MANUFACTURING OF NANO HYBRID SOL- GEL COATING AND STUDYING THE RAMAN STRUCTURAL PROPERTIES, MORPHOLOGICAL CHARACTERISTICS AND THEIR APPLICATION AS ANTIOXIDANT FOR CONTAMINATE ROHDAMINE B (RhB) PIGMENT

Z. N. JAMEEL[a,*], M. R. HUSSAN [a]
[a] *Communication Engineering Department, University of Technology, Baghdad, Iraq*

Titania have been extremely investigated for employing in the paint fields due to its importance as pigments. Therefore, TiO_2 particles are perfect candidates in the paint industry. The nanoparticles were mixed with coating solution (i.e. hybrid sol-gel and organosilicate nanoparticles (OSNP) at concentration (1%wt) for both anatase and rutile. Films were prepared by spin coating method which has been studied by the (Electron Dispersive X-ray Spectroscopy) (EDS)/ (Scanning Electron Microscope) to define the components of concentrations. Results of Raman Spectroscopy to distinguish between crystalline phases, Raman shift resulted for anatase about (142.1, 411.1, 547.4 and 669.6) cm^{-1}, rutile (190,272,452 and 616) cm^{-1}. Additionally, the films were studied the thickness and refractive index (n) by Spectroscopic Ellipsometer(SE) for nano-anatase (1%wt) film thickness (128)nm and n equal (2.25), for nano-rutile films thickness (313.5)nm and n equal (2.5). Profilometer investigated the coating topography to demonstrate the Root Mean Square (RMS) to identify the roughness which increased by increasing particle size. Fourier Transform Infrared (FTIR) analysis showed the strong bonds of the nanoparticles in frequency region between (400-1000) cm^{-1} corresponds to Ti-O-Ti, also the bands at cm^{-1} were for a symmetric Si-O-Si stretching and vibration, respectively. Self-cleaning tests on the films were performed using Rhodamine B (RhB) as an antioxidant indicator.

(Received December 14, 2019; Accepted January 29, 2020)

Keywords: Tio_2 Nanoparticles, Raman Spectroscopy, Hybrid Sol- Gel , Spectroscopic Ellipsometery, Rhodamine B (RhB)

1. Introduction

Hybrid Solution- gel coating means the composition of more than one substance, antibacterial or prepared laboratory coating synthesis by solution-gel method, every substance in this paint necessary in composition of this paint [1,2]. TiO2/SiO2 hybrid solution-gel consist of TiO2 and SiO2, the effect importance of TiO2 in paint as pigment and photocatalyst, one of the basic prerequisites for getting perfect stability and dispersant is the preparation of the balanced hydrosol, in addition to robust laboratory paint [2]. For that, Silica is considered to be one of the convenient modifiers for preparing hybrid solution-gel paint, because of its real warm and thermo oxidative stability, prime humidity impedance, incomplete ionic nature, less surface ability, and free alternation of chains about Si O bonds, great hydrophobicity, compressively and doping activity. In any case, silicones have poor mechanical characteristics [3].

The conjunction of silicone in hybrid solution-gel outcomes in the upgrade of physicochemical characteristics, thermal stabilization and anti-corrosive properties, that incorporate a valid processibility, adaptability, sturdiness, solidness, UV, substance and climate impediment alongside thermo oxidative. Solution-gel based on silicate substances are useful concerning this matter since a suitable control is available on locale elective of regular dissemination of TiO2 within the silicate matrices with clear stabilization [4]. Solution-gel inorganic system are supplemental highly inactive and indispensible, besides to thermal stability [5].

