

CHITOSAN FILM COMPOSITE WITH SUGARCANE BAGASSE-DERIVED CELLULOSE FILLER FOR METHYLENE BLUE ADSORPTIVE REMOVAL

H. Fathana¹, Rahmi^{2,✉}, M. Adlim^{1,3}, S. Lubis² and M. Iqhrammullah⁴

¹Graduate School of Mathematics and Applied Sciences, Universitas Syiah Kuala, Kopelma Darussalam, Banda Aceh 23111, Indonesia.

²Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Syiah Kuala, Kopelma Darussalam, Banda Aceh 23111, Indonesia.

³Department of Chemistry Education, Faculty of Teacher Training and Education, Universitas Syiah Kuala, Banda Aceh 23111, Indonesia.

⁴Innovative Sustainability Lab, PT. Biham Riset dan Edukasi, Banda Aceh 23243, Indonesia.

✉Corresponding Author: rahmi@fmipa.unsyiah.ac.id

ABSTRACT

Sugarcane bagasse (SCB) was used in this study as a source to produce cellulose (Cell), which was then utilized as filler in modified chitosan (Chi) as a film composite. The purpose of this study was to develop an affordable adsorbent with a high adsorption capability for methylene blue (MB) removal from an aqueous solution, as well as having improved mechanical properties. Based on the result, the tensile strength of chi-cell was increased (from 2.95 kgf/mm² to 14.50 kgf/mm²). Infrared spectra show the intensity of the chi-cell increased in wavenumber 3471 cm⁻¹, associated with higher abundance of OH groups in the chi-cell which act as active site in the adsorptive removal of methylene blue. According to X-ray diffractogram, the presence of cellulose had no significant effect on the crystallinity of chitosan. TGA data show that cellulose improved the thermal resistance of chi-cell. The adsorption performance of chi-cell reached optimum adsorption after 80 minutes at pH 10. Adsorption was shown to be Langmuir isotherm model dependent (adjusted-R² = 0.998), with Q_{max} = 3348.14 mg/g.

Keywords: Chitosan; Sugarcane Bagasse; Cellulose; Adsorption; Methylene Blue.

RASĀYAN *J. Chem.*, Vol. 16, No.2, 2023

INTRODUCTION

Dyeing agents contamination in an aquatic environment is concerning which is majorly contributed by the mismanagement of wastewater effluent from textile industries.^{1,2} Synthetic dye discharge to the environment not only impacts the aquatic organism but also exposes humans to multiple health risks.³ Due to the high cost of wastewater treatment, several textile industries are exploring loopholes in wastewater treatment agency laws to minimize operational expenses.⁴ Naturally, this has attracted the attention of researchers, who are hoping to produce a breakthrough. The development of adsorbents for removing dye waste from the textile industry is continuously increasing. Chitosan is a biopolymer with potential applications as an adsorbent.⁵ The most important characteristic of the adsorbent in the adsorption process is its high adsorption capacity.⁶ Lately, cellulose is in great demand by various industries because of its superior properties as a polymer material.^{3,7} Due to its ability to establish connected network structures via hydrogen bonding, cellulose can impart greater mechanical properties to composites even at low concentrations when integrated into a polymeric matrix.^{8,9} Sukyai *et al.* (2018) studied the influence of bagasse cellulose on protein isolates in the fabrication of films used in food packaging materials, where they reported improved tensile strength from 2.3 mPa to 4.9 mPa. Previously, we modified chitosan using amino acids from tofu waste and TiO₂.¹² The results show an improved adsorption capacity as compared to unmodified. Furthermore, amino acids-based modification lowered the mechanical characteristics of chitosan.

Herein, we investigated the effect of modification using a filler in the form of cellulose deriving from sugarcane bagasse in enhancing the adsorption capacity and also mechanical characteristics of the chitosan.

EXPERIMENTAL

Materials

HCl, NaOH, toluene, ethanol, distilled water, NaClO₂ 15%, and Methylene Blue were used in this study. All of the materials were of analytical quality (provided by Sigma-Aldrich, Selangor, Malaysia). The chitosan was supplied by Tokyo Chemical Industry Co., Ltd. in Japan and was manufactured from shrimp shells with a deacetylation degree of 75.0-85.0%. Sugarcane bagasse (SCB) was collected from a supplier of sugarcane drinks in Banda Aceh, Indonesia.

