

THE EFFECT OF COATING IN INCREASING THE EFFICIENCY OF SOLAR CELLS BY USING QUERCETIN POLY AS A DYE

Hardeli^{1,✉}, F. Hijri¹, H. Sanjaya¹, Y.P. Putri¹ and P. Permatasari²

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Padang, Jl. Prof. Dr. Hamka, Padang 25131, Indonesia

²Department of Materials Science and Processing Graduate School of Natural Sciences and Technology, 1-1 Yanagido, Gifu City 501-1193, Japan

✉Corresponding Author: hardeli22@fmipa.unp.ac.id

ABSTRACT

The efficiency obtained by using TiO₂ semiconductors is still low due to interfacial charge recombination. In this research, two coating methods were carried out, namely doping and bilayer using ZnO as a semiconductor to reduce recombination to collect charge and increase the efficiency of Dye-Sensitized Solar Cells. The use of UV-DRS in this study to see the band gap shows a decrease in the band gap after doping and bilayer processes. The XRD used in the study to look at the phase and molecular structure showed that the intensity of TiO₂ was lower due to doping and bilayer. The dye used is Quercetin which is polymerized to increase conjugated bonds. To see the polymerized Quercetin tested using FTIR. In the quercetin crosslinker polymerization process varied to 1.5 ml; 2.5 ml; and 3.5 ml to see how many conjugate bonds are formed so that the efficiency obtained is also high. Efficiency measurement using a multimeter. Based on the results of this study, it was found that the efficiency of solar cells increased. In the doping process, the highest efficiency was 11.3%, while the highest efficiency in the coating process was 9.1%.

Keywords TiO₂ Doping ZnO, TiO₂ Bilayer ZnO, Poly Quercetin, Crosslinker, DSSC, Efficiency

RASAYANJ. Chem., Vol. 16, No. 3, 2023

INTRODUCTION

Dye-Sensitized Solar Cell (DSSC) is a solar cell of the latest generation which is now being developed as an alternative energy. The advantage of DSSC is that it does not require high purity so the required production costs are low. DSSC is composed of a pair of glass electrodes, namely a counter electrode and the working electrode. The working electrode is TCO (Transparent Conducting Oxide) glass with a semiconductor and dye coating.¹ The counter electrode is made of carbon-coated TCO as a catalyst. DSSC has a working principle as an electron transfer reaction.² Titanium dioxide (TiO₂) is the most widely used semiconductor in the manufacture of DSSC solar cells. Titanium oxide (TiO₂) has the disadvantage that the recombination of TiO₂ takes place quickly so photodegradation does not run optimally.³ Titanium dioxide (TiO₂) is the most widely used semiconductor in the manufacture of DSSC solar cells. Titanium oxide (TiO₂) has the disadvantage that the recombination of TiO₂ takes place quickly so photodegradation does not run optimally.^{4,5} To overcome this, modifications such as doping and bilayers are carried out using ZnO semiconductors to increase DSSC efficiency. Doping and bilayer processes can generate an electric field that can separate the electrons at the interface so that charge recombination does not occur.^{6,7,8} Zinc Oxide is used for doping and bilayer because its photovoltaic properties are similar to TiO₂ and the band gap of ZnO (3.17 eV) approaches that of TiO₂ (3.2 eV).^{9,10,11,12} Therefore, in this study, the method of coating TiO₂-doped ZnO and TiO₂ bilayer ZnO was carried out to see the efficiency values obtained. The sensitizer used is an organic dye derived from the flavonoid group which consists of a complex mixture of polyphenolic atoms C, H, and O.¹³ In quercetin there is a double bond between C2 and C3, as well as the hydroxyl group on C4 which plays a role in inhibiting the oxidation process.^{14,15} Quercetin has anti-radical activity influenced by the presence of a hydroxyl group attached to C4. Quercetin has effectiveness in counteracting free radicals because there is an ortho-hydroxy on ring B.^{16,17,18}