* Corresponding author: 11042@uotechnology.edu.iq

Solution-gel chemical explained the preparation of substances by hydrolysis and (poly) condensation of adequate molecular prospectors, which introduces a straightforward and cheap significances for manufacturing inorganic coating [6]. Yet synthesis elastic and durable coating by utilizing the intended technique stays a serious difficulty. The most widespread issue with solution-gel based process for preparing hybrid solution-gel paint is drying–induced retraction and subsequent cracking [7]. In addition, these are so liable to humidity and substances synthesis typically friable unless polymeric additives, which may seriously overlap with the substances, intended functionality. Poly MethylSilsesQuioxane (PMSSQ) OSNPs that is able to be utilized in corporation with solution-gel techniques to investigate Nano-composite laboratory paint substances with not advanced ability to be tuned with their physical and chemical properties. PMSSQ NPs solution-gel composite as a new host matrix for the solidification of convenient additives for different implementations [8]. Within different substances that are able to be in combination with laboratory paints solution AminoPropylTriEthoxySiline (APTES) to enhance the cross-linking of the solution-gel matrix with the PMSSQ NPs thereby reducing phase separation of the nanoparticles upon curing and producing in a perfect cross-linked coating at minimum temperatures [9]. Some processes have been implemented, inclosing enhancement the titanium dioxide surface by hydrophilic polymer dispersants. Clear surface occurrence, perfect chemical resistance, reduce in ability to be permeated to destructive environment, therefore, clear corrosion characteristics, optical clarity, increase in modulus and thermally stable, simple for cleaning the surface, anti-skid, anti-fogging, anti-fouling and anti-graffiti characteristics, perfect thermal and electrical conductivity, perfect retention of gloss and other mechanical characteristics such as scratch resistance, anti-reflective in nature, chromate and lead free, clear adherence on various kind of substances. Nano-coating can be related with self-cleaning painting [10, 11].

2. Experimental

2.1. Materials and methods

a. Laboratory paint manufacturing (hybrid solution-gel with OSNPs)

TetraEthylOrthoSilicate (TEOS), Ti Ethoxide (TEOT), Hydrochloric Acid and Propylene Glycol Monomethyl Ether Acetate (PMA) were utilized for making the combination of Laboratory coating using glove box in a clean room with ratios 10:18:1:12, respectively [3]. The Nitrogen was utilized in this reaction for reducing humidity. The previous reaction must stay under using magnetic stirrer for (3-4) days for producing a pure solution. After that, filtering the hybrid solution- gel, and OSNPs, from nanoparticles of Poly Methyle SilseS Quioxane (PMSSQ) in PMA, has been supplemented, APTES (2% by mass) has been supplemented to a bulk formulation drop wise with the existence of magnetic stirrer at 80˚C for 5 minutes for further activation, cross linking and cohesion [8,12].

b. Combination of the Nanoparticles into the synthesis Lab. paint

In coating solutions various concentrations of TiO2 NPs (10 wt%, and 1 wt%) with APTES at 80˚C are synthesized. In ethanol TiO2 nanoparticles are initially re-dispersed**.** A filter is made with PTFE 0.2 μm titan 3 for the painting solution before coating. Thin films are synthesis by using spin coater technique at alternative concentrations of TiO2 nanoparticles (1wt%. and 10wt %) added to the bulk formulation and 2% APTES under using magnetic stirring. The manufactured thin films are desiccated after using spin coater technique via locating them above a hot plate at 70 ˚C for 5 min. After that, coated both of the Si and glass samples with hybrid solution-gel and OSNPS (bulk formulation) with and without TiO2 nanoparticles, are synthesized by the Spin Coater process under vacuum and Nitrogen in a clean room.

c. Cleaning, cutting and preparing samples

Acetone, Methanol and De-ionized water (AMD) method was used for cleaning Silicon and glass samples, the cutting and cleaning of Si substrates detached from glass substrates, samples has been cleaned utilizing acetone to five minutes for removing dust and organic, moreover, swilled with methanol for removing organics. Then, a De-ionized water rinse and drainage were used for removing remaining methanol. The intended process, as well has been utilized for substrates on glass. Particularly, for the Si substrates, after AMD process, HF (48% diluted to a ratio 1:10) was employed for removing the layer oxide. At last, the Si substrates were desiccated using Ni [8].

d. Characterization of Coating Films TiO2/ SiO2

The morphological characterization of the films Scanning electron microscope with EDX (EDX/SEM), also thickness and refractive index of coating films were studied by Ellipsometery. Films roughness measured by Profilometer. The structural and spectral properties were studied using Raman spectrometer (Renishaw Invia, Germany). FTIR spectroscopy has been employed to study the related functional groups of TiO2 NPs and prepared films surfaces (hybrid solution-gel and bulk formulation) and chemical distribution of TiO2 NPs was mixed with dried KBr powder and pressed to form the semitransparent pellets.

