BRIGHT STAR JOURNAL FOR SCIENTIS RESEARCH Local Number: 512/2019-00008
Vol.1, No.x (2020) PP 01 –10 Available at http://bsjsr.bsu.edu.ly
Received July 04, 2019, Accepted August 08, 2019, Published online Jan 01, 2020

Preparation of Nano- Natural Betalain Pigments from Red Beet Roots with Some Metals and Study the Physical Properties of these Compounds

Hamdy Abdel Baky Matter[*a] Tariq Mohamed Ayad[*b] and Abdel Rhman Elkatly*[c]

[*a] Ph.D. Physical Chemistry, [*b] Organic Chemistry and [*c] Physical Chemistry

[*a, *b *c] University of Benghazi, Faculty of Arts and Science, Chemistry Department Al-Wahat

*[a] Higher Institute Engineering and Technology, Egypt, El-Arish

E-mail: hamdy.matter@gmail.com

Abstract

Betalain dyes are extracted from beetroots by ethanolic method and determined the concentration of Betalain dyes spectrophotometrically at λ_{max} = 480 nm, calibration curve is draw with straight line at 50-1000 ppm. Effect of pH and physical properties of Nano-compounds are measured for Ni^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Bi^{2+} and Sb^{2+} ions. The particles which precipitate by betalain dyes with metal ions Hg^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, and Bi^{2+} are measured the conductivity which indicate that these Nano- metal dyes may be used as photo-electric cells.

الملخص العربي

يتم استخراج أصباغ البيتالين من جذر الشمندر(البنجر) بالطريقة الإيثانولية وتحديد تركيز الأصباغ البيتالين طيفيًا عند λ max = 480 nm ، يتم رسم منحنى المعايرة بخط مستقيم عند 50−1000 جزء في المليون. يتم قياس تأثير الأس الهيدروجيني والخواص الفيزيائية للمركبات النانونية للأيونات النيكل الثنائية والزئبق الثنائية والرصاص الثنائي والكوبلت الثنائي والكادميوم الثنائي والبزموت الثنائي والأنتيمون الثنائي. يتم قياسالتوصيلية الكهربية للجسيمات النانونية التي تترسب بواسطة أصباغ البيتالين مع أيونات المعادن المذكورة التي تشير إلى أن هذه الأصباغ النانوية مع أيونات الوئبق خاصة يمكن أن تستخدم كمواد حساسة للضوء أو كخلايا كهروضوئية لتحويل الطاقة الشمسية الى طاقة كهربية.

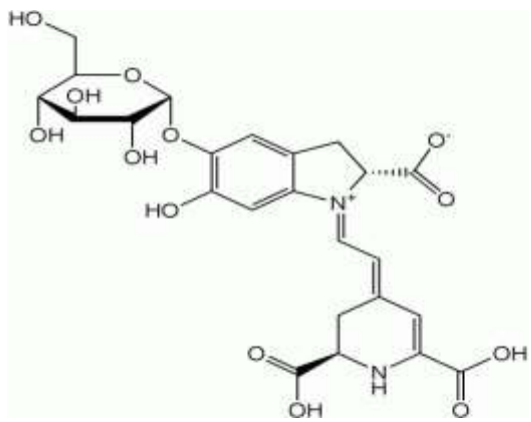
Key words

Spectrophotometry, Nano-compounds, Betalain dyes, and Beetroots

1. Introduction.

Betalains are a class of red and yellow indole-derived pigments found in plants of the Caryophyllenes, where they replace anthocyanin pigments. Betalains also occur in some higher order fungi [1]. They are most often noticeable in the petals of flowers, but may color the fruits, leaves, stems, and roots of plants that contain them. They include pigments such as those found in beets.