Cellulose Isolation

SCB was washed and dried at 60°C using the oven. Then, SCB was cut up into small parts and immersed for 24 hours at room temperature in ethanol:toluene (1:2). It was then filtered and neutralized using distilled water. Filtering was accomplished with a Buchner funnel and a vacuum, subsequently oven-dried (20 h; 50°C). The suspension was immersed in NaOH 5% for 4 h at 50°C and 500 rpm. It was then rinsed with distilled water to a pH 7 after being filtered through a Buchner funnel. The cellulose was then hydrolyzed in 5 M HCl for 12 h at 50°C. Afterward, the mixture was filtered, vacuumed, and neutralized. It was dried in an oven at 50°C. Cellulose was soaked in a 4:1 mixture of NaClO₂ and CH₃COOH and stirred for 2 hours at a 500-rpm speed and a temperature of 60°C using a magnetic stirrer. It was oven-dried after being neutralized. Ultrasonication was performed using a 600 W voltage. At a maximum temperature of 60°C, the suspension in 100 mL was sonicated for 60 minutes.

Preparation of Chitosan-Cellulose Film Composite

100 mL of acetic acid (2%) was used to dissolve 0.95 g of chitosan, and it was stirred for two hours using a magnetic stirrer. Thereafter, 0.05 g cellulose (powder) was added to the mixture and stirred for another 2 hours. Once it reached homogeneity, the mixture was casted onto a 17x12 cm acrylic and put in an oven at 40°C for 48 h. The product of the chitosan modification using SCB-derived cellulose was labeled as Chi-Cell.

Characterization

To assess how the functional groups on modified chitosan have changed, chitosan and modified chitosan were studied using Fourier-transformed infrared spectroscopy (FTIR). Crystal structure investigation was performed using X-Ray Diffractometer (Shimadzu XRD-700 Series). Cu K $\alpha_{1,2}$ radiation (1.54060 nm) was used to scan the samples from 10° to 60° (2 θ), at a speed of 8/min. The X-ray generator worked at 40 kV with a tube current of 30 mA. Tensile strength testing was performed at a speed of 20 mm/min on a Universal Testing Machine HT8503 (Hung Ta Instrument Co., Ltd, Taichung, Taiwan) to determine the effect of chitosan modification using cellulose on the mechanical properties. Thermal gravimetric analysis (TGA) was performed to determine changes in the thermal resistance of modified chitosan.

Batch Adsorption Study

0.1 g film composite (1x1 cm) was added into 20 mL methylene blue 30 mg/L in a 250 mL Erlenmeyer. Rotary shaker was used at 250 rpm for a variation of contact time (30, 40, 50, 60, 70, 80, and 90 min). Following the determination of the optimal time, the step was repeated with changes in solution pH of 2, 4, 6, 8, and 10 by applying HCl 0.1 M or NaOH 0.1 M. Then, methylene blue's absorbance was measured at the highest wavelength with a spectrophotometer UV-Vis. The step was also repeated for the initial concentration variation of methylene blue (30, 40, 50, 60, and 70 mg/L) using the optimized parameter.

RESULTS AND DISCUSSION

Cellulose Isolate

The type of SCB used in this research was identified via herbarium analysis. The dewaxing procedure is started at this point to remove the wax content contained in the bagasse.¹⁴ The alkalization process followed. This process aims to eliminate the amount of lignin and hemicellulose in SCB. The amorphous part of hemicellulose is soluble in NaOH,¹⁵ causing the color of the solution to become darker as a result of the lignin and hemicellulose dissolution. This is referred described as "black liquor".¹⁶ SCB was hydrolyzed using acid after being alkalized. The elimination of the amorphous part aided in the isolation of the crystalline part of the cellulose.¹⁷ After that, the resultant CNCs were bleached. The purpose of this

method was to make the cellulose having a brighter appearance.¹⁸ Water-insoluble lignin was oxidized to separate particular bonds including aryl ether bonds, carbon-carbon bonds, and β -O-4 bonds, resulting in water-soluble substances which included aldehydes and carboxylic acids.¹⁹ Following the bleaching procedure, cellulose was ultrasonicated. Cavitation was produced by ultrasonic vibrations, which aided damage minimization to the cell walls by rupturing the amorphous components.²⁰

Adsorption Capacities of Unmodified versus Cellulose-Based Modified Chitosan

Chitosan modified with cellulose and that unmodified were evaluated for MB adsorption to determine the best adsorbent. Figure-1 shows the results of the MB adsorption test on the chitosan modified with cellulose and unmodified. Based on these results, it is clear that the cellulose-modified chitosan had improved adsorption performance. The adsorption capacity of chitosan was 3.286 mg/g and chitosan-cellulose was increased to 4.93 mg/g.

