Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 90 (2) 247–255 (2025)
JSCS–5833
Original scientific paper
Published 5 November, 2024

Efficiency of physical–chemical treatment of wastewater of the paper and cardboard factory

LARYSA SABLII[1], OLEKSANDR OBODOVYCH[2] and VITALII SYDORENKO[2]*

[1]*Department of Bioenergy, Bioinformatics and Environmental biotechnology, National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Prospect Beresteiskyi 37, 03056, Kyiv, Ukraine and* [2]*Department of Heat and Mass Transfer in Disperse Systems, Institute of Engineering Thermophysics of NAS of Ukraine, Akademika Bulakhovskoho 2, 03164 Kyiv, Ukraine*

(Received 6 December 2023, revised 25 January, accepted 19 February 2024)

Abstract: The purpose of the work is to study the wastewater treatment of a cardboard and paper factory in the Khmelnytskyi region using physicochemical methods, namely coagulation and oxidation, to increase the efficiency of removing organic pollutants according to *COD* and *BOD* indicators. The use of coagulation and chlorination methods, before biological treatment in aeration tanks, was proposed. Alumofloc 18 % was used as a coagulant, PAA was used as a flocculant and sodium hydroxide was used as an alkalizing reagent. The study was conducted on a mixture of industrial and sewage wastewater with *COD* and BOD_5 – 3200 and 1575 mg L^{-1}, respectively, and on industrial wastewater with *COD* and BOD_5 – 4480 and 1960 mg L^{-1}, respectively. The effects of reducing *COD* and BOD_5 indicators in the first case after coagulation were 30 and 40 %, after chlorination – 37.82 and 43.18 %, respectively, and in the second after coagulation – 28.58 and 47.25 %, respectively. The effects of wastewater treatment of a cardboard and paper factory using coagulation and oxidation methods will allow for a reduction in the concentration of organic substances according to *COD* and *BOD* indicators before the biological treatment of wastewater in aeration tanks and also will ensure an increase in the efficiency of biological treatment.

Keywords: liquid waste; organic pollutants; coagulation; alumofloc; chlorination.

INTRODUCTION

Wastewater from cardboard and paper factories cause great damage to environment and water body. Such waters are a stable colloidal system. Organic substances presented in wastewater cause complex changes in water bodies.[1] They disrupt the established abiotic factors and are involved in chemical and

* Corresponding author. E-mail: V.V.Sydorenko@nas.gov.ua
https://doi.org/10.2298/JSC231206014S

biochemical processes. As a result, non-negotiable changes occur in the composition of biocenoses and the river water quality decreases significantly. Wastewater contains cellulose fibers, paper, fillers, dyes, latexes, emulsions, adhesives, *etc*. They have a high content of suspended solids and organic substances, as well as specific smell. Sources of organic substances are products of cellulose destruction, formed during bleaching and processing. These are substances such as aliphatic (alcohols, amines, acids, aldehydes, *etc*.) and terpene hydrocarbons, aromatic hydrocarbons of the phenolic series, low molecular weight alcohols, fatty acids, *etc*.[2] Due to the significant content of organic substances, wastewater is characterized by high *COD* values ranging from 800 to 2000 mg L^{-1} and BOD_5 values are within 500–800 mg L^{-1}. The BOD_5/COD ratio has average values, which indicate the possibility of applying a biological method of wastewater treatment. BOD_5/COD has a value in the range from 0.2 to 0.7. Suspended solids range from 900 to 3000 mg L^{-1}. Therefore, factory wastewater requires mechanical pretreatment, as a result of which coarse and suspended solids and some colloidal particles are removed.[3] The presence of low concentrations of phosphorus and nitrogen compounds in wastewater indicates that they should be added to water for biological processes.

Today, the most widespread methods of wastewater treatment in cardboard and paper factories are physico-chemical, namely reagent treatment, coagulation, flocculation, chemical, electrochemical oxidation[4] and biological. The use of reagent methods requires the purchase of chemical reagents, namely coagulants based on iron, aluminum, expensive flocculants or strong oxidizers as ozone[5,6] or hydrogen peroxide (Fenton method),[4] which does not ensure high purification efficiency in conditions of multicomponent pollution. Adsorption methods[7] can be used for wastewater treatment but require sophisticated equipment.