The name "betalain" comes from the Latin name of the common beet (*Beta vulgaris*), from which betalains were first extracted. The deep red color of beets, bougainvillea, amaranth, and many cactuses results from the presence of betalain pigments [2]. The particular shades of red to purple are distinctive and unlike that of anthocyanin pigments found in most plants. There are two categories of betalains [3]. It was once thought that betalains were related to anthocyanins, the reddish pigments found in most plants. Both betalains and anthocyanins are water-soluble pigments found in the vacuoles of plant cells. However, betalains are structurally and chemically unlike anthocyanins and the two have never been found in the same plant together [4], [5]. Betalains contain nitrogen whereas anthocyanins do not [6]. It is now known that betalains are aromatic indole derivatives synthesized from tyrosine. They are not related chemically to the anthocyanins and are not even flavonoids [7]. Each betalain is a glycoside, and consists of a sugar and a colored portion. Their synthesis is promoted by light. The most heavily studied betalain is betanin, also called beetroot red after the fact that it may be extracted from red beet roots. Betanin is a glucoside, and hydrolyzes into the sugar glucose and betanidin [8]. It is used as a food coloring agent, and the color is sensitive to pH. Other betalains known to occur in beets are isobetanin, probetanin, and neobetanin. The color and antioxidant capacity of betanin and indicaxanthin (betaxanthin derived of L-proline) are affected by dielectric microwave heating [9]. Addition of TFE (2, 2, 2-trifluoroethanol) is reported to improve the hydrolytic stability of some betalains in aqueous solution [10]. Furthermore, a betanin-europium(III) complex has been used to detect calcium dipicolinate in bacterial spores, including *Bacillus anthracis* and *B. cereus* [11]. Other important betacyanins are amaranthine and isoamaranthine, isolated from species of *Amaranthus*.



Betalain dye

Herein, chlorophyll and betalain dyes are extracted from fresh spinach leaves and beetroots [12]. Nine solvents, namely, *n*-hexane, ethanol, acetonitrile, chloroform, ethyl-ether, ethyl-acetate, petroleum ether, *n*-butyl alcohol, and methanol were used to extract natural dyes from Cordyline fruticosa, Pandannus amaryllifolius and Hylocereus polyrhizus [13]. The feasibility of using sugar-beet pectin gels for the removal of heavy metals from aqueous solutions. Sugar-beet pectin hydro- and xerogels were tested in the batch biosorption and desorption of cadmium, lead and copper. Pectins were successfully extracted and demethylated from the sugar-beet pulp, an agricultural residue, and gelled in the presence of $CaCl_2$ [14]. Beetroot (*Beta vulgaris*) pomace, processing by-product from food industry, was investigated as a starting raw material. The contents of phenolics (1.87–11.98 mg GAE/g of dry weight) and betalains

(0.75–3.75 mg betalains/g of dry weight) in the extracts were determinate spectrophotometrically [15]. Betalain was extracted from bougainvillea flower. Alumina, layered double hydroxides (LDHs) and zeolites were tested as adsorbents of the chromophore. Gamma alumina stabilized betalains over a long period [16]. In the palm oil industry, the deacidification process is performed by steam stripping which causes the loss of most of palm oil's natural antioxidants due to high temperature. The liquid–liquid extraction process which is carried out at low temperature is preferable in order to preserve these compounds [17]. A dye-sensitized solar cell based on natural betalain pigments from red beet roots is described. Reddish-purple betanin is an easily oxidized, water-soluble pigment with strong visible light absorption, having a maximum molar absorptivity of about 65,000 M^{-1} cm^{-1}at 535 nm [18]. The photoelectrochemical properties of dye-sensitized solar cells using natural pigments containing betalains and anthocyanins as sensitizers are descripted [19].

1.1. A Beer's Law Experiment

The ratio of I_t and I_o can be called the percent transmittance.

$$\% T = \left(\frac{I_t}{I_0}\right) \times 100 \ \ldots \ldots \ldots \ldots (1)$$

A more useful quantity is the absorbance (A) defined as

$$A = -\log\left(\% \frac{T}{100}\right) \ldots \ldots \ldots \ldots (2)$$

The higher the absorbance of light by a solution, the lower the percent transmittance, the wavelength at which absorbance is highest is the wavelength to which the solution is most sensitive to concentration changes. This wavelength is called the maximum wavelength or $\lambda_{max.}$

The molar absorptivity depends on the substance, the solvent and λ. The units for molar absorptivity are L/mole· cm for concentration in mole/L. Beer's law states the following:

$$A = \varepsilon bc \ldots \ldots \ldots \ldots \ldots (3)$$

With this equation (a calibration curve based on it), you can determine an unknown concentration or estimate what the absorbance of a certain solution will be as long as three of the four values in the equation are known.

