Asian Journal of Chemistry; Vol. 27, No. 10 (2015), 3745-3748

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18950

Evaluation of Anthocyanin, a Rose Residue Extract, for Use in Dye-Sensitized Solar Cell

ESIN EREN[1], ELIF CEREN GOK[2], BUSRA NUR SEYHAN[2], NESLIHAN NOHUT MASLAKCI[3] and AYSEGUL UYGUN OKSUZ[3,*]

[1]Hydrogen Technologies Research and Application Center, Suleyman Demirel University, 32260 Isparta, Turkey
[2]Bedri Ayhan Altinbasak High School, 32040 Isparta, Turkey
[3]Department of Chemistry, Faculty of Arts and Science, Suleyman Demirel University, 32260 Isparta, Turkey

*Corresponding author: Fax: +90 246 2371106; Tel: +90 246 2114082; E-mail: ayseguluygun@sdu.edu.tr

Received: 22 December 2014; *Accepted*: 20 January 2015; *Published online*: 22 June 2015; AJC-17338

Using a natural dye (anthocyanin), extracted from a wasted rose residue and characterized by FTIR and UV-visible spectroscopy, a dye-sensitized solar cell (DSC) was fabricated and the current-voltage (I-V) characteristics of the solar cell were studied. The best photovoltaic parameters like short-circuit photocurrent (I_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) were 0.291 mA/cm^2, 300 mV, 0.426, respectively, with an energy conversion efficiency of 0.04. Due to environmental friendliness, low-cost production and ease of waste management, natural dyes from rose residue can provide a wide venue for commercial applicability in dye-sensitized solar cells.

Keywords: Anthocyanins, Rose residue, Dye-sensitized solar cell, Natural dyes.

INTRODUCTION

Since 1991, much scientific research focused on the study of dye-sensitized solar cells (DSCs) due to their flexibility, environmental friendliness, colourful design and cost-effective alternative to the p-n junction solar cells[1-5]. A typical dye-sensitized solar cell is composed of a nanocrystalline mesoporous semiconductor electrode-absorbed molecular dye, a counter electrode and an appropriate electrolytic solvent[4]. Dye-sensitized solar cells are devices used for the conversion of solar energy to electrical energy based on sensitization of wide band gap semiconductors[6,7]. Titanium dioxide nanocrystalline thin film is one of the best photoanode of dye sensitized solar cells due to its low cost, non-toxicity and stable photoelectrode[8,9]. The conduction band edge of TiO_2 coincides well with the excited electronic level of natural anthocyanin-based dyes, presenting the necessary configuration for the injection of electrons from the dye molecule to the semiconductor[9,10]. An efficient solar cell primarily depends on the dye used as photosensitizer. The absorption spectrum of the dye and anchoring groups (=O, -OH, -COOH, *etc.*) of the dye to surface of TiO_2 has some significant parameters that allow the production of the efficient solar cells[11].

Natural dye is obtained from plants, insects/animals and minerals[12]. Natural dyes are an effective alternative to expensive and rare organic based dye-sensitized solar cells due to their cost efficiency, ease of attainability, abundance in supply of raw materials, non-toxicity and complete biodegradation making the dyes a popular subject of research[4,9,12]. In most cases, the natural dye's photoactivity is related to the anthocyanin family[13]. The chemical structure of anthocyanin contains chelating groups like hydroxyl (-OH) that can bind with Ti(IV) sites on the TiO_2 surface[14-16]. Anthocyanins, proanthocyanidins and flavonols are three major subclasses of flavonoid compounds[9,17]. The word anthocyanin, derived from two Greek words was originally used to mean plant and blue[13,18]. Work on dye-sensitized solar cells based on natural dye containing anthocyanin has been reported in literature. An anthocyanin pigment extracted from flower was first used as photosensitizer in dye-sensitized solar cell by Tennakone *et al.*[19]. Fernando and Senadeera[20] studied various natural pigments including anthocyanins for use as photosensitizer in dye-sensitized solar cells. Photocurrent densities ranging from 1.1 to 5.4 mA cm^{-2} and photovoltages ranging from 390 to 410 mV were obtained. Of the different flowers studied, the extract from Hibiscus surattensis-HST gave the best photosensitized effect with a reasonable efficiency of 1.14 %[20]. Kumara *et al.*[21] researched Shiso leaf pigments for dye-sensitized solid-state solar cell. Shiso plant is a well-known vegetable in Japan and its leaf extract is used as a food colorant. Leaves of this plant have two anthocyanin pigments including shisonin and malonylshisonin. The dye-sensitized solar cell (DSC) based on extract containing shisonin exhibits a promising performance with an efficiency of 1.01 %[21]. The efficiency and stability of devices based on natural dyes such as mulberry, blueberry and jaboticaba's skin were studied by Patrocínio *et al.*[22]. Mulberry sensitized cells gave the best performance among the extracts studied. Okoli *et al.*[23] made an anthocyanin-dyed TiO_2 electrode and studied its performance on dye-sensitized solar cell. Their results showed that the overall conversion efficiency of the stained and unstained cells were 0.58 and 0.03 %, respectively. Anthocyanins from various plants gave different sensitizing performances[9,24].