The most accessible and effective both from the point of view of high efficiency of the treatment, low costs for construction and operation and the impact on the environment and natural water bodies is the biological method,[8–11] namely the aerobic[12,13] and anaerobic[14–20] methods.

At a cardboard and paper factory in the Khmelnytskyi region, wastewater is treated at a wastewater treatment plant, which includes grit traps, primary radial sedimentation tanks, aeration tanks with activated sludge regenerators, secondary radial sedimentation tanks and biopонds (Fig. 1).

The productivity of the treatment plant is 7000 m^3 per day. Aeration tanks are designed for 14 h of aeration and 12 h of regeneration. The main drawback of the treatment plant is the insufficient efficiency of wastewater treatment from organic pollutants according to *COD* and *BOD* indicators, which necessitated research to find and use methods of pretreatment of factory wastewater using physical and chemical treatment.

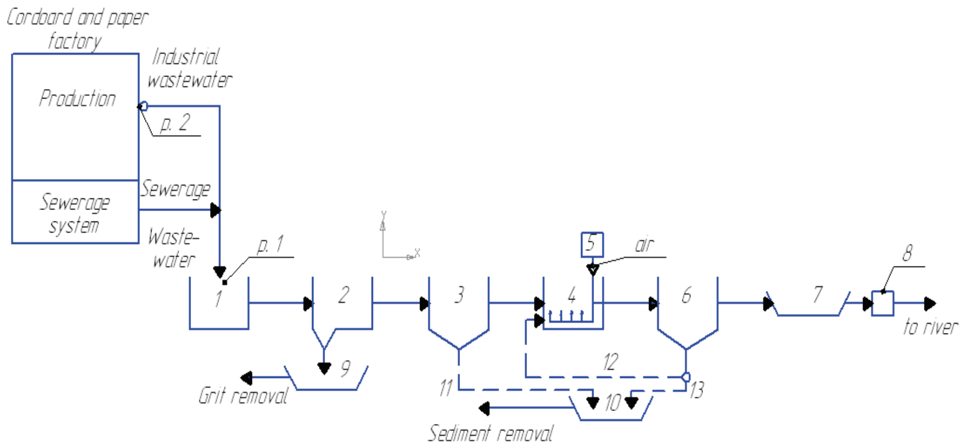

Fig. 1. Block diagram of waste water removal and treatment of cardboard and paper factory: 1 – Inlet chamber; 2 – grit traps; 3 – primary sedimentation tanks; 4 – aeration tanks; 5 – air blower; 6 – secondary sedimentation tanks; 7 – biopounds; 8 – disinfection; 9 – grit beds; 10 – sludge beds; 11 – sediment; 12 – recirculated activated sludge; 13 – surplus activated sludge. p.1 – sampling site of the mixture of industrial and sewerage wastewater from the inlet chamber; p.2 – sampling site of industrial wastewater in the well at the outlet of industrial wastewater from the workshop.

The purpose of the work is to study the wastewater treatment of a cardboard and paper factory using physicochemical methods, namely, coagulation and oxidation, for increasing the efficiency of removing organic pollutants according to *COD* and *BOD* indicators.

EXPERIMENTAL

A series of samples of the following wastewater were selected for analysis:

1) a mixture of industrial and sewage wastewater from the inlet chamber of the wastewater treatment plant of the cardboard and paper factory (Table I);

2) wastewater directly from production (Table II).

Samples were taken at points p.1 and p.2, shown in the block diagram shown in Fig. 1. Coagulation and chlorination of samples were carried out in laboratory conditions. Samples were taken at the indicated points three times: at 9 a.m., 2 p.m. and 7 p.m.

The analysis results of the samples taken at sampling site p.1 and p.2 were averaged according to the indicators. The average values are shown in the Tables I and II. In the first case (Table I), the following indicators were determined: pH, suspended solids, *COD*, BOD_5 of untreated wastewater, water after coagulation, as well as chlorinated coagulated water. In the second case (Table II), the same indicators were determined for the untreated and water after coagulation.

Reagents with the following doses were used for the study for coagulation: alumofloc 18 % – 0.6 mL L^{-1}; sodium hydroxide – 55 mg L^{-1} and PAA flocculant – 2 mg L^{-1}. The volume of sediment after coagulation and settling for 2 h was 20 %.