1.2. Nanoparticles

Nanoparticles in general refer to particles having internal structural measurement or external dimensions within the size range of a few nanometers, preferable up to 100 nm size. According to the European Committee for Standardization, nanomaterials are defined as the materials with any external dimension at the nanoscale, or that possess nanoscale internal or surface structures. Nanoscale describes the size range from approximately 1–100 nm [20]. It is most frequently used as a specific size description (usually <100 nm, though sometimes <50 nm). The major synthesis routes are liquid phase, gas-phase, and biological methods [21-23]. The main liquid phase syntheses of inorganic NPs are co-precipitation, solgel processing, micro-emulsions, hydrothermal or solvothermal methods, template synthesis, and biometric synthesis [24]. The biological method can be approached for synthesis of NPs, which is rapid and cost-effective [25]. The gas-phase synthesis methods are of interest because they allow elegant way to control process parameter in order to be able to produce size-, shape-, and chemical composition-controlled nanostructures, and also can be used to prepare the large quantity of NPs [26, 27]. Nanoparticles are of two types: non-engineered and engineered NPs. Non-engineered NPs present in the environment are derived from natural events such as terrestrial dust storms, erosion, volcanic eruption, and forest fires [28]. Engineered NPs (ENPs) are intentionally produced by man using many different materials, such as metals (including Au, Ag, Zn, Ni, Fe, and Cu), metal oxides (TiO_2, Fe_2O_4, SiO_2, CeO_2, and Al_2O_3) [29], nonmetals (silica and quantum dots) [30], carbon (graphene and fullerene) [31], polymers (alginate, chitosan, hydroxyethylcellulose, polyhydroxyalkanoates and polyhydroxyalkanoates, and poly-Ecaprolactone) [32], and lipids (soya bean lecithin and stearic acid) [34].

Physical properties of NPs include shape, size, specific surface area, agglomeration/ aggregation, state of size distribution, surface morphology/topography, and structure including crystallinity, defect structure, and solubility [35, 36]. The size, shape, surface area, and size distribution of NPs are important deciding factors controlling their uptake by plants as it is highly dependent on cell wall pores and size of stomata [37-39]. The following section will describe the basics of each physical property of NPs.

1.3. Size and Shape

The size and shape can be identified as the most important parameter to define the nanomaterial in general. [40] postulated that NPs below 20–30 nm in size are characterized by an excess of energy at the surface and are thermodynamically unstable because of the interfacial tension, acting as a driving force, which leads to a spontaneous reduction of the surface area. However, most types of particles have a critical size of about 30 nm below which NPs exhibit their typical "nano" properties from their bulk material. When the size of a nanoparticle decreases, the amount of molecules present at the particle's surface increases in an exponential trend [41] studied the size-dependent effects of silica particles on Arabidopsis (Arabidopsis thaliana) plants. The studies showed reduced development of plants for treatment with 50 and 200 nm silica NPs.

The design of NPs has gained a lot of attention, resulting in particles with various shapes such as spheres, rods, tubed, fibers, and disks, and more extraordinary geometries such as worms, squares, urchins, and ellipsoids. The optical properties of NPs also depend on its size and shape.

1.4. Surface and Size Distribution of Nanoparticles

The surface morphology and surface area of NPs can be analyzed using scanning electron microscope (SEM) and Brunauer–Emmett–Teller (BET), respectively [42]. To get a higher resolution of approximately 0.2 nm, atomic force microscopy (AFM) can be used. It provides real topographical images of sample surfaces. Dynamic light scattering (DLS) enables evaluation of the size distribution of NPs, and zetasizer can be used to determine the surface charge of NPs. The attachment of NPs to cell membrane seems to be most affected by the surface charge of the NPs [43]. The plant cellular uptake is usually a prerequisite and is also governed by surface hydrophobicity and charge in addition to size. Compared to NPs having a neutral or negative charge, positively charged NPs are taken up at faster rate. The dispersion status of NPs in aqueous media principally depends on the surface charge of the given NPs. A number of invitro studies with different NPs have been published in which the effect of the different parameters such as dispersion, surface properties, and agglomeration and de-agglomeration can be controlled using ultrasonication, ionic strength and pH of aqueous solutions, physiological buffers, and cell culture media [44,45].

1.5. Structural and Species Specifics of Nanoparticles

Determinations of purity of NPs are important in biological application. X-ray diffraction (XRD) is the most essential tool used to characterize crystal structures [46]. The most commonly used database for the identification of crystal structures is the Joint Committee on Powder Diffraction Standards—International Center for Diffraction Data (JCPDS-ICDD) system. Detailed profile analysis of experimental XRD patterns provides information about a given material's space group and structural parameters. [47-49] studied the effects of size and shape of silver NPs on growth and gene expression in Arabidopsis plants and found that the application could result in a complex physiological response in the treated tissues. The literature reported the species specificity of NPs in which their effects vary with the type of NPs and type and nature of biological systems that got treated with NPs [50, 51].