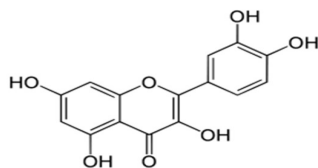


Fig.-1: Quercetin Structure

The quercetin used is polymerized to increase conjugated bonds because the ability of sunlight to convert into electricity depends on the existence of bonds between molecules that cause the electrons in the dye to be excited to the semiconductor. In the crosslinker polymerization process used, namely glutaraldehyde, it is varied to see how many conjugate bonds are formed so that the resulting efficiency is getting better.^{19,20}

EXPERIMENTAL

Instruments and Material

The tools used are a beaker, round bottom flask, stirring rod, spatula, ultrasonic cleaner, measuring flask, oven, hot plate, analytical balance, magnetic stirrer, measuring cup, vacuum, and water bath. The instrument used in this research is the FTIR, multimeter, UV-DRS, and XRD. The materials used in this study were quercetin from sigma-Aldrich, glutaraldehyde, NaOH, distilled water, acetonitrile, Potassium Iodide/I₂, alcohol, indicator paper, TiO₂, PEG, filter paper, aluminum foil, ZnO, 36% HCl p.a. And 34% HCHO.

General Procedure

ITO Glass Preparation

The material used as a substrate for the DSSC is Indium Tin Oxide (ITO) glass. The ITO glass was cut to a size of 1.25 cm x 1.25 cm, then the sides of the glass were sanded. The ITO glass was put into a 200 mL beaker containing 70% alcohol and then put into the ultrasonic cleaner. In the ultrasonic cleaner setting, the time is 60 minutes for the cleaning process. The ultrasonic cleaner is used to remove material that cannot be removed with water.

Preparation of TiO₂ Paste and Doped ZnO

TiO₂ as much as 0.0475 grams and ZnO as much as 0.025 grams mixed in methanol pa 100mL then stirred for 60 minutes until a homogeneous sol is formed. The TiO₂-ZnO sol was sonicated for 30 minutes, then heated for 60 minutes in the oven at 95°C, then evaporated all the solvents were.

Preparation of TiO₂ Paste Bilayer ZnO Paste

0.5 grams of TiO₂ powder was weighed and then dissolved in 4 ml of methanol solution. The mixture was then stirred in a beaker with a magnetic stirrer for 30 minutes at a speed of 300 rpm. The paste that had been formed was then placed in the oven at a temperature of 80°C for 15 minutes, and 0.5 grams of ZnO powder was weighed and then dissolved in 4 ml of methanol solution. The mixture was then stirred in a beaker with a magnetic stirrer for 30 minutes at a speed of 300 rpm. The paste that has been formed is then placed in the oven at a temperature of 80°C for 15 minutes.

Dye Preparation

In the first step, 2.5 grams of Quercetin was weighed and then dissolved in a 500 ml reflux flask containing a mixture of 25 ml (36% HCl and 37% HCHO) and stirred at 200°C for 2 hours. The reflux results were then filtered and washed with aquabidest and dried in an oven at 80°C for 1 hour. In the second the step was weighed 0.25 grams of quercetin formaldehyde and dissolved in 25 ml of 1% NaOH solution with a magnetic stirrer stirred and heated to a temperature of 60-70% continuously, then added (1.5; 2.5; 3.5) ml of the glutaraldehyde crosslinker and the heating temperature were increased to 100°C and then stirred for 1 hour. The resin obtained was cooled at room temperature.

Electrolyte Preparation

This stage begins by preparing 0.498 grams of KI and 0.076 grams of I₂ in 6 ml of acetonitrile in two different beakers. The KI and I₂ solutions were mixed with stirring until they were homogeneous, and then 2.4 grams of PEG were added while stirring until they formed a gel.

Counter Electrode Preparation

Counter electrodes were prepared by coating the ITO glass with carbon. The carbon source used is obtained from the smoke of burning candles. The process of coating carbon on ITO glass is by heating the conductive part of the ITO glass with wax until a black layer is formed. The edges of the ITO glass were trimmed using a cotton bud. The carbon layer is formed according to the size of 1 cm x 1 cm.

