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The biological synthesis of anatase titanium dioxide nanoparticles using *Arnicae anthodium* extract

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The aim of this study was to presentation of the novel ecofriendly method of synthesis of anatase titanium dioxide nanoparticles. In this work, TiO_2 nanoparticles were synthesized using *Arnica montana L*. by reduction method. The prepared titanium dioxide nanoparticles were characterized using Ultraviolet–Visible Spectroscopy (UV-VIS), Total Reflection X-Ray Fluorescence Analysis (TXRF) and Fourier-Transform Infrared Spectroscopy (FTIR). The morphology of the synthesized titanium dioxide nanoparticles was verified by SEM-EDS. X-ray diffraction (XRD) was used to calculate crystallite size. The size of titanium nanoparticles was about 30 nm.

Also, this work presents alterative to chemical methods of synthesis titanium dioxide nanoparticles.

Key words: nanotechnology, nanoparticles, titanium dioxide

INTRODUCTION

Nanotechnology is emerging as a rapidly growing field with its application in science and technology for the purpose of manufacturing new materials at the nanoscale level [1]. In results, nanotechnology has gained massive applications in the fields of biology and pharmacology [2]. Nanoparticles have become significant in recent years and have created an impact in the areas of chemical, energy, electronic, and biological sciences. Although such particles can be synthesized by physical, chemical and biological methods, in the past few years, the last option has gained importance [3]. Preparation of nanoparticles using green technologies is advantageous over chemical agents due to their less environmental consequences. In the biosynthesis method, extracts from plant may act both as reducing and capping agents in synthesis of nanoparticles [4].

TiO_2 is one of the most widely used material owing to its many applications in the field of photocatalysis, gas and humidity sensors, water treatment, selfcleaning, solar cells, photo electrochemical cells, protective coatings on optical elements and bioanalytical chemistry [5]. However, the performances of TiO_2 is strongly influenced by the crystalline structure, the morphology and the size of the particles [6]. Also, among various phases of titania reported, anatase shows a better photocatalytic activity and antibacterial performance [7]. Besides, titanium oxide (TiO_2) is still believed as the most efficient and environmentally [8. TiO_2 nanoparticles have been synthesized using natural products like *Nyctanthes arbortristis* extract, *Catharanthus roseus* aqueous leaf extract, *Eclipta prostrate* aqueous leaf extract and *Aspergillus flavus*. So there is a pressing need to develop clean non-toxic and eco-friendly procedures for the synthesis and assembly of nanoparticles [9].

Arnica montana L. (*Asteraceae family*) is a rhizomatous herbaceous perennial herb originated from the high mountains of the Alps and the Carpathians. Arnica is a medicinal plant widely used as an herbal remedy as well as in cosmetic and liqueur industry [10]. *Arnica montana L.* contains volatile oils, terpenoides, sesquiterpenes lactones, flavonoides [11, 12]. Sesquiterpene lactones are the most active components [13]. In this study TiO_2 nanoparticles were synthesized using *Arnica montana L*. by reduction method.

EXPERIMENTAL

Synthesis of anatase titanium dioxide nanoparticles

5 g powder of *Arnicae anthodium* was boiled for 40 minutes at 80°C with 200 ml of doubly distilled water. 30 ml of the aqueous extract of *A. anthodium* was added in 30 ml of 5mM TiO_2 at room temperature. This solution was stirred at room temperature for 24 h. After this time the solution was heated to 100 °C for the time 30 minutes. The solution was filtered by 0,45 μm Milipore membrane filter and followed by 0,2 μm Millipore membrane filter. TiO_2 nanoparticles solution was stored during 24, 48, and 72 hours.

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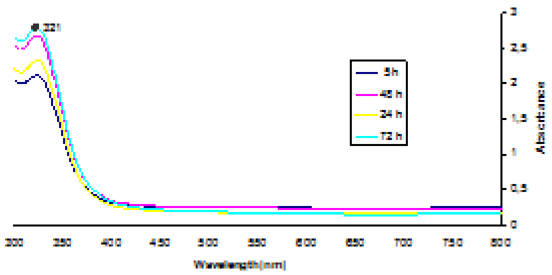

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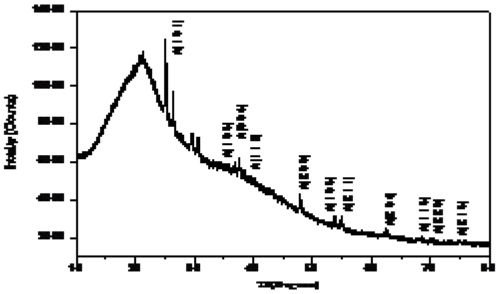