Isparta is a city in southwestern Turkey that is widely known as "the city of roses" for its beautiful roses and rosewater production. Rose residue forms an enormous amount of organic material that is not being used and has to be disposed of. Disposal is both costly and environmentally polluting[25]. The aim of the present study is to evaluate Isparta's rose residue seen as waste product for use in dye-sensitized solar cells. The natural dye was extracted from dried and washed rose residue and characterized by UV-visible spectroscopy and Fourier Transform Infrared spectroscopy (FTIR). The natural dye was then used as a sensitizer in the dye-sensitized solar cell and the photovoltaic properties of dye-sensitized solar cell were studied.

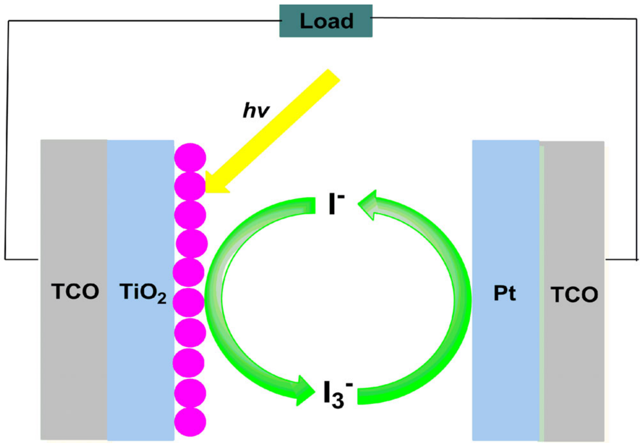
EXPERIMENTAL

Rose residue was purchased from Isparta Sebat Rose Oil Factory. Test Cell Kits containing titania electrodes, platinum electrodes, iodolyte and sealings (Solaronix) were used for dye-sensitized solar cell studies. All solvents were of spectroscopic grade and were used without any further purification.

Preparation of natural dye sensitizer: The rose residue was kept in a vacuum furnace for 24 h at 80 °C to remove the moisture. Anthocyanins were extracted from rose residue by immersing the residue in 0.1 % HCl (v/v) in methanol for 4 h at 65 °C without exposure to direct sunlight. The mixture was filtered on a Buchner funnel and the remaining solids were washed with 0.1 % HCl (v/v) in methanol until a clear solution was obtained. The natural dye solutions were dried at 60 °C using a rotary evaporator. The obtained natural dye was properly stored, protected from direct sunlight and used as a sensitizer in dye-sensitized solar cell.

Fabrication of dye-sensitized solar cell (DSC): For dye uptake, the TiO_2 electrode (Solaronix) was immersed in a methanol solution containing a natural dye for 24 h at room temperature. Natural adsorbed TiO_2-coated ITO glass was washed with methanol to remove unadsorbed dye. A platinum-covered glass (Solaronix) was used as a counter electrode, because of the stability and catalytic activity of Pt for I_2 reduction[26]. Both the photoanode electrode and the platinized glass counter electrode were sealed *via* heating at 110 °C. A dye-sensitized solar cell was obtained after filling the electrolyte iodolyte (Solaronix) in the space between the working and counter electrodes. A secondary sealing was also used for protecting the electrolyte solution from leaking.[27] The active area of the cell was 0.36 cm^2. Schematic diagram of a dye-sensitized solar cell is shown in **Scheme-I**.