Solar Cell Fabrication

After the dssc component is made the dssc is assembled into a sandwich. Efficiency is then measured using a digital multimeter so that the voltage and resistance values are obtained.

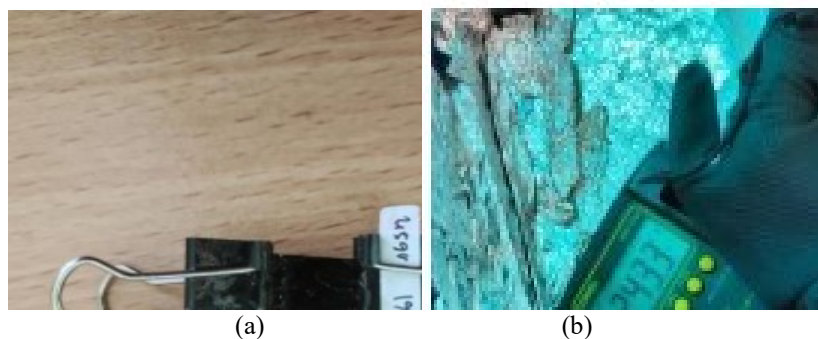


Fig.-2: (a) DSSC That Has Been Prepared (b) The Process of Measuring Efficiency Using a Multimeter

RESULTS AND DISCUSSION

TiO₂ Doping ZnO and TiO₂ Bilayer ZnO

Band Gap Analysis of TiO₂ Doping ZnO and TiO₂ Bilayer ZnO with UV-DRS

The analysis that has been carried out using UV-DRS shows that the band-gap value is decreasing. This can be seen in Fig.-3 below. TiO₂ doping ZnO obtained a band gap of 2.64 eV while TiO₂ bilayer ZnO obtained a band gap of 2.83 eV. The band gap resulting from TiO₂ doping ZnO is smaller due to an increase in the absorption intensity of the visible light region so that it can excite the 3d electrons belonging to Zn to the conduction band of TiO₂.²¹ An increase in the band gap can cause the photocatalyst activity to increase.²² Reducing the band-gap also causes the valence band of TiO₂ to be closer to its conduction band and this will not cause intercharge recombination so that efficiency can increase.²³

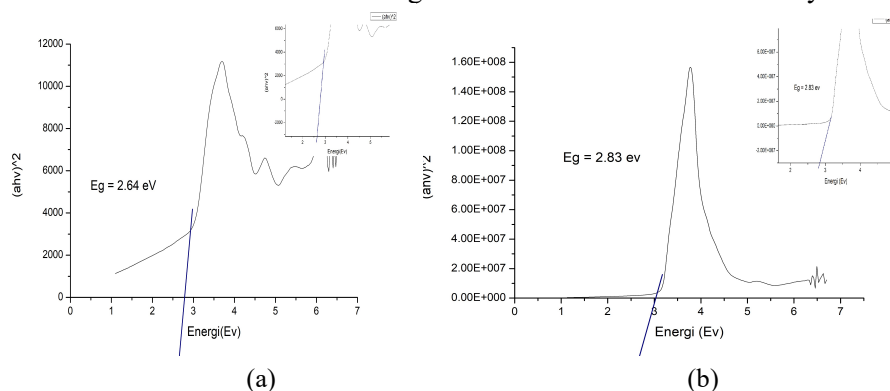


Fig.-3: Graph of Band Gap Values (a) TiO₂ Doping ZnO (b) TiO₂ Bilayer ZnO

From the table, it can be explained that Zinc Oxide plays a major role in reducing the band gap so that it can increase photocatalytic activity and reduce recombination between charges.

Table-1: Band Gap Values of TiO₂ Doped ZnO and TiO₂ Bilayer ZnO

	Band gap Value
TiO ₂ doping ZnO	2.64 eV
TiO ₂ bilayer ZnO	2.83 eV

Characterization of TiO₂ Doped ZnO and TiO₂ Bilayer ZnO by XRD

Characterization with this method was carried out to obtain information about the crystal structure, crystal size, and phases present in TiO₂-doped ZnO and TiO₂ bilayer ZnO.