For chlorination active chlorine – 42 mg L^{-1} was used. The duration of settling after coagulation and chlorination was 2 h. Coagulation was successful in both cases. In the water obtained after settling, in the first case suspended solids decreased from 127 to 15 mg L^{-1} and in the second – from 162 to 20 mg L^{-1}. The results of the conducted analyses according to average values are summarized in Tables I and II.

The dissolved oxygen concentration in both cases was close to zero (0–0.1 mg L^{-1}), so the oxidation of water impurities with the participation of dissolved oxygen was not considered.

The error, of the results of experimental measurements, was not higher than 5 %.

To increase the efficiency of removing pollutants from wastewater of a cardboard and paper factory during primary sedimentation, it is possible to apply pre-reagent treatment of wastewater with the help of a coagulant, for example alumofloc. This reagent forms colloidal particles of aluminum hydroxide in water, capable of coagulation and forming flakes. Suspended particles (cellulose fibers, paper particles, fillers, *etc.*) colloidal and dissolved organic substances (hydrocarbons, fatty acids, *etc.*) contained in wastewater are adsorbed on the surface of the flakes, thus forming aggregates that settle in sedimentation tanks. As a result of coagulation, the concentration of suspended substances in wastewater and the concentration of organic substances according to *COD* and BOD_5 indicators are reduced to a greater extent than with simple settling.

In order to increase the efficiency of removal of organic substances from wastewater, the chlorination was used for pretreatment. The action of active chlorine consists in the chemical oxidation of organic substances, which are contained in large quantities in wastewater of the cardboard and paper factory, namely aliphatic (alcohols, amines, acids, aldehydes, ketones, *etc.*) and terpene hydrocarbons, aromatic hydrocarbons of the phenolic series, low molecular weight alcohols, fatty acids, *etc*.

These substances are determined by *COD* and BOD_5 indicators. Moreover, most of these substances are difficult to oxidize biologically (during wastewater treatment in aeration tanks), so pretreatment is needed.

The purpose of oxidation is to decompose hard-to-oxidize substances into biodegradable substances for microorganisms in the biological treatment. When oxidized with chlorine, simpler compounds are formed. For example, acids or ketones are formed when alcohols are oxidized and acids are formed when aldehydes are oxidized. The formed reaction products are biologically degradable with the participation of active sludge of aeration tanks, which increases the efficiency of biological wastewater treatment. For example, when ketones are oxidized with chlorine, mixtures of organic acids are formed, which are easily decomposed by activated sludge microorganisms.

When ketones are oxidized, C–C bonds between the carbon atoms of the carbonyl group and the carbon radical are broken with the formation, for example, of a mixture of formic, acetic, propionic, or other biodegradable acids.

RESULTS AND DISCUSSION

Rows 5 to 10 of Tables I and II show the results of some calculations that characterize the efficiency of wastewater treatment using the applied coagulation and chlorination methods.

Studies of the wastewater treatment in the factory using the coagulation method showed the following.

In a case of an industrial and sewage wastewater mixture (Table I) in the mixture of wastewater from the inlet chamber of the wastewater treatment plant, after coagulation, BOD_5 decreases by 40 % and *COD* by 30 %. The BOD_5/COD ratio for the next biological treatment in the aeration tanks of the wastewater treatment plant should be greater than 0.5. In this case, as the results showed, coagulation worsened the ratio from 0.49 to 0.42.

TABLE I. Change in indicators of the mixture of industrial and sewage wastewater of the cardboard and paper factory after coagulation and chlorination

Ser. no	Indicator	Unit	Value		
			Initial	After coagulation	After coagulation and chloration
1	pH	–	6.3	7.1	7.25
2	Suspended solids	$mg\ L^{-1}$	127	15	15
3	*COD*	$mgO_2\ L^{-1}$	3200	2240	1990
4	BOD_5	$mgO_2\ L^{-1}$	1575	945	895
5	COD/BOD_5 ratio	–	2.03	2.37	2.22
6	BOD_5/COD ratio	–	0.49	0.42	0.45
7	$COD - BOD_5$ ("pure" *COD*)	$mg\ O_2\ L^{-1}$	1625	1295	1095
8	Decrease of the BOD_5	$mg\ O_2\ L^{-1}$		630 (40 %)	50 (43.18 %)
				680 (43.17 %)[a]	
9	Decrease of the *COD*	$mg\ O_2\ L^{-1}$		960 (30 %)	250 (37.82 %)
				1210 (37.81 %)[a]	
10	Decrease of "pure" *COD*	$mg\ O_2\ L^{-1}$		330 (20.3 %)	200 (12.4 %)
				530 (32.62 %)[a]	