1.6. Chemical Properties of Nanoparticles

Chemical properties include the elemental composition of nanomaterials and its surface chemistry such as zeta potential and photocatalytic properties. The chemical properties of a material are determined by the type of motion of its electrons. There is a wide range of NPs contributing to many different chemical properties [52]. Here, we describe the chemical characteristics separately with different kinds of NPs.

1.7. Metallic Nanoparticles

Compared with other nanostructures, metallic NPs have been proven to be the most flexible nanostructures owing to the synthetic control of their size, shape, composition, structure, assembly, and encapsulation, as well as the resulting tunability of their optical properties. Compared with other metallic nanostructures, colloidal gold and silver NPs are especially promising in nanobiotechnology because of their simple and fast preparation and bioconjugation. The attraction of surface plasmon excitations for the applications typically arises from the large electromagnetic field enhancement near the metal surface and the dependence of the resonance wavelength on the size, shape, and local dielectric properties of NPs. Such nanoparticles work as platform materials for biomolecular ultrasensitive detection, hyperthermal treatment for cancer, cell and protein labeling, and targeted delivery of therapeutic agents within the cells. Whereas silver NPs have a comparatively high cytotoxicity [53], gold NPs are biologically almost inert [54], and have a remarkable role on seed germination and antioxidant systems in Arabidopsis and altered levels of micro-RNAs expression that regulates various morphological, physiological, and metabolic processes in plants.

1.8. Metal Oxide Nanoparticles

Metal oxide NPs can exhibit unique chemical properties due to their limited size and a high density of corner or edge surface sites. Particle size is expected to influence important groups of basic properties in any material. The properties such as structural characteristics, namely the lattice symmetry, cell parameters, and effect of size, are related to the electronic properties of the oxide and structural and electronic properties obviously drive the chemical properties of the solid and also by size in a simple classification [55]. Metal oxide particles serve many functions in the various field of plant technology [56-58]. For example, nanosized silicon dioxide (SiO_2) treatments in proper concentration increased the percentage germination [59]. It was also reported that alumina NPs increased the root growth of plants [60]. Magnetic NPs exhibit a wide variety of attributions, which make them highly promising connection with biological system and bioapplications usually exists or can be prepared in the form of either single domain or superparamagnetic magnetite (Fe_2O_3) or greigite (Fe_3S_4). Due to their favorable beneficial effects, magnetic NPs approved for clinical use by Food and Drug Administration.

2-Experimental

2.1. Apparatus

All spectroscopic measurements were made at 25 ± 1°C with Jenway 6300 spectrophotometer and pH meter (Orion Model 81-02) was used for all pH measurements. Measuring flasks and glasses are used.

2.2. Reagents and materials

All chemicals were of analytical reagent grade unless otherwise stated distilled water was used throughout. The following cations and compound solutions were prepared and standardized using the standard methods. Dilute solutions (10^{-1}-10^{-6}) (M) mole. L^{-1} of these cations and compounds were prepared by distilled water at pH 7-8. Ni^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Ag^{+} , Bi^{2+} , Sb^{2+} and Mn^{2+} ions.

2.3. Extraction of Betalain dyes from beetroots and purification

Betalain dyes are extracted from beetroots method filtrated, dry and weigh 1 g of dry dye in

1 liter of solution in distilled water at 7-8 pH (1000 ppm) and by dilution prepared 900 - 100 ppm, calibration curve has obtained as a relation between concentration and the absorbance of light by a solution. The wavelength at which absorbance is highest is the wavelength to which the solution is most sensitive to concentration changes. This wavelength is called the maximum wavelength or $\lambda_{max.}$ = 470 nm.

2.4. Effect of pH

Betanin is a glucoside, and hydrolyzes into the sugar glucose and betanidin [8]. It is used as a food coloring agent, and the color is sensitive to pH. Other betalains known to occur in beets are isobetanin, probetanin, and neobetanin. The color and antioxidant capacity of betanin and indicaxanthin (betaxanthin derived of L-proline) are affected by dielectric microwave heating [9]. The change of the colour is studies in different pH solutions. 10-1-10-6 M HCl having theoretical pH 1-6 prepared and 10^{-6}-10^{-1} M NaOH having theoretical pH 8-14 prepared, then add anthocyanins different colour are formed, it may be used as pH indicators.