Fourier transform infrared (FTIR) spectra were recorded between 4000 and 400 cm^{-1} with a 4 cm^{-1} resolution from KBr pellets on a Perkin Elmer Spectrum BX FTIR system (Beaconsfield, Beuckinghamshire, HP91QA, England). The absorption spectra were measured using 1 cm path length



Scheme-I: Schematic diagram of a dye-sensitized solar cell (●: dye)

quartz cuvette on Perkin Elmer Lambda 20 UV-visible spectrophotometer. I-V characteristics were measured with Keithley 2400 sourcemeter (2400 model) and Labview data acquisition software under 100 mW/cm^2 light intensity and AM1.5 conditions. The overall energy conversion efficiency (n) and the fill factor (FF) were calculated using the eqns. 1 and 2[9,24,28]:

$$\text{Energy conversion efficiency (n)} = \frac{I_{sc}V_{oc}FF}{P_{in}} \quad (1)$$

$$\text{Fill factor (FF)} = \frac{V_m I_m}{V_{oc} I_{sc}} \quad (2)$$

where P_{in} is the power of incident light per unit area, I_m and V_m are maximum current and voltage, I_{sc}, V_{oc} are short-circuit photocurrent and open-circuit voltage, respectively.

RESULTS AND DISCUSSION

Fig. 1 shows the FTIR spectrum of the natural dye extracted from the rose residue. The -OH stretching vibration band belonging the anthocyanin dye of rose residue is observed[29] at 3303 cm^{-1}. The asymmetric and symmetric C-H stretching modes are observed at 2933 and 2841 cm^{-1}, respectively. The band at 1729 cm^{-1} is typical of the C=O stretching vibration of anthocyanins used as dyes of rose residue[30]. The C=O is also an indication that anthocyanin in dye of rose residue has a partially quinoidal form[31,32]. The peak at 1653 cm^{-1} belongs to the stretching of aromatic C=C in the anthocyanin content[33]. FTIR results indicate that the natural dye obtained from rose residue exhibits most of the characteristic peaks of the anthocyanin.

UV-visible absorption: The UV-visible absorption spectra have been studied at different pH values (0.86, 1.76, 2.70, 12.10, 12.47) and the wavelength of maximum absorbance have been listed in Table-1. The different pH value is adjusted using an HCl solution, a NaOH solution and water for UV-visible measurements. UV-visible absorption spectra are shown in Fig. 2. The synthesized samples showed two main peaks experimentally located at 268-284 and 329-366 nm. No clear maximum absorption peak in the visible light region from about 390 to 700 nm was observed. This result can be explained based on the superposition of the absorption peaks[4]. The peak