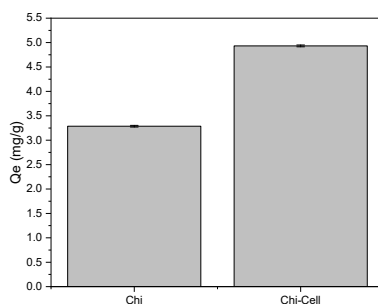


Fig.-1: The adsorption capacity of chitosan before and after modification

Characteristics

The chitosan-cellulose (Chi-Cell) was further characterized by tensile strength test, FTIR, and XRD. Tensile strength tests were carried out, and the results have been presented in Figure 2a. The tensile strength value increased significantly after the modification using SCB-derived cellulose. The existence of hydrogen bonds between cellulose and chitosan enhances the film's tensile characteristics.²¹ The tensile strength of chitosan was 2.95 kgf/mm² with an elongation of 18.48%; following the addition of cellulose, the film had a tensile strength of 14.5 kgf/mm² with an elongation of 34.3%.

The FTIR spectrum is used to identify the functional groups in a material. Figure-2b shows a slight change in the absorption band on the FTIR spectra of chitosan film with cellulose addition. In chitosan, wavenumber 3471 cm⁻¹ shows the existence of stretching vibrations of hydrogen bonds from the -OH group.²² The intensity of the chi-cell increases in the wave number region, indicating an increase in the amount of OH groups in the composite as a result of the addition of cellulose, which has numerous OH groups on its surface. It discovered the presence of CH₂ scissoring vibrations in cellulose at a wavenumber of 1420 cm⁻¹.²³ Several reports state that the wavenumber range of 850-1500 cm⁻¹ is a critical peak for the cellulose crystal structure.^{14,24,25} Taken altogether, the change in FTIR spectra is indicative to the successful insertion of cellulose into chitosan in this study.

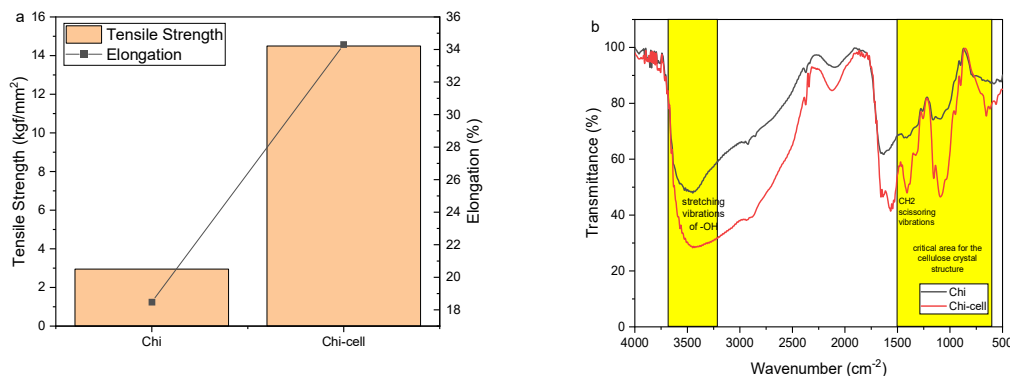


Fig.-2: Tensile strengths (a) and FTIR (b) of neat chitosan (Chi) and cellulose-modified chitosan (Chi-Cell)