2.5. Treatment of Waste-Water

Sugar-beet pectins could be used as an efficient biosorbent for the treatment and recovery of Cu, Pb and Cd from wastewater [14]. 10^{-1}-10^{-6} M from Ni^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Ag^{+}, Mn^{2+} ions solutions were prepared, red cabbage dye was added to heavy metal ions different precipitates are formed, filtrated and measured the absorption of filtrate to know concentration of dye from calibration curve of dye.

2.6. Preparation of betanin nanoparticles

10^{-3} M of Hg^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, and Bi^{2+} were adding to[g/L] betanin solution let the solution about 24h until nanoparticles are formed filtrated and dried. Nanoparticles are compressed as a disc and measuring conductivity with effecting of sunlight which gives activity of photosensitive will be expected to use at photocell.

3. Results and discussion

The wavelength at which absorbance is highest is the wavelength to which the solution is most sensitive to concentration changes. This wavelength is called the maximum wavelength or $\lambda_{max.}$ = 470 nm

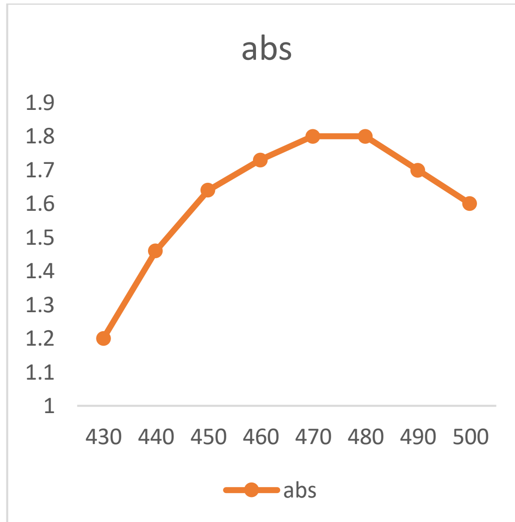


Fig. 1: For measuring λ_{max} of betalain dyes

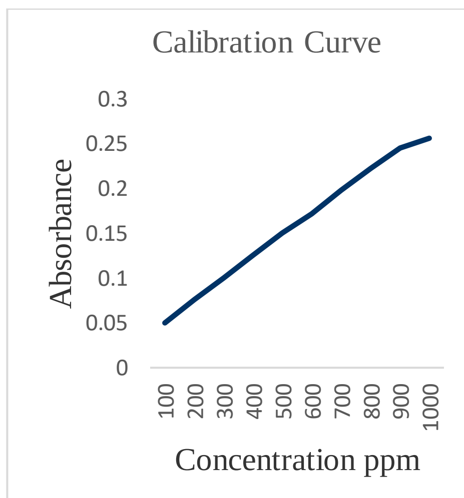


Fig 2: Calibration curve of betalain dyes.

3.1. Betalain dyes were measuring spctrophotomitrically and treatment of waste water:

1 g in liter of solution (1000) ppm diluted to 100 ppm and measuring the absorbance by Jenway

6300 spectrophotometer then, obtains a calibration curve.

Betalain dyes used as pH indicator and used with $KMnO_4$ or $K_2Cr_2O_7$ as oxidizing agent and betalain dyes as a chelating agent for precipitation some heavy metal ions like Ni^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Ag^{+}, Mn^{2+}, and measuring the concentration of betalain dye from filtrate spectrophotometry until precipitate all heavy metal ions in solution or waste water. Betalain dye is a good material, nature source, safety, not expensive for treatment of waste water from poisons heavy metals as the following arrangement Hg^{2+}> Cd^{2+}> Pb^{2+}> Ni^{2+}> Co^{2+}> Mn^{2+}> Ag^{+}. Betalain dyes have many hydroxyl groups as chelating agents formed complexes with heavy metals and precipitated so betalain dyes can used for treatment of waste water.

3.2. Betalain dyes complexes uses as photoelectric sensitive and photoelectric cells

Betalain dyes complexes with Hg^{2+}> Cd^{2+}> Pb^{2+}> Ni^{2+}> Co^{2+}> Mn^{2+}> Ag^{+} have photoelectric sensitive due to its colored and it's effected by oxidizing agents.

Table 1: For measuring conductivity of nanoparticles complexes

Metals	Conductivity ohm^{-1} in sun light	Conductivity ohm^{-1} without sun light
Hg^{2+}	60	40
Cd^{2+}	50	35
Pb^{2+}	40	38
Ni^{2+}	35	32
Co^{2+}	30	25
Mn^{2+}	25	23
Ag^{+}	24	23

5. References

[1] Strack, D. Vogt, T. and Schliemann, W. (2003) *Recent advances in betalain research*, Phytochemistry 62 (3): 247–69.

