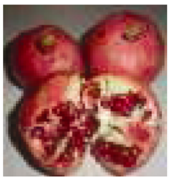
Figure 1. Molecular structure of anthocyanin.

molar extinction coefficients of sour and sweet pomegranate extract in solution at their respective λ_{max} are also shown in Table 1, indicating that these natural dyes have good light-harvesting abilities[16].

DSSCs are constructed and compared to clarify the relationship between the sensitizing behaviours of natural dye molecules. The DSSCs utilized these natural dyes as sensitizers for nanocrystalline anatase TiO_2. Figure 3 presents a schematic diagram of the solar cell. Figure 4 shows a typical photocurrent–photovoltage (J–V) curve for the cells based on natural dyes and a mixture of extract. Table 2 presents the detailed photovoltaic parameters of DSSCs in terms of short-circuit photocurrent (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and conversion efficiency (η).

Table 2 shows that under the standard global AM 1.5 solar condition, the conversion efficiencies of cells containing sour pomegranate, sweet pomegranate and the mixed extract are 0.73%, 1.57% and 0.91% respectively.

Table 1. Absorption of natural dyes

Natural dye source	λ_{max} (nm) (in solution)	ε (M^{-1} cm^{-1})	λ_{max} (nm) (on TiO_2)
Sour pomegranate 	511	24,887	520
Sweet pomegranate 	529	26,661	536

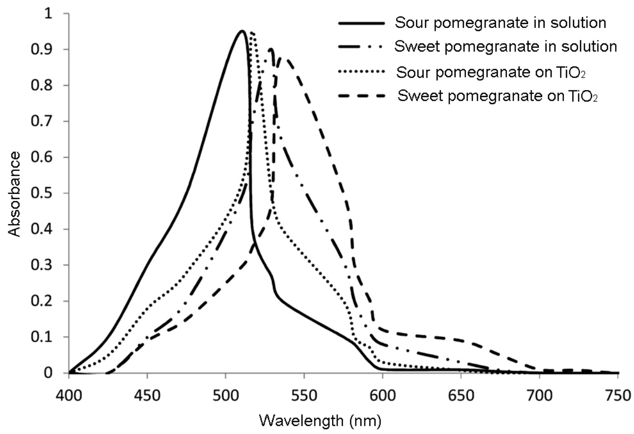


Figure 2. UV–Vis absorption spectra for natural dyes.

The larger conversion efficiency of sweet pomegranate extract sensitizer is probably due to higher intensity and broader range of light absorption of the extract on TiO_2, and higher interaction between TiO_2 and anthocyanin in sweet pomegranate extract leads to a better charge transfer[17]. A DSSC sensitized by a mixed extract has a conversion efficiency close to the average value of those sensitized with sweet and sour pomegranate. This result is in agreement with that of Wongcharee *et al.*[2]. Under similar conditions, DSSCs sensitized by sweet pomegranate extract showed good performance compared to those prepared from other natural dyes based on anthocyanin[7,18].

Table 2. Photovoltaic performance of dye-sensitized solar cells based on sour pomegranate extract, sweet pomegranate extract and mixed extract

Dye source	V_{OC} (V)	J_{SC} (mA cm^{-1})	Fill Factor (%)	η (%)
Sour pomegranate	2.97	0.50	49.00	0.73
Sweet pomegranate	4.60	0.62	55.01	1.57
Mixed extract	3.25	0.56	50.13	0.91

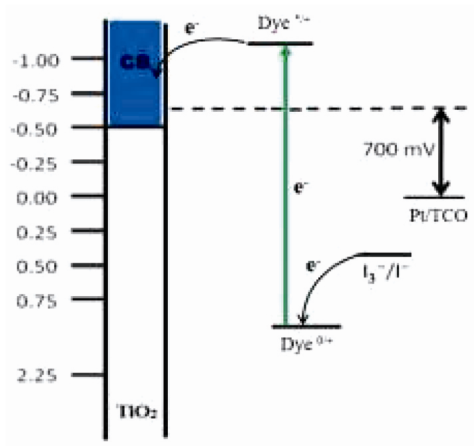


Figure 3. Schematic diagram of the solar cell.

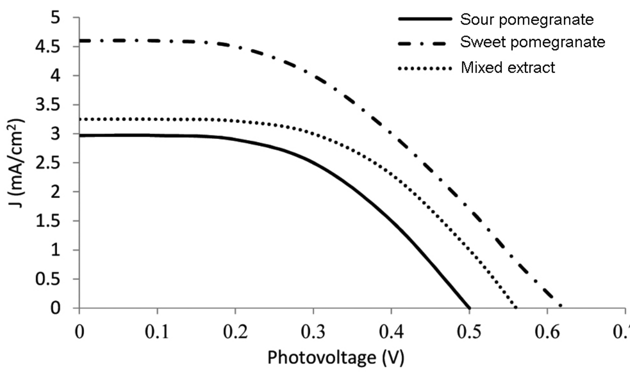


Figure 4. Current density–voltage characteristics for sweet pomegranate, sour pomegranate and mixed extract.

Two natural dyes were extracted from sour and sweet pomegranate grown in Iran. Natural dyes are an environmental-friendly and low-cost source as sensitizer for DSSCs. The spectrophotometric properties of the natural dyes in solution and on TiO_2 substrate were examined. Sour and sweet pomegranate extracts showed absorption maxima in solution at 511 and 529 nm respectively. The absorption maxima of both natural dyes separately applied on TiO_2 films gave bathochromic shifts compared to the corresponding dye spectra in solutions. Finally, the natural extract dyes were utilized in constructed DSSCs and their photovoltaic behaviours were assessed. A solar energy to electricity conversion efficiency of 0.73%, 1.57% and 0.91% was achieved for sour pomegranate, sweet pomegranate and mixed extract respectively. The mixed extract has a conversion efficiency close to the average value of those sensitized with sour pomegranate and sweet pomegranate extracts. From the results of the present study, it is clear that sweet pomegranate extract presents the best photosensitized effect in DSSCs, which is due to the better interaction between the carbonyl and hydroxyl groups of anthocyanin on sweet pomegranate extract and the TiO_2 substrate in DSSCs.

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Vegetation and climatic variability in southeastern Madhya Pradesh, India since Mid-Holocene, based on pollen records

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Pollen analysis of 1.75 m deep sediment core from Tula-Jalda (Amarkantak) in Anuppur district, Madhya Pradesh shows that around 4500–3600 cal years BP, this region supported open mixed tropical deciduous forests comprising chiefly *Madhuca indica* followed by *Terminalia*, *Mitragyna parvifolia*, *Haldina cordifolia*, *Emblica officinalis* and *Acacia*, under a warm and relatively less humid climate. The retrieval of Cerealia and other cultural plants, viz. *Artemisia*, Cheno/Am and Caryophyllaceae signifies that the region was under cereal-based agricultural practice. The open mixed deciduous forests got enriched and dense around 3600–2761 cal years BP with the expansion of trees that already existed coupled with invasion of *Symplocos*, *Diospyros*, *Lannea coromandelica* and *Radermachera* with the inception of a warm and moderately humid climate in response to increased monsoon precipitation. Around 2761–2200 cal years BP, much expansion of the forests took place owing to

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