3. Results and discussion

In this paper, Electron Dispersive X-ray Spectrometer (EDS) spectrum results had been collected. It has been separated in a way where the white assembles localized upon the Titanium Dioxide surface includes basically Si, Ti, Cl, C and O. Besides, composites of the specimen were shown by the additional EDX (XRD pattern and the EDX spectra) and defined the synthesized films contain the materials of hybrid solution-gel, OSNP and TiO2 nanoparticles. Homogeneity main factor in paint application to be uniform and well coating, also the observed results are agreed with the research introduce by Jingli Yue *et. al.* [13]. Figure 1 shows 1%wt concentration for anatase TiO2 NPs into hybrid solution-gel (Lab. paint). Figure 2 explain rutile NPs at 1%wt.

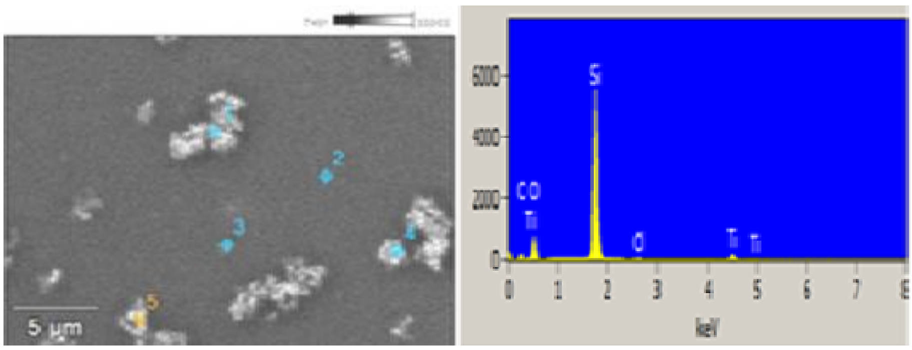


Fig. 1. Scanning Electron Microscope image& the Electron Dispersive X-ray Spectrometer of the manufactured TiO_2/ SiO_2 hybrid Sol-Gel with Anatase NPs at 1% wt .

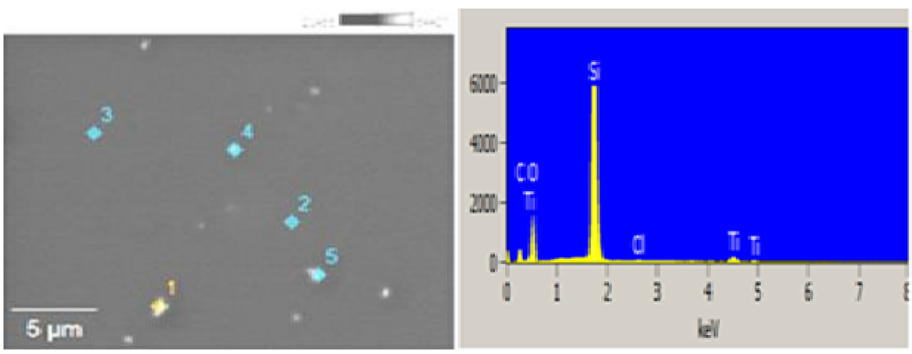


Fig. 2. Scanning Electron Microscope image& the Electron Dispersive X-ray Spectrometer of the manufactured TiO_2/ SiO_2 hybrid Sol-Gel with Rutile NPs at 1% wt .

Raman spectrum of TiO2 after calcination at two temperatures 500˚C and 900°C. The amorphous TiO2 does not possess quite determined Raman peaks. Intensity peaks concerning the anatase and rutile are described by A and R, sequentially. While the specimen is calcined at 500 °C, the Raman spectrum introduces four characteristic peaks with wave numbers or Raman shift of about (142.1, 411.16, 547.44 and 669.66)cm-1; these peaks are able to be attached with the anatase phase. There are no peaks either attached to rutile or other TiO2 polymorphs were spotted for this specimen. When the substance increasing calcination temperature, the anatase phase is incompletely changed to rutile. The optimal intensity peaks of the rutile phase (190, 272, 452, and 616) cm-1 have been noticed and control the Raman spectrum for the specimen calcined at 900 °C. Phase variations are often obviously distinguished within the spectrum; however other structural variation such as polymorphism can detect themselves just through very accurate spectral variations. Results for anatase and rutile show in Fig. 3. These results are in agreement with those reported by Dong Fang *et. al.* [14].