Table-2: TiO₂ Doping ZnO

2-θ	I/I ₀	FoM	Phase
0.8275	0.7611	0.7692	Anatase
0.7501	0.7710	0.7520	Anatase
0.9784	0.5998	0.7657	Zincite
0.9767	0.6054	0.7580	Zincite

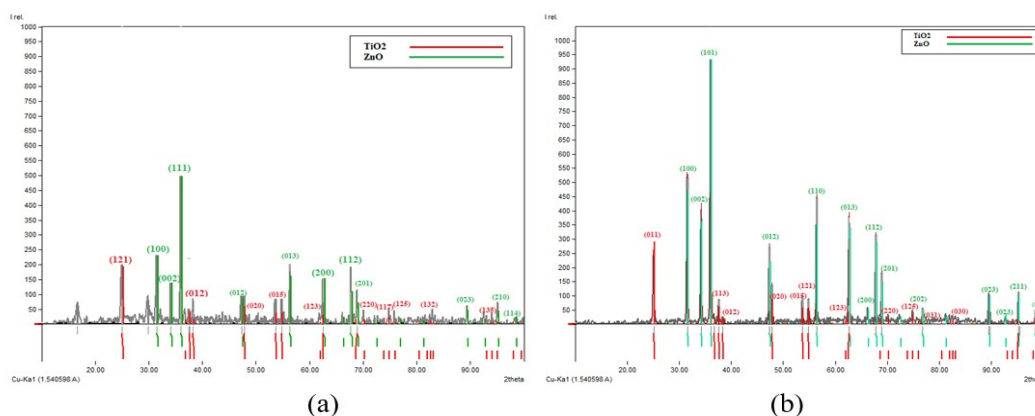


Fig.-4: Difactogram (a) TiO₂ Doped ZnO (b) TiO₂ Bilayer ZnO

Table-3: TiO₂ Bilayer ZnO

2-θ	I/I ₀	FoM	Phase
0.8454	0.7776	0.7755	Anatase
0.8427	0.6757	0.7626	Anatase
0.9784	0.5998	0.7657	Zincite
0.7842	0.6929	0.7288	Zincite

Based on the results of integration outside the area of the sample peaks, the crystallinity of TiO₂ doped ZnO was 41.3% with a crystalline size using the Scherrer equation of 40.2 nm and TiO₂ bilayer ZnO of 45.9% with a crystalline size using the Scherrer equation of 43.8 nm. The size of the crystal in nano form can accommodate more dye due to the small cavity formed, which causes the photocatalytic activity to increase.²⁴ The addition of doping and bilayer causes the TiO₂ intensity to decrease and a new peak appears which indicates that the doping and bilayer process has been carried out successfully.²⁵

Dye Characterization

The dyes used were characterized by a Fourier-transform infrared spectroscopy (FTIR) instrument that aims to see the functional groups and types of polyquercetin bonds (Qp) obtained. The wavelengths used in testing dyes using the FTIR instrument are 500-4000 cm⁻¹. Characterization of Quercetin and Poly Quercetin using the FTIR instrument found three functional groups in pure Quercetin and four functional groups in poly Quercetin.

The characterization results obtained showed quercetin monomer there is a functional group in the form of O-H Phenol in the absorption area of 3289.3 cm⁻¹ where the intensity is strong and the band is wide, the absorption obtained indicates the presence of a group (-OH) attached to an aromatic ring due to intramolecular hydrogen bond vibrations. Quercetin has double-bond conjugates that absorb visible light. This is indicated by the presence of a carbonyl C=O bond in the absorption area of 1024.64 cm⁻¹, and the presence of a carbonyl C=O functional group in the absorption area of 1617.2 cm⁻¹. The polymerized quercetin shows a shift in the peak of the spectrum in the (-OH) namely from the absorption area of 3289.3 cm⁻¹ becomes 3363.9 cm⁻¹ with a strong intensity. In the polymerized quercetin (poly-quercetin) there are C=C aromatic, C=O carbonyl groups, and aromatic C-O.²⁶