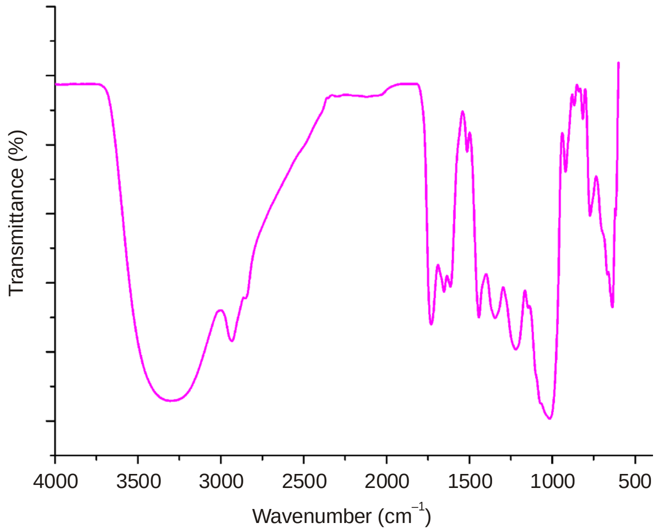


Fig. 1. FTIR spectra of natural dye extracted from rose residue

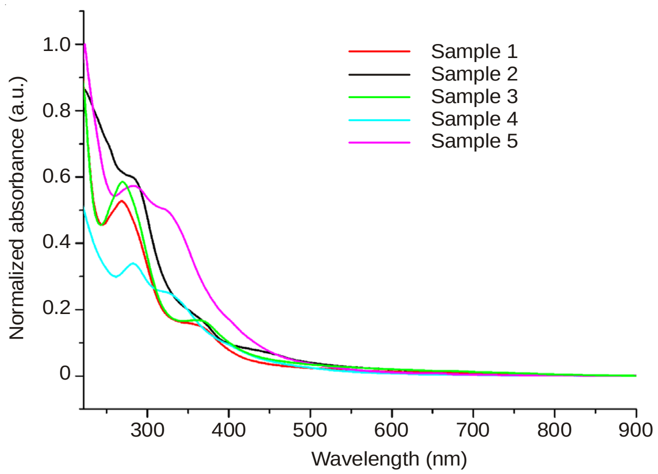


Fig. 2. Normalized absorption spectra of the samples

between 268 and 284 nm belongs to the absorption characteristic of anthocyanin in the UV region[34,35]. It is known that the common copigments associated with anthocyanin are flavonols like quercetin and kaempferol, that show absorption peaks between 300 and 400 nm[28]. The degree of acidity and alkalinity are among the factors that may affect the chemical structure of anthocyanins, including flavylium cation, quinoidal bases, the presudobase or carbinol and the chalcones[36]. The anthocyanin pigments in rose residue change the wavelength of maximum absorbance with pH (Table-1). For example, the band around 364 nm shifts to lower wavelength (about 333 nm) under basic conditions. This blue shift may reveal an interaction between anthocyanins and copigments like flavonol and is indicative of the formation of a cluster[37].

TABLE-1
WAVELENGTH OF MAXIMUM ABSORBANCE AT DIFFERENT pH VALUES

Sample	pH	Solvent	λ_{max} (nm)
1	0.86	HCl solution	268, 366
2	1.76	HCl solution	284, 364
3	2.70	H_2O	269, 366
4	12.10	NaOH solution	282, 333
5	12.47	NaOH solution	283, 329

Photoelectrochemical properties of dye-sensitized solar cells sensitized with natural dye: The performance of a natural dye, anthocyanin, as sensitizer in dye-sensitized solar cells was evaluated by short-circuit photocurrent (I_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and an energy conversion efficiency (n). The effect of the amount of anthocyanin extract at constant volume solvent on the performance of the dye-sensitized solar cell was also investigated. The photoelectrochemical parameters of a dye-sensitized solar cell sensitized with a natural dye are collected in Table-2. The best light-to-electricity conversion efficiency (n) was obtained as 0.04 when the amount of natural dye was 50 mg. Our study indicates that the natural dye sensitized solar cell has higher efficiency than the dye-sensitized solar cell sensitized by lithospermum flowers with energy conversion efficiency of 0.03[4,9]. Moreover, the dye obtained from rose residue showed better performance than anthraquinone dyes, especially for the 1-amino-4-hydroxy-9,10-dihydroanthracene-2-carboxylic acid (four times increase in energy conversion efficiency), on dye-sensitized solar cells applications[38]. The best I-V curves of dye-sensitized solar cell using the sensitizer extracted from rose residue are given in Fig. 3. Our results also indicate that the efficiency of the rose residue is low when compared to that of the rose flower used as sensitizer for dye-sensitized solar cell (Table-3), as, we didn't use rose flower itself in our study. Rose flower undergoes processes such as dissolution, filtration and boiling during rose oil solid production at rose processing factory. At the end of these processes, rose residue is discharged and thrown away as waste product. Some of the reasons for the low efficiency of the rose residue are:

TABLE-2
EFFECTS OF AMOUNT OF NATURAL DYE IN METHANOL (5 mL) ON THE PERFORMANCE OF DYE-SENSITIZED SOLAR CELL

Amount (mg)	Open-circuit voltage (mV)	Short-circuit photocurrent (mA/cm^2)	Fill factor	n (%)
25	400	0.102	0.407	0.017
50	300	0.291	0.426	0.040
100	400	0.092	0.443	0.016

n = Energy conversion efficiency

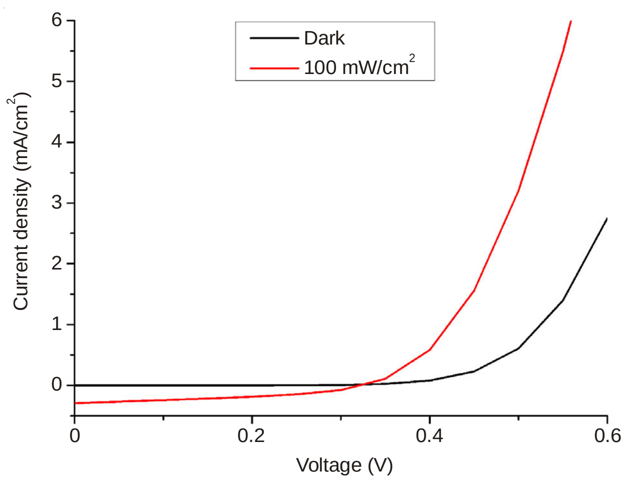


Fig. 3. Current-voltage curves for dye-sensitized solar cell prepared with a natural dye (50 mg) as sensitizer in the dark (——), under 100 mW/cm^2 light source and AM 1.5 illumination (——)