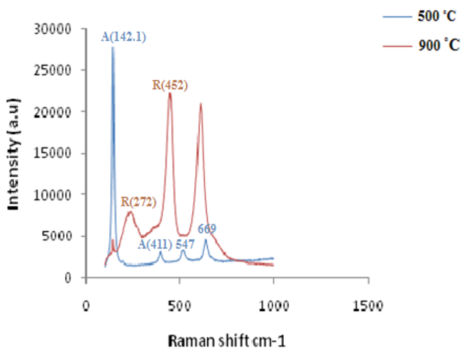


Fig. 3. Raman modes of anatase and rutile phases at 500˚C and 900˚C respectively.

Coating solution films deposited on silicon (n-type) substrates were studied the surface topography and morphology of the hybrid solution-gel and bulk formulation films with nano-TiO_2 as additive into laboratory paint (coating solution) with two phases as observed from the optical profilometer micrographs, proves that the grains are uniformly distributed. Surface characteristic is important for applications such as paint [15, 16]. From the topographic images it can be seen that the films deposited at room temperature and heating treated at 80˚C on hot plate. The RMS roughness also increased with increasing substrate temperatures (T_s) and particle size of additive nanoparticles. Surface area has been increased with particle size decreases for nanoparticles. Figure 4 shows bulk formulation, APTES surface roughness and surface area (0.287 mm^2). Figure 5 photograph illustrated Bulk formulation, APTES in addition to anatase TiO_2 at concentration 1%wt and Figure 6 displays the roughness shown in figure and surface area (3.7 mm^2) for films coated by Bulk formulation, APTES and Rutile nano-TiO_2 at concentration 1%wt.

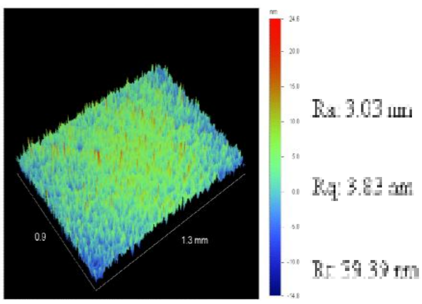


Fig. 4. Profilometer image of Bulk formulation (hybrid sol-gel and OSNP) and APTES.

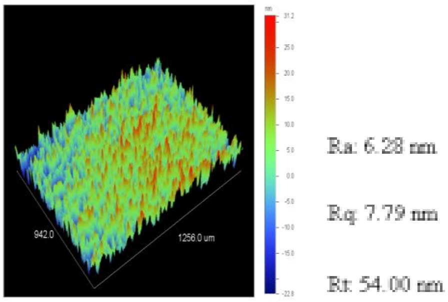


Fig. 5. Profilometer image for Bulk formulation, APTES and 1%wt. anatase TiO_2 NPs.

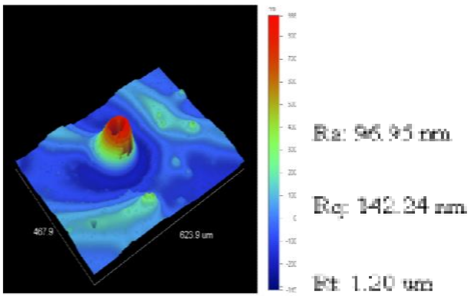


Fig. 6. Profilometer image for Bulk formulation, APTES and 1%wt rutile TiO_2 NPs.

Researchers have built a physical model in order to characterize physically prospective bulk formulation and TiO_2 thin films, characterization for bulk formulation with APTES the thickness of film was 57 nm with refractive index 1.83 on the other hand, the thickness of bulk formulation with APTES and incorporating anatase TiO_2 nanoparticles with two concentration (1%wt) was (128) nm, respectively and refractive index (2.25). For nano-rutile thickness measurements indicated in the range of (313.5) nm at 1%wt from concentration, and refractive index in the range of (2.5), previous results of the prepared films with TiO_2 nanoparticles possess a refractive index larger than the rest of the films with just bulk formulation with APTES.

The FTIR spectra of TiO_2/SiO_2 hybrid solution-gel and TiO_2/SiO_2 bulk formulation are shown in figures (7a) and (7b). Regarding the overview, the featured band for Ti-O-Si vibration between (860-1000) observed in both figures of TiO_2/SiO_2 solution-gel. The bands at (1420, 1440) cm^{-1} for both figures are assigned to the Ti-O-Ti vibration. Bands at 793 and 1100cm^{-1} are for symmetric Si-O-Si stretching vibration sequentially. It appears that Si can be found as both isolated amorphous SiO_2 and some Ti-O-Si bonds. Furthermore, rising the stabilization and dispersity of TiO_2/SiO_2 solution-gel is based on the existence of chemical bonding between titania and silica.