[a]Estimated differences in the values of the indicators of the untreated wastewater and water after coagulation and chlorination

The difference between *COD* and BOD_5 ("pure" *COD*) is:

$$3200 - 1575 = 1625\ mg\ O_2\ L^{-1};$$

$$2240 - 945 = 1295\ mg\ O_2\ L^{-1}.$$

The difference of "pure" *COD* of wastewater from the inlet chamber of the wastewater treatment plant before and after coagulation is: 1625 – 1295 = 330 $mg\ O_2\ L^{-1}$.

The "pure" *COD* of wastewater (without taking into account its BOD_5) after coagulation decreased by only 330 $mg\ O_2\ L^{-1}$ or 20.3 %.

As a result of chlorination, the following indicators were obtained.

After coagulation and chlorination, BOD_5 decreases by 43.18 % and *COD* – by 37.82 %, in wastewater from the inlet chamber of the wastewater treatment plant. Chlorination (separately, after coagulation) decreased BOD_5 by 3.18 % and *COD* by 7.82 %.

Chlorination, in comparison with coagulation, additionally reduced BOD_5 by 5.3 % and *COD* by 11.17 %.

The BOD_5/COD ratio in the case of using coagulation and chlorination decreased from 0.49 to 0.45.

"Pure" *COD* (minus BOD_5) will be:

$$3200 – 1575 = 1625 \text{ mg } O_2 \text{ L}^{–1};$$
$$2240 – 945 = 1295 \text{ mg } O_2 \text{ L}^{–1};$$
$$1990 – 895 = 1095 \text{ mg } O_2 \text{ L}^{–1}.$$

TABLE II. Change in indicators of industrial wastewater cardboard and paper factory after coagulation

Ser. no	Indicator	Unit	Value	
			Initial	After coagulation
1	pH	–	6.5	7.2
2	Suspended solids	mg L^{-1}	162	20
3	*COD*	mgO$_2$ L^{-1}	4480	3200
4	BOD_5	mgO$_2$ L^{-1}	1960	1034
5	COD/BOD_5 ratio	–	2.28	3.09
6	BOD_5/COD ratio	–	0.43	0.32
7	$BOD – COD_5$ ("pure" *COD*)	mg O$_2$ L^{-1}	2520	2166
8	Decrease of the BOD_5	mg O$_2$ L^{-1}	926 (47.25 %)	
9	Decrease of the *COD*	mg O$_2$ L^{-1}	1280 (28.58 %)	
10	Decrease of the "pure" *COD*	mg O$_2$ L^{-1}	354 (14.05 %)	

The difference of "pure" *COD* of wastewater from the inlet chamber of the wastewater treatment plant before and after coagulation and chlorination will be:

$$1625 – 1095 = 530 \text{ mg } O_2 \text{ L}^{–1}.$$

After coagulation and chlorination, the "pure" *COD* of wastewater (excludeing its BOD_5) decreased by only 530 mg O_2 L$^{–1}$ or 32.62 %.

The difference between "pure" *COD* of wastewater from the inlet chamber of the wastewater treatment plant before and after coagulation will be:

$$1625 – 1295 = 330 \text{ mg } O_2 \text{ L}^{–1}.$$

The "pure" *COD* of wastewater (without taking into account its BOD_5) after coagulation decreased by only 330 mg O_2 L$^{–1}$ or by 20.3 %.

The difference between the "pure" *COD* of wastewater from the inlet chamber of the wastewater treatment plant between coagulated and chlorinated wastewater will be:

$$1295 – 1095 = 200 \text{ mg } O_2 \text{ L}^{–1}.$$

The "pure" *COD* of wastewater (excluding its BOD_5) between coagulated and chlorinated wastewater decreased by only 200 mg O_2 L$^{–1}$ or 12.4 %.

In the case of production wastewater from a cardboard and paper factory (Table II), the BOD_5 indicator after coagulation decreases by 47.25 % and the *COD* by 28.58 %. In this case, coagulation decreases the BOD_5/COD ratio from 0.43 to 0.32.