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Fig. 1. a) UV-Vis absorption spectrum of TiO_2 nanoparticles from water extract of *A.anthodium* b**)** XRD patterns of synthesized TiO_2 nanoparticles

Characterization of anatase titanium dioxide nanoparticles

The optical property of TiO_2 nanoparticles was analyzed UV-VIS absorption spectroscopy (spectrophotometer Cary E 500) in the range 300 nm-800 nm. The morhology of TiO_2 nanopraticles was examined scaning electron microscopy (SU3500, Hitachi with spectral imaging system Thermo Scientific NSS (EDS), the tape of detector (BSE-3D), acceleration voltage (15.0kV), working distance (11,6 mm), the pressure (in the case of a variable vacuum conditions)(40 Pa). The binding properties of TiO_2 nanoparticles were investigated by FTIR analysis. Characterization involved Fourier transform infrared spectroscopy (FTIR) analysis of the dried powder of synthesized TiO_2 nanopraticles by Perkin Elmer Spectrum 1000 spectrum in attenuated total reflection mode and using spectral range of 4000–400 cm−1 with a resolution of 4 cm−1. To confirm the presence of TiO_2 nanoparticles using X-ray fluorescence spectrometer Bruker S2 TXRF Picofox (50 kV and 600 uA). X-ray diffraction (XRD) studies of the nanoparticles were carried out using a BRUKER D8 ADVANCE brand *-2* configuration (generator-detector) x-ray tube copper S = 1.54 A and LYNXEYE PDS detector. The size of particles estimation was performed by the Scherrer's formula.

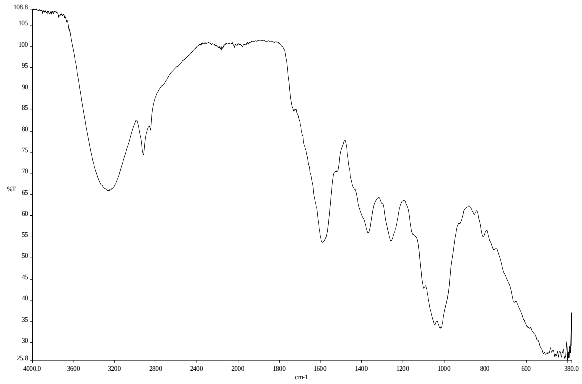


Fig. 2. FTIR spectrum of TiO_2 nanoparticles from water extract of *A. anthodium*

RESULTS AND DISCUSSION

UV VIS and XRD analysis

The absorption spectra were taken at different time intervals. Moreover, 5, 24, 48 and 72 hours after preparation of the solution, absorbance was measured. Figure 1a shows the UV-vis absorption spectrum of TiO_2 nanoparticles between 300 and 800 nm. Figure 1b presents XRD patterns of TiO_2 nanoparticles from water extract of *A. anthodium.*

The peak was observed at 321 nm which is a characteristic band for TiO_2 nanoparticles. According to Silija et al. [14], the intense band with absorption maxima around 300 to 350 nm is associated to the $Ti^{4+}O^{2-}$charge-transfer, corresponding to the electronic excitation from the valence band to the conduction band. The UV–Visible spectra of the resulting solutions were monitored as a function of reaction time. Also, it is observed the increase in absorbance in time. UV-Vis absorption spectrum is compatible with X-ray diffraction profile of titanium nanoparticles. Figure 1b shows the X-ray diffraction profile of titanium nanoparticles. The size of titanium nanoparticles was obtained by Debye-Scherrer's formula given by equation

$D=K\lambda/(\beta\cos\theta)$

where D is the crystal size;

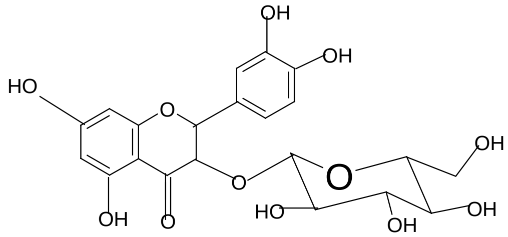
λ is the wavelength of the X-ray radiation (λ=0.15406 nm) for CuKα;

K is usually taken as 0.89;

and β is the line width at half-maximum height [15].

Also, the crystallite sizes were calculated using Scherrer's formula applied to the major intense peaks and found to be the size of 30 nm. TiO_2 nanoparticles synthesized from water extract of *Arnicae anthodium* shows peaks corresponds to the planes at 2θ=25,27° (101), 2θ=36,70° (103), 2θ

=37,80° (004), 2θ = 41, 25° (112), 2θ =47,90° (200), 2θ=53,59° (105), (211), 2θ =62,36° (204), 2θ =54, 39° (211), 2θ =56,64° (220), 2θ = 75,01° (215) indicate anatase form.