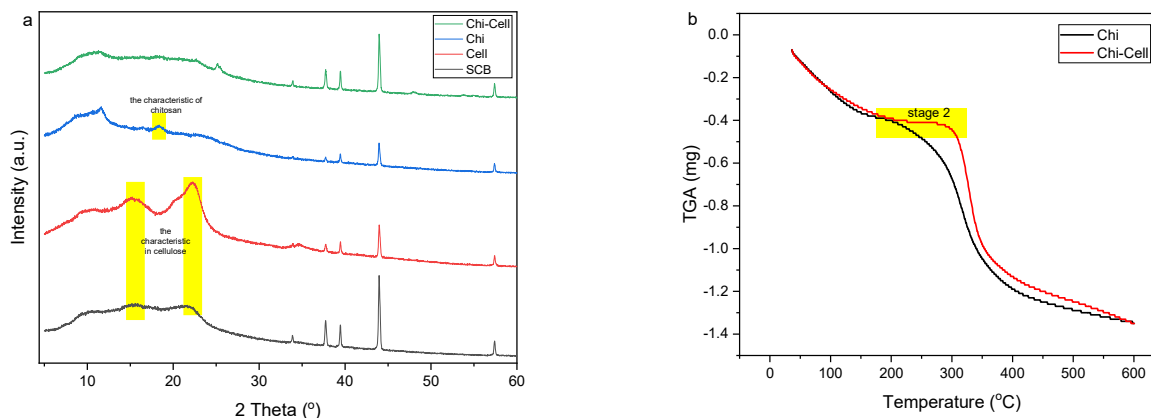


Fig.-3: Diffractograms (a) and thermograms (b) of neat chitosan (Chi) and cellulose-modified chitosan (Chi-Cell)

According to XRD data (Fig.-3a), the characteristic diffractogram in cellulose is at angles of $2\theta=15.4^\circ$ and 22.3° .²¹ In chitosan, the characteristic diffractogram was at an angle of $2\theta=19.5^\circ$.²⁶ The peaks correspond to JCPDS no. 84-1286. The presence of sharp diffractogram peaks in the sample suggests high crystallinity. The peak of cellulose in the SCB was still highly amorphous, but following the processes of alkalization, hydrolysis, bleaching, and sonication, the peak intensity of cellulose has grown dramatically. This demonstrates that cellulose crystalline was successfully extracted from sugarcane bagasse. The presence of cellulose did not affect the crystallinity of chitosan. According to Fig.-3b, chitosan and chitosan-cellulose biosorbent thermograms demonstrate a two-step thermal reaction. The first stage occurs at temperatures from 50° to 100°C and is associated with the evaporation of water bonded to the sample. This was observed in both samples. The second stage, between 279° and 317.07°C , was assigned to sample degradation. It was clear that the cellulose improved the composite's thermal resistance. This is caused by the thermal dissociation of chitosan and OH groups from cellulose.^{27,28}

Adsorption Performance

Based on the results of MB adsorption with time variations, the best contact time obtained was 80 minutes (Figure 4a). When the contact time between the Chi-Cell and the MB increases, so does the adsorption efficiency of the MB, and remained constant when equilibrium was achieved. When the amount of MB dye adsorbed by the Chi-Cell was kept constant, the Chi-Cell has reached equilibrium, indicating that it had been saturated with MB adsorption. The adsorption kinetics of MB might be calculated using data on adsorption capacity vs time. Based on the nonlinear equations, the pseudo-second-order adsorption kinetics model has a higher R^2 value (0.9207) than the pseudo-first-order adsorption kinetics model (0.7999). R^2 close to 1 indicates that the match between the experimental and modeled Q_e .^{29,30} For pseudo-second-order, the Q_e was 5.15 mg/g. The k_2 for pseudo-second-order was 0.019.

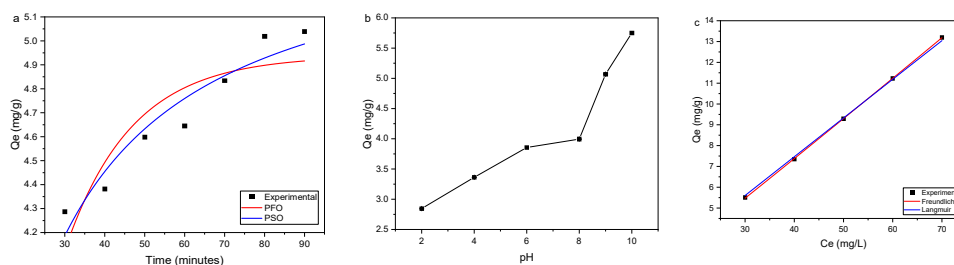


Fig.-4: Kinetic adsorption (a), pH optimum adsorption (b), and isotherm adsorption (c) of MB using Chi-Cell