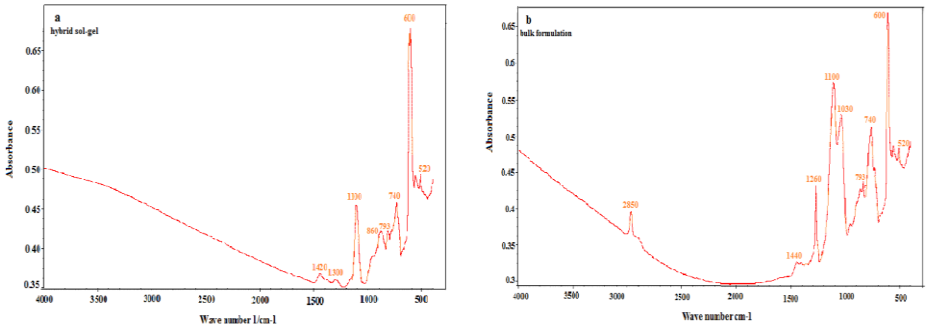
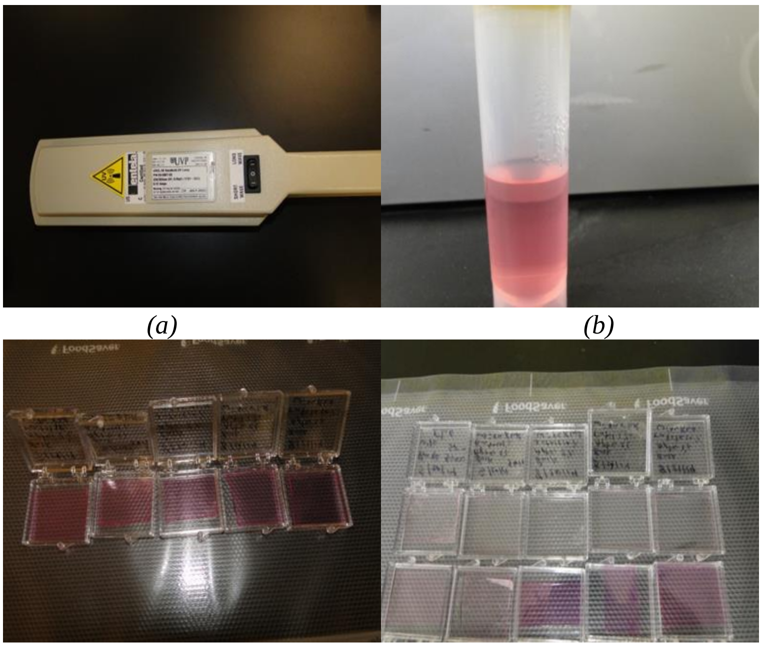


Fig. 7. (a) FTIR spectra of hybrid sol-gel with TiO_2 NPs; (b) hybrid sol-gel& OSNP and TiO2 NPs(Bulk Formulation).

3.1. Antioxidant test

The antioxidant for self-cleaning test utilizing (RhB) pigment as the pollutant indicator [17]. The concentration of 1mg/ml from ethanol (200 proof) dissolving the RhB pigment. A (RhB) coating is applied by using spin coater over the samples (films) after drying. The procedure is refined for other laboratory paint with RhB pigment (1 mg/ml). At last, various conditions with the films (bulk formulation and APTES with and without RhB on glass and Si, bulk formulation, APTES and TiO2 nanoparticles (1 wt%) with and without RhB on glass and silicon, bulk formulation, APTES and TiO2 nanoparticles (10 wt%) with and without RhB on glass and silicon were synthesized. Specimens on Si were synthesized to measure the thickness of the film by ellipsometry. The whole specimens were dried on a hot plate at (70˚C) for (5min) after the laboratory painting with RhB (610) pigment is used. Utilizing UV-lamp irradiation (254 / 365 nm UV, 6 Watt, 115V, 60 Hz) at a short wavelength with films samples painted with RhB pigment (610) as shown in figure 8, the self-cleaning and antioxidant test of TiO2 was demonstrated in terms of photocatalytic activity for the disintegration of the pigment to measure the changing in absorption regarding UV irradiation time[18,19].