"Pure" *COD* (minus BOD_5) will be:

$$4480 – 1960 = 2520 \text{ mg } O_2 \text{ L}^{-1};$$

$$3200 – 1034 = 2166 \text{ mg } O_2 \text{ L}^{-1}.$$

The difference of "pure" *COD* of industrial wastewater before and after coagulation will be:

$$2520 – 2166 = 354 \text{ mg } O_2 \text{ L}^{-1}.$$

The "pure" *COD* (excluding BOD_5) decreased by only 354 mg O_2 L^{-1} or 14.05 % after coagulation.

As can be seen from Tables I and II (rows 7 and 8), the coagulation and settling allow a reduction of BOD_5 in the first and second cases by 40 (Table I) and 47.25 % (Table II) and *COD* by 30 % (Table I) and 28.58 % (Table II), respectively. These indicators indirectly indicate percentages of organic pollutants (according to BOD_5) and the total amount of organic matter (according to *COD*) that are in wastewater in suspended and colloidal states. At the same time, it is worth noting that coagulation reduces BOD_5 more effectively than *COD*, which indicates that most of the hard-to-oxidize compounds are dissolved.

CONCLUSION

As a result of studies of the coagulation process for the treatment of wastewater from a cardboard and paper factory, a decrease in the indicators of suspended solids, *COD* and *BOD* was obtained.

The BOD_5/COD ratio was less than 0.5 and this must be taken into account when adjusting the composition of wastewater (by changing the ratio of easily and hard-oxidizing substances due to the detection and reduction of chemical components coming from production).

It was determined that 60–70 % of organic substances, according to the *COD* indicator, are in a dissolved state. During the coagulation of wastewater, the efficiency of purification according to the BOD_5 indicator was determined to be 40–47 %. It has been determined that as a result of chlorination, the maximum reduction of "pure" *COD* is achieved; therefore, the possibility and expediency of chlorination of water after the secondary settling tank in increased doses, should be considered in the wastewater treatment technology of the cardboard and paper factory.

It should be noted that the use of reagents in the doses adopted in the study is unlikely to be economically justified, but it will be advisable to arrange an oxidizer-biocoagulator in front of the primary settling tank, in which activated sludge is used instead of reagents.

И З В О Д

ЕФИКАСНОСТ ФИЗЧКО-ХЕМИЈСКИХ МЕТОДА У ПРЕЧИШЋАВАЊУ ОТПАДНИХ ВОДА ФАБРИКЕ КАРТОНА И ПАПИРА

LARYSA SABLII[1], OLEKSANDR OBODOVYCH[2] и VITALII SYDORENKO[2]

[1]*Department of Bioenergy, Bioinformatics and Environmental biotechnology, National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Prospect Beresteiskyi 37, 03056, Kyiv, Ukraine* и
[2]*Department of Heat and Mass Transfer in Disperse Systems, Institute of Engineering Thermophysics of NAS of Ukraine, Akademika Bulakhovskoho 2, 03164 Kyiv, Ukraine*

Сврха рада је проучавање пречишћавања отпадних вода фабрике картона и папира у Khmelnytskyi региону коришћењем физичко–хемијских метода, односно коагулације и оксидације, како би се повећала ефикасност уклањања органских загађивача према *COD* и *BOD* индикаторима. Предложена је употреба метода коагулације и хлорисања пре биолошког третмана у аерационим резервоарима. Алумофлок 18 % је коришћен као коагулант, PAA је коришћен као флокулант, а натријум-хидроксид је коришћен као алкализирајући реагенс. Студија је спроведена на мешавини индустријских и канализационих отпадних вода са *COD* и BOD_5 – 3200 и 1575 mg L^{-1}, редом, и на индустријским отпадним водама са *COD* и BOD_5 – 4480 и 1960 mg L^{-1}, редом. Ефекти смањења *COD* и BOD_5 индикатора у првом случају након коагулације били су 30 и 40 %, након хлорисања – 37,82 и 43,18 %, редом, а у другом случају након коагулације – 28,58 и 47,25 %, редом. Ефекти пречишћавања отпадних вода из фабрике картона и папира методама коагулације и оксидације омогућиће смањење концентрације органских материја према *COD* и *BOD* индикаторима пре биолошког третмана у аерационим резервоарима и обезбедиће повећање ефикасности биолошког третмана.