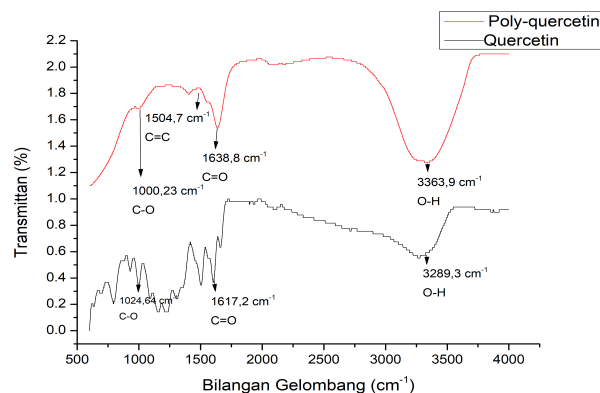


Fig.-5: FTIR Spectra of Poly Quercetin and Quercetin

Table-3: Interpretation of Quercetin and Poly Quercetin Data

No	Functional groups	Data Interpretation		
		Quercetin (cm ⁻¹)	Poly quercetin (cm ⁻¹)	Literature data
1.	O-H	3289.3	3363.9	3500-3000
2.	C=O	1617.2	1638.8	1600-1820
3.	C=C	-	1504.7	1500-1675
4.	C-O	1024.64	1000.23	1000-1100

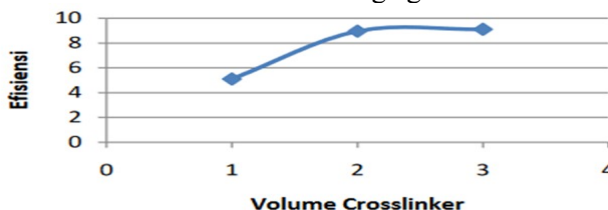
Efficiency Measurement

The previously assembled solar cells were measured for efficiency to determine the effect of polymerization on the ability of solar cells to convert photon energy into electrical energy by measuring current and voltage using a digital multimeter. This solar cell test uses a UV lamp that has 24 watts of power. The test was carried out under a UV lamp by measuring the conductive side of the ITO glass. From the measurement results with a digital multimeter, the efficiency of the doping or bilayer process is obtained. Here are the data obtained.

Table-4: Measurement Results with TiO₂ Bilayer ZnO Crosslinker Variations

Crosslinker Volume	Voltage(V)	Obstacle	Efficiency(%)
1.5 ml	0.173	243.3	5.1
2.5 ml	0.248	285.5	9.1
3.5 ml	0.265	318.9	8.95

Crosslinking agent or crosslinker is one of the factors that influence the polymerization process in the formation of poly-quercetin. The volume of the crosslinking agent affects the formation of poly-quercetin in the polymerization process, the less the volume of the crosslinking agent, the fewer free radicals so that fewer quercetin monomers can be bound to the crosslinking agent.

Fig.-6: Graph of TiO₂ Bilayer ZnO Crosslinker Efficiency Variation

The large volume of the crosslinking agent causes more free radicals so that more quercetin monomers are bound to the crosslinking agent, but the greater volume of the crosslinking agent also does not make the polymer obtained because this is not followed by the addition of an initiator concentration that will open the polymer. The epoxy group in Glutaraldehyde makes the polymer chain length.^{27,28} In the table, it can be seen that the volume of the crosslinking agent is 2.5 ml, which at optimum conditions has the highest efficiency value of 9.1%, while the lowest efficiency value is found in the volume of 1.5 ml of the crosslinking agent with an efficiency value of 5.1%.