TABLE-3
PHOTOELECTROCHEMICAL PARAMETERS OF THE DYE-SENSITIZED SOLAR CELLS USING THE EXTRACTS OF ROSE

Sample	Open-circuit voltage (mV)	Short-circuit photocurrent (mA/cm^2)	Fill factor	n (%)	Ref.
Rose residue	300	0.291	0.426	0.04	This work
Rose	595	0.970	0.659	0.38	4
Yellow rose	609	0.740	0.571	0.26	4
Chinese rose	483	0.900	0.619	0.27	4

1) inefficient light-harvesting ability of the natural dye 2) inefficient charge injection into the conduction band of TiO_2, or 3) inefficient collection of the injected electrons[3].

Conclusion

A natural dye, anthocyanin, was extracted from rose residue through a simple extraction technique without any further purification. The dye's structure, optical properties and performance in dye-sensitized solar cells were studied. It was observed that the different dye baths containing different amount of the natural dye gave different performance of dye-sensitized solar cells. The difference in performance is mainly due to the amount of dye adsorption; for example, when the amount of natural dye was 25 and 100 mg, the energy conversion efficiency was found to be almost same. When using the same volume of solvent for comparison, the optimal amount of dye for photovoltaic measurements was found to be 50 mg. The resulting maximal photovoltaic characteristics were a short-circuit photocurrent (I_{sc}) of 0.291, an open-circuit voltage (V_{oc}) of 300 mV and a fill factor (FF) of 0.426, with an energy conversion efficiency of 0.04. Compared to previous studies, our result showed that the natural dye dye-sensitized solar cells efficiency is better than that of dye-sensitized solar cells based on lithospermum, some anthraquinone dyes and coumarin dyes[4,9,38,39]. The quick and simple preparation procedures presented in this study make anthocyanin extracted from rose residue a good sensitizer for use in dye-sensitized solar cells. The importance of our work lies not only in the use of anthocyanin in dye-sensitized solar cells but also in the reevaluation of the disposal of and recycling of environmentally friendly and readily available natural waste products, a topic of study popular in industry, Universities and Even High Schools research energy based projects.

ACKNOWLEDGEMENTS

The authors are grateful to Assoc. Prof. Dr. Mahmut Kus from Chemical Engineering Department and Advanced Technology R&D Center, Selcuk University, Konya, Turkey and research assistant Canan Baslak from Chemistry Department, Science Faculty, Selcuk University Konya, Turkey for their help during photovoltaic measurements to this study. Special thanks goes to Ms Layla Rahhal-Irabi from Henry Ford Community College, Dearborn, MI for her support and valuable contribution to this paper.