(Примљено 6. децембра 2023, ревидирано 25. јануара, прихваћено 19. фебруара 2024)

REFERENCES

1. *The Global Paper Packaging Market: Growth, Trends, Competitive Landscape and Forecasts Report*, Globe Newswire, Dublin, 2020
2. M. A. Hubbe, J. R. Metts, D. Hermosilla, M. A. Blanco, L. Yerushalmi, F. Haghighat, P. Lindholm-Lehto, Z. Khodaparast, M. Kamali, A. Elliott, *BioRes*. **11** (2016) 7953 (https://doi.org/10.15376/biores.11.3.Hubbe)
3. O. Ashrafi, L. Yerushalmi, F. Haghighat, *J. Environ. Manage.* **158** (2015) 146 (https://doi.org/10.1016/j.jenvman.2015.05.010)
4. K. Eskelinen, H. Särkkä, N. A. Kurniawan, M. E. T. Sillanpää, *Desalination* **255** (2010) 179 (https://doi.org/10.1016/j.desal.2009.12.024)
5. N. Kishimoto, T. Nakagawa, H. Okada, H. Mizutani, *J. Water Environ. Technol.* **8** (2010) 99 (https://doi.org/10.2965/jwet.2010.99)
6. W. De los Santos Ramosa, T. Poznyaka, I. Chairez, I. Córdova, *J. Hazard. Mater.* **169** (2009) 428 (https://doi.org/10.1016/j.jhazmat.2009.03.152)
7. S. Kakkar, A. Malik, S. Gupta, *J. Appl. Nat. Sci.* **10** (2018) 695 (https://doi.org/10.31018/jans.v10i2.1769)
8. C. Ram, P. Rani, K.A. Gebru, *Phys. Sci. Rev.* **5** (2020) 8 (https://doi.org/10.1515/psr-2019-0050)
9. P. Singh, A. Srivastava, *Int. J. Pharm. Biol. Sci.* **5** (2014) 773 (https://api.semanticscholar.org/CorpusID:98160371)

10. M. Cabrera, A. Zaki, in *Biological Wastewater Treatment and Resource Recovery*, F. Robina, A. Zaki, Eds., InTech, Rijeka, 2017, p. 256 (https://doi.org/10.5772/62795)
11. A. Schnell, P. V. Hodson, P. Steel, H. Melcer, J. H. Carey, *Water Res.* **34** (2000) 501 (https://doi.org/10.1016/S0043-1354(99)00161-X)
12. C. W. Bryant, *Water Sci. Technol.* **62** (2010) 1248 (https://doi.org/10.2166/wst.2010.934)
13. C. V. Dubeski, R. M. Branion, K. V. Lo, *J. Environ. Sci. Health* **36** (2001) 1245 (https://doi.org/10.1081/ese-100104875)
14. M. Tielbaard, T. Wilson, E. Feldbaumer, W. Driessen, in *Proceedings of TAPPI International Environmental Conference* (2002), TAPPI Press, Atlanta, GA, 2002, pp. 621–634
15. L. Habets, W. Driessen, *Water Sci. Technol*. **55** (2007) 223 (https://doi.org/10.2166/wst.2007.232)
16. N. B. Golub, M. V. Potapova, Yu. V. Karpenko, *IBB* **3** (2019) 96 (https://doi.org/10.20535/ibb.2019.3.2.166429)
17. N.B. Golub, M.V. Shinkarchuk, O.A. Kozlovets, B. V. Morgun, O. R. Lakhneko, A. I. Stepanenko, M. V. Borisjuk, *Water Air Soil Pollut*. **231** (2020) 445 (https://doi.org/10.1007/s11270-020-04805-6)
18. R. Chhotu, R. Pushpa, G. A. Kibrom, M. G. M. Abrha, ,*Phys. Sci. Rev.* **5** (2020) 20190050 (https://doi.org/10.1515/psr-2019-0050)
19. M. A. Hubbe, J. R. Metts, D. Hermosilla, M. A. Blanco, L. Yerushalmi, F. Haghighat, P. Lindholm – Lehto, Z. Khodaparast, M. Kamali, A. Elliott, *BioRes.* **11** (2016) 7953 (https://doi.org/10.15376/biores.11.3.hubbe)
20. S. R. Hassan, N. Q. Zaman, I. Dahlan, *Prep. Biochem. Biotechnol*. **50** (2019) 234 https://doi.org/10.1080/10826068.2019.1692214).