(a) *(b)* *(c)* *(d)*

Fig. 8. Image illustrates a): UV lamp, b): RhB Dye as solution, c) & RhB, d) glass samples coated bulk formulation after exposure to UV source.

4. Conclusion

New approach from TiO_2/SiO_2 hybrid solution-gel was synthesized as laboratory paint, and utilizing prepared TiO_2 nanoparticles as an additive in to the laboratory coating for improving their properties. Proved de-polluted and anti-oxidant surfaces test on lab. Paint. The films (Si and glass) have been coated utilizing spin coater technique. The EDS, Profilometer and Ellipsometer measurements were used for showing the concentrations, morphological properties for all materials used for preparing the lab paint, surface topography, roughness and the thickness of the prepared films, respectively, Raman spectra and FTIR results have been demonstrated the structural characteristics and chemical bonds between the lab paint contents (Tio_2/SiO_2) sequentially. Coated films with nanoparticles utilizing Rhodamine B (RhB) pigment as pollution indicator and UV lamp as exposure source, these films have been proved successfully results as an anti-oxidant and self-cleaning films.

Acknowledgements

The authors gratefully acknowledge the support provided by University of Missouri-Columbia, USA, in experimental work. Authors also thank Communication Engineering Department in University of Technology/Baghdad/Iraq for supporting.

References

[1] Y. Zhang, Y. Lia, S.-Yun Fu, J. H. Xinb, W. A. Daoudb, L.-Feng Lia. Polymer **46**, 8373 (2005).
[2] Z. N. Jameel, A. J. Haider, S. Y. Taha. Eng. & Tech. Journal, **32**(3), part (B), 418 (2014).
[3] Z. N. Jameel, A. J. Haider, S. Y. Taha, S. Gangopadhyay, S. Bok, AIP Conference Proceeding **1750,** 020001 (2016).
[4] V. Korampally, V. K Mamidi, B. Harris, K. Gangopadhyay, G. A Baker, S. Gangopadhyay, J. Colloid Interface Sci. **364**, 546 (2011).
[5] A. J. Haider, Z. N. Jameel, I. H. M.Al-Hussaini. Energy Procedia **157**, 17 (2019).
[6] A. J. Haider, Z. N. Jameel, S. Y. Taha, Eng. & Tech. Journal **33**(5) part (B), 761 (2015).
[7] Z. N. Jameel, O. A. Mahmood, F. L. Ahmed, International Journal of Nanoelectronics and Materials **12**(3), 329 (2019).
[8] S. C. Hamm, R. Shankaran, V. Korampally, S. Bok, S. Praharaj, G. A. Baker, J. D. Robertson, B. D. Lee, S. Sengupta, K. Gangopadhyay, S. Gangopadhyay, ACS Appl. Mater. Interfaces **4**(1), 178 (2012).
[9] A. Gupta, V. K. Patel, R. K., Shantanu Bhattacharya. Rev. Adhesion Adhesives **4**(2), 166 (2016).
[10] A. J. Haider, R. Al- Anbari, G. Kadhim, Z. N. Jameel. MATEC Web of Conferences **162**, 05006 (2018**).**
[11] N. M. Bedford, A. J. Steck. Applied Materials Interfaces **2**(8), 2448 (2010).
[12] K. K. Gupta, M. Jassal, A. K. A Grawal, Indian Journal of Fiber& Textile Research **33**, 443 (2008).
[13] J. Yue, Z. Chen, Yifeng , L. Chen, J. Zhang , Y. Song, Y. Zhai. Nanoscale Research Letters **9**, 465 (2014).
[14] D. Fang, K. Huang, S. Liu, J. Huang, J. Braz. Chem. Soc. **19**(6), (2008).
[15] Sulistyani, Proceeding of International Conference on Research, Implementation and Education of Mathematics and Sciences, Yogyakarta State University, 203 (2014).
[16] Z. Pu, Z. Dianmo, L. Zhihong. J. Jiangxi, Chemical Industry **4**, 20 (2004).
[17] E. S. Hadas, H. Mamane. Chemosphere **184**, 1020 (2017).
[18] L. Bergamonti, G. Predieri, Y. Paz, L. Fornasini, P. P. Lottici, F. Bondioli Microchemical Journal **133**, 1(2017).
[19] M. Rochkind, S. Pasternak, Y**.** Paz**.** Molecules **20**(1), 88 (2015).