Adsorption is the adhesion of adsorbate molecules to the adsorbent's surface. The electrostatic force was affected by the adsorbent's surface charge. According to this, pH has a significant impact on the adsorption process. In Fig.-4b, the amine group of chitosan was observed to be possibly protonated in the

presence of H⁺ ions, which resulted in a very poor adsorption capacity at pH 2 and 4. At pH 8, the adsorption capacity of the Chi-Cell was found in an increasing trend until the pH reached 10. Higher pH causes the adsorbent's surface to become negatively charged, causing a greater adsorption capacity. Adsorption isotherms can be used to calculate an adsorbent's maximum adsorption capacity. According to Fig.-4c, the methylene blue adsorption process using Chi-Cell was expected to follow the Langmuir isotherm model since the R² value is near one (0.999). Therefore, the MB adsorption onto Chi-Cell was in line with the Langmuir's assumption that the adsorption is monolayer with homogenous binding energy across the adsorbent surface. According to the nonlinear equation, the chitosan-cellulose biosorbent has a maximum adsorption capacity (Q_{max}) of 3348.14 mg/g.

CONCLUSION

Based on FTIR and XRD data, cellulose was successfully isolated from sugarcane bagasse. The addition of cellulose to chitosan modification considerably increased its adsorption efficiency. It can also increase the mechanical characteristics and thermal resistance of the composite. Due to its high performance in MB removal, Chi-Cell has the potential to be employed to treat textile effluent.

ACKNOWLEDGMENTS

The authors acknowledge Universitas Syiah Kuala for funding this work with Grant No. 332/UN11/SPK/PNBP/2021. The authors appreciate those who provided suggestions while authoring this work.

CONFLICT OF INTERESTS

The authors confirm that none of their known financial conflicts of interest or close personal connections might have seemed to have influenced the research presented in this study.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this work, took part in its reviewing, editing, and characterizing, and gave their final approval for publication. The author's ORCID IDs which is listed below can be used to confirm their research profile.

H. Fathana  <https://orcid.org/0000-0001-8774-4157>

Rahmi  <https://orcid.org/0000-0003-3622-907X>

M. Adlim  <https://orcid.org/0000-0001-6278-7775>

S. Lubis  <https://orcid.org/0000-0002-1711-3509>

M. Iqhrammullah  <https://orcid.org/0000-0001-8060-7088>

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. S. S. Vedula and G. D. Yadav, *Journal of the Indian Chemical Society*, **99**, 100263(2022), <https://doi.org/10.1016/j.jics.2021.100263>
2. D. Wahyudin and R. S. Malik, *Journal of Sustainable Development Education and Research*, **3**, 51(2019), <https://doi.org/10.17509/jsder.v3i1.17172>
3. A. I. Waly, M. A. M. Khedr, H. M. Ali, and I. M. Ahmed, *Egyptian Journal of Chemistry*, **63**, 2673(2020), <https://doi.org/10.21608/ejchem.2020.26122.2522>
4. N. Mohammed, *et al. Chemical Engineering Journal*, **417**, 129237(2021), <https://doi.org/10.1016/j.ccej.2021.129237>
5. H. Fathana, Rahmi, Susilawati, M. Adlim, and S. Lubis, *Rasayan Journal of Chemistry*, **14**, 2292(2021), <https://doi.org/10.31788/RJC.2021.1445944>
6. S. Sabar, *et al. Reactive and Functional Polymers*, **151**, 104584(2020), <https://doi.org/10.1016/j.reactfunctpolym.2020.104584>