[2] Robinson, T. (1963) *"The Organic Constituents of Higher Plants*, Minneapolis Burgess Publishing p 292.

[3] Salisbury, F.B. and Ross, C.W. (1991). *Plant Physiology (4th ed.). Belmont, California*: Wadsworth Publishing. pp. 325–326.

[4] Kimler, L.M. (1975) *Betanin, the red beet pigment, as an antifungal agent*, Botanical Society of America, p 36.

[5] Gandía, H.F. García, C.F. and Escribano J. (2005). *Botany: floral fluorescence effect*. Nature. 437 (7057): 334.

[6] Francis F. (1999) Colorants. Egan Press.

[7] Stafford, H.A. (1994) *Anthocyanins and betalains: evolution of the mutually exclusive pathways*, Plant Science 101 (2): 91–98.

[8] Raven, P.H. Evert R.F. and Eichhorn S.E. (2004) *Biology of Plants* (7th Ed.). New York: W. H. Freeman and Company p 465

[9] Gonçalves, L.C. Di Genova, B.M, Dörr, F.A. Pinto, E. and Bastos, E.L. (2013) *Effect of dielectric microwave heating on the color and antiradical capacity of betanin*, Journal of Food Engineering 118 (1): 49–55.

[10] Bartoloni, F.H. Gonçalves, L.C. Rodrigues, A.C. Dörr, F.A. Pinto, E. and Bastos, E.L. (2013) *Photophysics and hydrolytic stability of betalains in aqueous trifluoroethanol*, Monatshefte für Chemie - Chemical Monthly 144 (4): 567–571.

[11] Gonçalves, L.C. Da Silva, S.M. DeRose, P.C. Ando, R.A. and Bastos, E.L. (2013) *Beetroot-pigment-derived colorimetric sensor for detection of calcium dipicolinate in bacterial spores*, PLOS One 8 (9): 673-701.

[12] Sengupta, D. Mondal, B. and Mukherjee, K. (2015) *Visible light absorption and photo-sensitizing properties of spinach leaves and beetroot extracted natural dyes*. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 148: 85-92.

[13]Al-Alwani, M.A. Mohamad, A.B., Kadhum, A. H., and Ludin, N.A. (2015) *Effect of solvents on the extraction of natural pigments and adsorption onto TiO_2 for dye-sensitized solar cell applications,* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 148: 130-137.

[14] Mata, Y.N. Blázquez, M.L. Ballester, A. González, F. and Muñoz, J.A. (2009) *Sugar-beet pulp pectin gels as biosorbent for heavy metals: Preparation and determination of biosorption and desorption characteristics,* Chemical Engineering Journal 150 (2–3): 289-301.

[15] Vulić, J. Brunet, J.Č. Ćetković, G. Tumbas, V. Djilas, S. Simin, D.Č. and Čanadanović V. (2012) *Antioxidant and cell growth activities of beet root pomace extracts,* Journal of Functional Foods 4 (3) 670-678.

[16] Lima, E. Bosch, P. Loera, S. Ibarra, I. A. Laguna, H. and Lara, V. (2009) *Non-toxic hybrid pigments: Sequestering betanidin chromophores on inorganic matrices,* Applied Clay Science 42 (3–4): 478-482.

[17] Zahrina, I. Nasikin, M. Krisanti, E. and Mulia, K. (2018) *Deacidification of palm oil using betaine monohydrate-based natural deep eutectic solvents,* Food Chemistry 240 490-495.

[18] Zhang, D. Lanier, S.M. Downing, J.A. Avent, J.L. Lum, J. and McHale, J.L. (2008) *Betalain pigments for dye-sensitized solar cells,* Journal of Photochemistry and Photobiology A: Chemistry, 195 (1): 72-80.

[19] Calogero, G. Yum, J. Sinopoli, A. Di Marco, G. Grätzel, M. and Nazeeruddin, M. K. (2012) *Anthocyanins and betalains as light-harvesting pigments for dye-sensitized solar cells,* Solar Energy 86 (5): 1563-1575.

[20] Lövestam, G. Rauscher, H. Roebben, G. Klüttgen, B.S. and Gibson, N. (2010) *Considerations on a definition of Nanomaterial for regulatory purposes*, Publications Office of the European Union.