In the doping process, the following data was obtained:

Table-5: Measurement Results with TiO₂ Doping ZnO Crosslinker Variations

Concentration	Voltage(V)	Barriers(Ω)	Efficiency(%)
1.5 ml	0.209	339.1	5.3
2.5 ml	0.293	316.0	11.3
3.5 ml	0.270	356.7	8.5

Based on the table, it can be seen that the efficiency of polyquercetin in a volume of 1.5 ml has an efficiency of 5.3%. Efficiency will increase as the volume of crosslinkers used increases. A volume of 2.5 ml is the optimum condition which has an efficiency value of 11.3%. Efficiency decreased at the crosslinker volume of 3.5 ml with an efficiency value of 8.5%

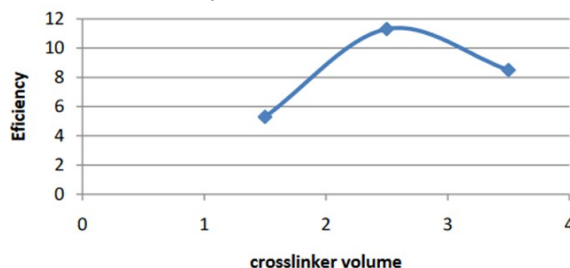


Fig.-7: Graph of TiO₂ Doping ZnO Crosslinker Efficiency Variation

CONCLUSION

Based on the results of the research that has been done are:

- 1) TiO₂ coating with doping and bilayer can reduce TiO₂ band gap and TiO₂ intensity
- 2) Polyquercetin contains many conjugated bonds
- 3) The highest efficiency obtained in the doping process is 11.3%
- 4) The highest efficiency is obtained in the bilayer process at 9.1%

ACKNOWLEDGMENTS

The author would like to thank the UNP Directorate of Research and Community Service for funding this research with the contract scheme number 093/E5/PG.02.00.PT/2022.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

Hardeli  <https://orcid.org/0000-0002-7124-7364>

P. Permatasari  <https://orcid.org/0000-0003-4262-3452>

Open Access: This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

REFERENCES

1. H. P. I. Subriadi, H. Hardeli, *REACTOR: Journal of Research on Chemistry and Engineering*, **4**(1), 2 (2023), <http://dx.doi.org/10.52759/reactor.v4i1.72>
2. R. Damayanti, H. Hardeli., H. Sanjaya, *Sainstek: Jurnal Sains dan Teknologi*, **6**(2), 148(2016), <http://dx.doi.org/10.31958/js.v6i2.114>
3. S. Haffad, K. K. Kiprono, *Surface Science*, **686**, 10 (2019), <https://doi.org/10.1016/j.susc.2019.03.006>
4. W. Amananti,, A. Susanto, A. Sunardi, *Journal of Natural Sciences and Mathematics Research*, **3**(2), 243(2017), <http://dx.doi.org/10.21580/jnsmr.2017.3.2.1960>