7. Y. Yang, *et al.* *International Journal of Polymer Science*, **2019**, (2019), <https://doi.org/10.1155/2019/1767028>
8. N. M. Barkoula, B. Alcock, N. O. Cabrera, and T. Peijs, *T. Polymers, and Polymer Composites*, **16**, 101(2008), <https://doi.org/10.1002/pc.23316>
9. D. Trache, *et al.*, *Frontiers in Chemistry*, **8** (2020), <https://doi.org/10.3389/fchem.2020.00392>
10. P. Maturavongsadit, G. Paravyan, R. Shrivastava, and S. R. Benhabbour, *Materialia*, **12**, 100681 (2020), <https://doi.org/10.1016/j.mtla.2020.100681>
11. P. Sukyai, *et al.* *Food Research International*. **107**, 528(2018), <https://doi.org/10.1016/j.foodres.2018.02.052>
12. H. Fathana, M. Iqhrammullah, and R. Rahmi, *Chemical Data Collections*, **35**, 100754(2021), <https://doi.org/10.1016/j.cdc.2021.100754>
13. A. A. El-Fattah, A. G. M. El Demerdash, W. A. Alim Sadik, and A. Bedir, *A. Journal of Composite Materials*, **49**, 3251(2015), <https://doi.org/10.1177/0021998314561484>
14. H. Abral, *et al.*, *Food Hydrocoll*, **98**, 105266(2020), <https://doi.org/10.1016/j.foodhyd.2019.105266>
15. Y. Cai, L. Liu., H. Tian, Z. Yang, and X. Luo, *Molecules*, **24(24)**, 4534 (2019), <https://doi.org/10.3390/molecules24244534>
16. Q. Lin, Y. Huang, and W. Yu, *Industrial Crops and Products*, **169**, 113640(2021), <https://doi.org/10.1016/j.indcrop.2021.113640>
17. A. salah omer, *et al.* *Journal of Materials Research and Technology*, **19**, 3241(2022), <https://doi.org/10.1016/j.jmrt.2022.06.045>
18. H. Abral, G. J. Putra, M. Asrofi, J. W. Park, and H. J. Kim, *Ultrasonics Sonochemistry*, **40**, 697(2018), <https://doi.org/10.1016/j.ultsonch.2017.08.019>
19. T. Wang and Y. Zhao, *Carbohydrate Polymers*, **253**, 117225(2021), <https://doi.org/10.1016/j.carbpol.2020.117225>
20. B. Zakani and D. Grecov, *Carbohydrate Polymers*, **291**, 119651(2022), <https://doi.org/10.1016/j.carbpol.2022.119651>
21. H. Z. Li, S. C. Chen, and Y. Z. Wang, *Composites Science, and Technology*, **115**, 60(2015), <http://dx.doi.org/10.1016/j.compscitech.2015.05.004>
22. K. Harini and C. Chandra Mohan, *International Journal of Biological Macromolecules*, **163**, 1375(2020), <https://doi.org/10.1016/j.ijbiomac.2020.07.239>
23. H. Ni, *et al.* *Bio-Medical Materials and Engineering*, **22**, 121(2012), <https://doi.org/10.3233/BME-2012-0697>
24. A. Kumar, Y. Singh Negi, V. Choudhary, and N. Kant Bhardwaj, *Journal of Materials Physics and Chemistry*, **2**, 1(2020), <https://doi.org/10.12691/jmpc-2-1-1>
25. J. Lamaming, *et al.* *Carbohydrate Polymers*, **134**, 534(2015), <http://dx.doi.org/10.1016/j.carbpol.2015.08.017>
26. K. Gul, S. Sohni, M. Waqar, F. Ahmad, N. A. N. Norulaini, and M. O. A. K, *Carbohydrate Polymers*, **152**, 520(2016), <http://dx.doi.org/10.1016/j.carbpol.2016.06.045>
27. S. S. Al-Taweel, H. R. Saud, A. A. H. Kadhum, and M. S. Takriff, *Results in Physics*, **13**, 102296(2019), <https://doi.org/10.1016/j.rinp.2019.102296>
28. M. Abbasi, *Journal of Cleaner Production*, **145**, 105(2017), <http://dx.doi.org/10.1016/j.jclepro.2017.01.046>
29. Z. M. Khoshhesab, Z. Ayazi, and M. Dargahi, *International Journal of Nanoscience and Nanotechnology*, **16**, 35(2020).
30. M. Massoudinejad, H. Rasoulzadeh, and M. Ghaderpoori, *Carbohydrate Polymers*, **206**, 844(2019), <https://doi.org/10.1016/j.carbpol.2018.11.048>

[RJC- 8204/2022]