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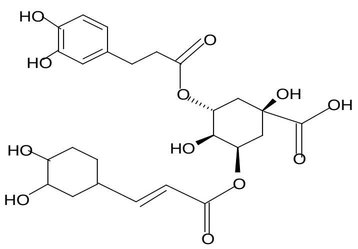

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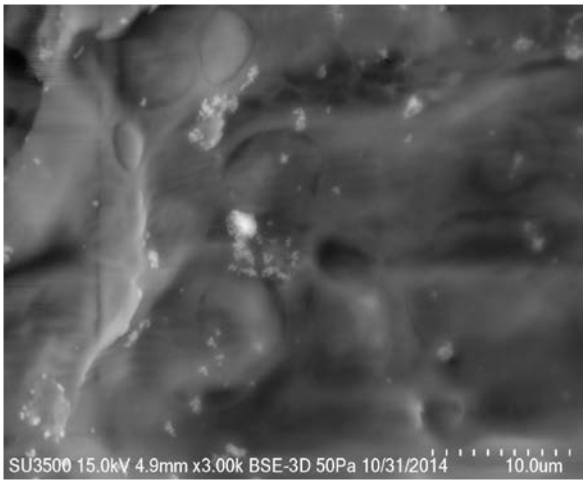
Fig. 3. The structure of a) quercetin 3-*O*-glucuronic acid and b) 3,5-dicaffeoylquinic acid

FTIR analysis

FTIR spectrum involves the correlation of the absorption bands (vibrational bands) with the chemical compounds in the sample. In effect, the biomolecules present in plant extracts that are responsible for the reduction and stabilization processes of the green synthesis of nanoparticles can be identified [16]. Also, FTIR spectroscopy was used to determine different groups on *A. anthodium* water extract and predict their role in nanoparticle synthesis (Figure 2). The strong IR bands it is observed at 3269 cm-1, 2924 cm-1, 1591 cm-1, 1369 cm-1, 1258 cm-1, 1020 cm-1 and 416 cm-1. The peaks at 1369, 1258 cm−1 and 1020 cm−1 may be attributed to –C–O and –C–O–C stretching alcohols, carboxylic acids, esters and ethers modes. The band at 1591 cm-11 indicate presence of C=C characteristic of saturated hydrocarbons Strong absorption peaks at 3269 and 2924 cm−1 correspond to -OH stretching and aliphatic methylene group -C-H stretching. The IR band observed at 416 cm-1 indicate presence of TiO_2 nanparticles.



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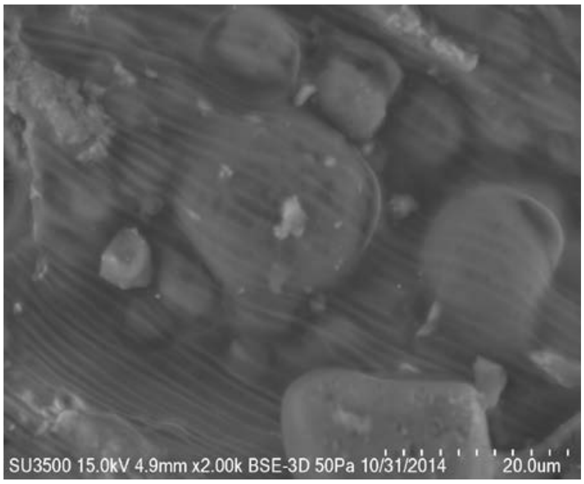

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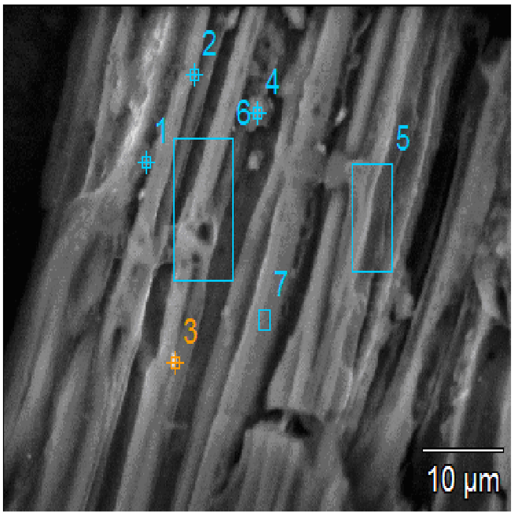
Fig. 4. SEM of TiO_2 nanoparticles from water extract of A. anthodium a) the scale bar is 10 µm, b) the scale bar is 20 µm

Also, FTIR analysis confirmed the presence of groups characteristic for flavonoids and phenolic acids. According to Ganzera et al. [17] the most dominant flavonoid was found to be quercetin 3-*O*-glucuronic acid, whereas 3,5-dicaffeoylquinic acid was the major phenolic acid. These compounds show significant antioxidant and antibacterial activities. Figure 3 presents the structure of quercetin 3-*O*-glucuronic acid and 3,5-dicaffeoylquinic acid which are present in extract of *A. anthodium*.