5. M. Daous, V. Iliev, L. Petrov, *Journal of Molecular Catalysis A: Chemical*, **392**, 194(2014), <https://doi.org/10.1016/j.molcata.2014.05.020>
6. M. R. D. Khaki, M. S. Shafeeyan, A. A. A. Raman, W. M. A. W. Daud, *Journal of Molecular Liquids*, **258**, 354 (2018), <https://doi.org/10.1016/j.molliq.2017.11.030>
7. G. K. Upadhyay, J. K. Rajput, T. K. Pathak, V. Kumar, L. P. Purohit, *Vacuum*, **160**, 154(2019), <https://doi.org/10.1016/j.vacuum.2018.11.026>
8. D. Tekin, H. Kiziltas, H. Ungan, *Journal of Molecular Liquids*, **306**, 112905(2020), <https://doi.org/10.1016/j.molliq.2020.112905>
9. N. G. Park, M. G. Kang, K. M. Kim, K. S. Ryu, S. H. Chang, D. K. Kim, A. J. x. Frank, *Langmuir*, **20(10)**, 4246(2020), <https://doi.org/10.1021/la036122x>
10. H. Cai, P. Liang, Z. Hu, L. Shi, X. Yang, J. Sun, J. Wu, *Nanoscale Research Letters*, **11**, 1(2016), <https://doi.org/10.1186/s11671-016-1309-9>
11. K. Shen, K. Wu, D. Wang, *Materials Research Bulletin*, **51**,141(2014), <https://doi.org/10.1016/j.materresbull.2013.12.013>
12. A. Ghobadi, T. G. Ulusoy, R. Garifullin, M. O. Guler, A. K. Okyay, *Scientific Reports*, **6(1)**, 30587(2016), <https://doi.org/10.1038/srep30587>
13. G. Torrisi, A. Di Mauro, M. Scuderi, G. Nicotra, G. Impellizzeri, *RSC advances*, **6(91)**, 88886 (2016), <https://doi.org/10.1039/C6RA13773C>
14. Y. J. Li, S. C. Wei, H. W. Chu, H. J. Jian, A. Anand, A. Nain, J. Y. Lai,. *Chemical Engineering Journal*, **437**, 135315(2022), <https://doi.org/10.1016/j.cej.2022.135315>
15. C. Zhao, G. P. Jin, L. L. Chen, Y. Li, B. Yu, *Food Chemistry*, **129(2)**, 595(2011), <https://doi.org/10.1016/j.foodchem.2011.04.072>
16. M. Tohidinia, M. Farsadrooh, S. Bahmanzadeh, N. Sabbaghi, M. J. R Noroozifar, *RSC Advances*, **8(3)**, 1237(2018), <https://doi.org/10.1039/C7RA11132K>
17. S. Bashir, Y. Y. Teo, S. Ramesh, K. Ramesh, *Polymer*, **147**, 108(2018), <https://doi.org/10.1016/j.polymer.2018.05.071>
18. E. Olewnik-Kruszkowska, M. Gierszewska, A. Richert, S. Grabska-Zielińska, A. Rudawska, M. Bouaziz,*Materials*, **14(7)**, 1643(2021), <https://doi.org/10.3390/ma14071643>
19. G. Sharma, J. Park, A. R. Sharma, J. S. Jung, H. Kim, C. Chakraborty, J. S. Nam, *Pharmaceutical Research*, **32**, 723(2015), <https://doi.org/10.1007/s11095-014-1504-2>
20. L. R. Braga, L. M. Pérez, M. D. V. Soazo, F. Machado, *LWT*, **101**, 491(2019), <https://doi.org/10.1016/j.lwt.2018.11.082>
21. C. Pragathiswaran, C. Smitha, B. M. Abbubakkar, P. Govindhan, N. A. Krishnan, *Materials Today: Proceedings*, **45**, 3357(2021), <https://doi.org/10.1016/j.matpr.2020.12.664>
22. S. P. Onkani, P. N. Diagboya, F. M. Mtunzi, M. J. Klink, B. I. Olu-Owolabi, V. Pakade, *Journal of Environmental Management*, **260**, 110145(2020), <https://doi.org/10.1016/j.jenvman.2020.110145>
23. L. M. Anaya-Esparza, E. Montalvo-González, N. González-Silva, M. D. Méndez-Robles, R. Romero-Toledo, E. M. Yahia, A. Pérez-Larios, *Materials*, **12(5)**, 698(2019), <https://doi.org/10.3390/ma12050698>
24. S. Siuleiman, N. Kaneva, A. Bojinova, K. Papazova, A. Apostolov, D. Dimitrov, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **460**,408(2014), <https://doi.org/10.1016/j.colsurfa.2014.01.010>
25. Y. Jing, H. Yin, C. Li, J. Chen, S. Wu, H. Liu, S. Yu, *Environmental Research*, **203**, 111819(2022), <https://doi.org/10.1016/j.envres.2021.111819>
26. N. Sahiner, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **452**, 173(2014), <https://doi.org/10.1016/j.colsurfa.2014.03.097>
27. H. Darmokoesoemo, H. Setyawati, A. T. A. Ningtyas, H. S. Kusuma, *Rasayan Journal of Chemistry*, **10(2)**, 313 (2017), <http://dx.doi.org/10.7324/RJC.2017.1021561>
28. H. Sanjaya, P. Permatasari, I. P. Novita, N. F. Agdisti, R. Luli, L. Yunita, *Rasayan Journal of Chemistry*, **15(1)**, 569(2022), <http://dx.doi.org/10.31788/RJC.2022.1516567>

[RJC- 8143/2022]