REFERENCES

1. B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991).
2. M. Grätzel, *Nature*, **414**, 338 (2001).
3. B. Pradhan, S.K. Batabyal and A.J. Pal, *Sol. Energy Mater. Sol. Cells*, **91**, 769 (2007).
4. H. Zhou, L. Wu, Y. Gao and T. Ma, *J. Photochem. Photobiol. Chem.*, **219**, 188 (2011).
5. K. Takagi, S. Magaino, H. Saito, T. Aoki and D. Aoki, *J. Photochem. Photobiol. Photochem. Rev.*, **14**, 1 (2013).
6. M. Thambidurai, N. Muthukumarasamy, D. Velauthapillai and C. Lee, *Mater. Lett.*, **92**, 104 (2013).
7. N.M. Gómez-Ortíz, I.A. Vázquez-Maldonado, A.R. Pérez-Espadas, G.J. Mena-Rejón, J.A. Azamar-Barrios and G. Oskam, *Sol. Energy Mater. Sol. Cells*, **94**, 40 (2010).
8. M. Thambidurai, N. Muthukumarasamy, D. Velauthapillai and C. Lee, *J. Mater. Sci. Mater. Electron.*, **24**, 1921 (2013).
9. M.R. Narayan, *Renew. Sustain. Energy Rev.*, **16**, 208 (2012).
10. A. Olea, G. Ponce and P.J. Sebastian, *Sol. Energy Mater. Sol. Cells*, **59**, 137 (1999).
11. K.H. Park, T.Y. Kim, J.Y. Park, E.M. Jin, S.H. Yim, J.G. Fisher and J.W. Lee, *J. Electroanal. Chem.*, **689**, 21 (2013).
12. M. Shahid, Shahid-ul-Islam and F. Mohammad, *J. Clean. Prod.*, **53**, 310 (2013).
13. G. Calogero and G.D. Marco, *Sol. Energy Mater. Sol. Cells*, **92**, 1341 (2008).
14. S. Hao, J. Wu, Y. Huang and J. Lin, *Sol. Energy*, **80**, 209 (2006).
15. N.J. Cherepy, G.P. Smestad, M. Grätzel and J.Z. Zhang, *J. Phys. Chem. B*, **101**, 9342 (1997).
16. G.P. Smestad, *Sol. Energy Mater. Sol. Cells*, **55**, 157 (1998).
17. P. Jing, S.-J. Zhao, S.-Y. Ruan, Z.-H. Xie, Y. Dong and L. (Lucy) Yu, *Food Chem.*, **133**, 1569 (2012).
18. P. Ponmozhi, M. Geetha, M.S. Kumar and P.S. Devi, *Asian J. Pharm. Clin. Res.*, **4(Suppl. 1)**, 41 (2011).
19. K. Tennakone, G.R.R.A. Kumara, A.R. Kumarasinghe, K.G.U. Wijayantha and P.M. Sirimanne, *Semicond. Sci. Technol.*, **10**, 1689 (1995).
20. J.M.R.C. Fernando and G.K.R. Senadeera, *Curr. Sci.*, **95**, 663 (2008).
21. G.R.A. Kumara, S. Kaneko, M. Okuya, B. Onwona-Agyeman, A. Konno and K. Tennakone, *Sol. Energy Mater. Sol. Cells*, **90**, 1220 (2006).
22. A.O.T. Patrocínio, S.K. Mizoguchi, L.G. Paterno, C.G. Garcia and N.Y.M. Iha, *Synth. Met.*, **159**, 2342 (2009).
23. L.U. Okoli, J.O. Ozuomba, A.J. Ekpunobi and P.I. Ekwo, *Res. J. Recent Sci.*, **1**, 22 (2012).
24. K. Wongcharee, V. Meeyoo and S. Chavadej, *Sol. Energy Mater. Sol. Cells*, **91**, 566 (2007).
25. H. Fazaeli and M. Zahedifar, *Turk. J. Vet. Anim. Sci.*, **33**, 265 (2009).
26. Y.L. Lee and Y.S. Lo, *Adv. Funct. Mater.*, **19**, 604 (2009).
27. L. Ciammaruchi, S. Penna, A. Reale, T.M. Brown and A. Di Carlo, *Microelectron. Reliab.*, **53**, 279 (2013).
28. C.Y. Chien and B.D. Hsu, *Sol. Energy*, **98**, 203 (2013).
29. K.V. Hemalatha, S.N. Karthick, C. Justin Raj, N.-Y. Hong, S.-K. Kim and H.-J. Kim, *Spectrochim. Acta A*, **96**, 305 (2012).
30. V. Shanmugam, S. Manoharan, S. Anandan and R. Murugan, *Spectrochim. Acta A*, **104**, 35 (2013).
31. P. Mazzaracchio, S. Tozzi, C. Boga, L. Forlani, P.G. Pifferi and G. Barbiroli, *Food Chem.*, **129**, 1100 (2011).
32. P. Luo, H. Niu, G. Zheng, X. Bai, M. Zhang and W. Wang, *Spectrochim. Acta [A]*, **74**, 936 (2009).
33. C.S. Pappas, C. Takidelli, E. Tsantili, P.A. Tarantilis and M.G. Polissiou, *Food Compost. Anal.*, **24**, 17 (2011).
34. G.S. Woodall and G.R. Stewart, *J. Exp. Bot.*, **49**, 1447 (1998).
35. C. Qin, Y. Li, W. Niu, Y. Ding, R. Zhang and X. Shang, *Czech. J. Food Sci.*, **28**, 117 (2010).
36. M.A.B. Levi, I.S. Scarminio, R.J. Poppi and M.G. Trevisan, *Talanta*, **62**, 299 (2004).
37. A.H. Nielsen, C.E. Olsen and B.L. Møller, *Phytochemistry*, **66**, 2829 (2005).
38. C. Li, X. Yang, R. Chen, J. Pan, H. Tian, H. Zhu, X. Wang, A. Hagfeldt and L. Sun, *Sol. Energy Mater. Sol. Cells*, **91**, 1863 (2007).
39. E.M. Abdou, H.S. Hafez, E. Bakir and M.S.A. Abdel-Mottaleb, *Spectrochim. Acta A*, **115**, 202 (2013).