[21] Klaus, T. Joerger, R. Olsson, E. and Granqvist, C.G. (1999) *Silver-based crystalline nanoparticles, microbially fabricated*, Proc. Nat. Acad. Sci. USA 96:13611–13614.

[22] Konishi, Y. Ohno, K. Saitoh, N. Nomura, T. and Nagamine, S. (2007) *Bioreductive deposition of platinum nanoparticles on the bacterium (Shewanella algae)*, J Biotechnol 128: 648–653.

[23] Raliya, R. Nair, R. Chavalmane, S. Wang, W.N. and Biswas, P. (2015) *Mechanistic evaluation of translocation and physiological impact of titanium dioxide and zinc oxide nanoparticles on the tomato (Solanum lycopersicumL.) plant*, Metallomics 7: 1584–1594.

[24] Cushing, B.L. Kolesnichenko, V.L. and O'Connor, C.J. (2004) *Recent advances in the liquid-phase syntheses of inorganic nanoparticles*, Chem Rev 104: 3893–3946.

[25] Gilaki, M. (2010) *Biosynthesis of silver nanoparticles using plant extracts*. J Biol Sci 10: 465–467.

[26] Jiang, J. Chen, D.R. and Biswas, P. (2007) *Synthesis of nanoparticles in aflame aerosol reactor with independent and strict control of their size, crystal phase and morphology*, Nanotechnology 18: 285-603.

[27] Thimsen, E. Rastgar, N. and Biswas, P. (2008) *Nanostructured TiO_2 films with controlled morphology synthesized in a single step process: Performance of dye-sensitized solar cells and photo water splitting*. J. Phys Chem C 112: 4134–4140.

[28] Nowack, B. and Bucheli, T.D. (2007) *Occurrence, behavior and effects of nanoparticles in the environment*, Environ Pollut 150: 5–22.

[29] Fernández G. M. and Rodriguez, J.A. (2011) *Metal oxide nanoparticles*. Encycl Inorg Bioinorg Chem. Instituto de Catálisis y Petroleoquímica, CSIC, Madrid, Spain and Brookhaven National Laboratory, Upton, NY, USA

[30] Ehrman, S.H. Friedlander, S.K. and Zachariah, M.R. (1999) *Phase segregation in binary SiO_2/TiO_2 and SiO_2/Fe_2O_3 nanoparticle aerosols formed in a premixed flame*, J. Mater Res 14: 4551–4561.

[31] Endo, M. Iijima, S. and Dresselhaus, M.S. (2013) *Carbon Nanotubes*, Elsevier, Shinshu University, Japan.

[32] Paques, J.P. van der Linden, E. van Rijn, C.J. and Sagis, L.M. (2014) *Preparation methods of alginate nanoparticles*, Adv Colloid Interf Sci 209: 163–171.

[33] Rao, J.P. and Geckeler, K.E. (2011) *Polymer nanoparticles: preparation techniques and size-control parameters*, Prog Polymer Sci 36: 887–913.

[34] Ekambaram, P. Sathali, A.H. and Priyanka, K. (2012) *Solid lipid nanoparticles: a review*, Sci Rev Chem Commun 2: 80–102.

[35] Cadden, A. (1987) *Comparative effects of particle size reduction on physical structure and water binding properties of several plant fibers*. J, Food Sci 52:1595–1599.

[36] Rao, C. and Biswas, K. (2009) *Characterization of nanomaterials by physical methods*, Annu Rev Analyt Chem 2: 435–462.

[37] Eichert, T. Kurtz, A. Steiner, U. and Goldbach, H.E. (2008) *Size exclusion limits and lateral heterogeneity of the stomatal foliar uptake pathway for aqueous solutes and water-suspended nanoparticles*, Physiol Planta 134:151–160.

[38] Schreck, E. Foucault, Y. Sarret, G. Sobanska, S. and Cécillon, L. (2012) *Metal and metalloid foliar uptake by various plant species exposed to atmospheric industrial fallout: Mechanisms involved for lead*, Sci Total Environ 427: 253–262.

[39] Wang, W.N. Tarafdar, J.C. and Biswas, P. (2013) *Nanoparticle synthesis and delivery by an aerosol route for watermelon plant foliar uptake*, J. Nanopart Res 15:1–13.

[40] Jolivet, J.P. Froidefond, C. Pottier, A. Chanéac, C. and Cassaignon, S. (2004) *Size tailoring of oxide nanoparticles by precipitation in aqueous medium*, A Semi-Quant Model J Mater Chem 14: 3281–3288.