SEM analysis

The morphology of TiO_2 nanoparticles from water extract of *A. anthodium* was verified by SEM-EDS. Figure 4a, 4b and 5a show the SEM images of TiO_2 nanoparticles. The size of TiO_2 nanoparticles was about 100 nm. The larger sizes are results of agglomeration of the particles. In result, agglomeration makes it difficult to study individual nanoparticles. EDS profile of the TiO_2 nanoparticles the presence of elemental metal signal was confirmed. Figure 5b presents four peaks between 0,5 and 5 kV which are characteristic for anatase for of TiO_2 nanoparticles.



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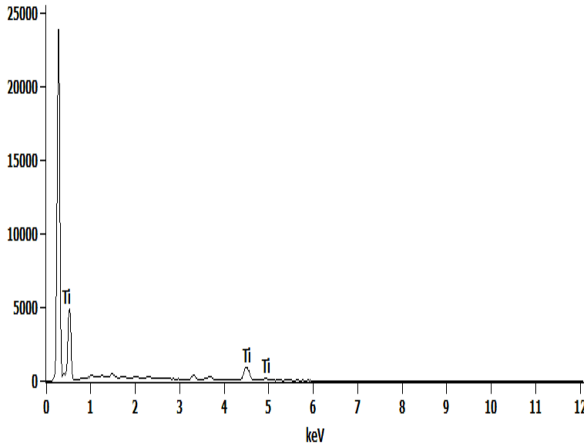

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Fig. 5. a) SEM and b) EDS profile of TiO_2 nanoparticles from water extract of *A. anthodium*

TXRF analysis

The sample was determined by X-ray fluorescence spectrometer TXRF Bruker S2 Picofox, operated at 50 kV and 600 µA. The strong signal at 4,62 5 keV suggest presence of titanium nanoparticles in water extract of *A. anthodium.* Figure 6 presents TXRF spectrum of TiO_2 nanoparticles from water extract of *A. anthodium.* Also, TXRF analysis confirmed the presence of anatase TiO_2 nanoparticles.

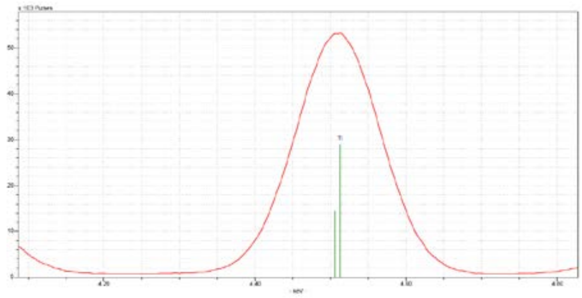

Fig. 6. TXRF spectrum of TiO_2 nanoparticles from water extract of *A. anthodium*

CONCLUSIONS

In the study, ecofriendly synthesis of anatase form of titanium dioxide nanoparticles in low temperature was presented. Titanium dioxide nanoparticles were characterized using UV-VIS, TXRF, FTIR and XRD. The morphology of titanium dioxide nanoparticles was verified by SEM-EDS. Anatase phase exhibits the highest photocatalytic activity. Such properties have led to use of nano-TiO_2 for a wide variety of applications. The water extract of *A. anthodium* could be used instead of chemical solvents. Also, this is eco-friendly and cheap method for the synthesis of photocatalytic form of titanium dioxide nanoparticles.

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БИОЛОГИЧНА СИНТЕЗА НА НАНОЧАСТИЦИ ОТ ТИТАНОВ ДИОКСИД (АНАТАЗ) ЧРЕЗ ЕКСТРАКТ ОТ *Arnicae anthodium*

Р. Добруцка

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(Резюме)

Цел на настоящата работа е да се представи нов, екологически съвместим метод за синтез на наночастици от титанов диоксид (анатаз). Наночастиците от TiO_2 са синезирани с помощта на *Arnica montana L*. чрез редукция. Получените частици са охарактеризирани чрез UV-VIS-спектроскопия, рентгеноструктурен флуоресцентен анализ с пълно вътрешно отражение (TXRF) и ИЧ-спектроскопия с Fourier-трансформация (FTIR). Морфологията на наночастиците от синтезирания титанов диоксид е потвърдена чрез сканираща електронна микроскопия (SEM-EDS), рентгеноструктурен анализ (XRD), като са определени и размерите на частиците (около 30 nm). Освен това, работата предлага и други химични методи за синтезата на наночастици от титанов диоксид.