[41] Slomberg, D.L. and Schoenfisch, M.H. (2012) *Silica nanoparticle phytotoxicity to Arabidopsis thaliana*, Environ Sci Technol 46(18):10247–10254.

[42] Hayat, M.A. (1974) *Principles and Techniques of Scanning Electron Microscopy*. Biological Applications, Vol. 1, Van N.R. Company, New Jersey, USA.

[43] Honary, S. and Zahir, F. (2013) *Effect of zeta potential on the properties of nano-drug delivery systems*, Trop J Pharmaceut Res 12: 255–264.

[44] Orts-Gil, G. Natte, K. Drescher, D. Bresch, and H. Mantion, A. (2011) *Characterization of silica nanoparticles prior to in vitro studies: from primary particles to agglomerates*. J. Nanopart Res 13:1593–1604.

[45] Barreto, Â. Luis, L.G. Girão, A.V. Trindade, T. Soares, A.M. and Oliveira, M. (2015) *Behavior of colloidal gold nanoparticles in different ionic strength media*, J. Nanopart Res 17:1–13.

[46] Warren, B.E. (1969) *X-ray Diffraction*, Courier Dover Publications Reprint of the Addison-Wesley Publishing Company, Inc., Reading Massachusetts, USA.

[47] Jain, D. Daima, H.K. Kachhwaha, S. and Kothari, S. (2009) *Synthesis of plant-mediated silver nanoparticles using papaya fruit extract and evaluation of their anti-microbial activities*, Digest J. Nanomater Biostruct 4: 557–563.

[48] Kumar, V. Guleria, P. Kumar, V. and Yadav, S.K. (2013). *Gold nanoparticle exposure induces growth and yield enhancement in Arabidopsis thaliana*, Sci. Total Environ 461: 462–468.

[49] Syu, Y.Y, Hung, J.H. Chen, J.C. and Chuang, H.W. (2014) *Impacts of size and shape of silver nanoparticles on Arabidopsis plant growth and gene expression*, Plant Physiol Biochem 83: 57–64

[50] Zhang, Y. Ren, L. Wang, S. Marathe, A. Chaudhuri, J. and Li, G. (2011)

Functionalization of grapheme sheets through fullerene attachment, J. Mater Chem. 21: 5386–5391.

[51] Song, L. Connolly, M. Fernández-Cruz, M.L. Vijver, M.G. and Fernández, M. (2014) *Species-specific toxicity of copper nanoparticles among mammalian and piscine cell lines*, Nano-toxicology 8: 383–393.

[52] Schmid, G. (2011) *Nanoparticles: From Theory to Application* Wiley-VCH Weinheim, Germany.

[53] Greulich, C. Kittler, S. Epple, M. Muhr, G. and Köller, M. (2009) *Studies on the biocompatibility and the interaction of silver nanoparticles with human mesenchymal stem cells (hMSCs)*, Lange beck's Arch Surge 394: 495–502.

[54] Mahl, D. Diendorf, J. Meyer-Zaika, W. and Epple, M. (2011) *Possibilities and limitations of different analytical methods for the size determination of a bimodal dispersion of metallic nanoparticles*, Colloids Surf A Physicochem Eng Asp 377: 386–392.

[55] Ayyub, P. Palkar, V. Chattopadhyay, S. and Multani, M. (1995) *Effect of crystal size reduction on lattice symmetry and cooperative properties*, Phys Rev B 51:6135

[56] Picó,Y. and Blasco, C. (2012) *Nanomaterials in food, which way forward?* Analys Risk Nanomater Environ Food Sump 59:305

[57] Raliya, R. Tarafdar, J. (2013) *ZnO nanoparticle biosynthesis and its effect on phosphorous-mobilizing enzyme secretion and gum contents in Clusterbean (Cyamopsis tetragonoloba L.)*, Agric Res 2: 48–57.

[58] Tarafdar, A. Raliya, R. Wang, W.N. Biswas, P. Tarafdar, J. (2013) *Green synthesis of TiO_2 nanoparticle using Aspergillus tubingensis*, Adv. Sci. Eng. Med 5: 943–949.

[59] Siddiqui, M.H. and Al-Whaibi, M.H. (2014) *Role of nano-SiO_2 in germination of tomato (Lycopersicum esculentum seeds Mill*, Saudi J. Biol. Sci. 21: 13–17.

[60]Lin, D. and Xing, B. (2007) *Phytotoxicity of nanoparticles: inhibition of seed germination and root growth*, Environ Pollut 150: 243–250.