

Short ozonation of municipal waste as effective pretreatment

Yan Rosen ^a

Hadas Mamane ^b

Yoram Gerchman ^c

^a Porter School of Environmental Studies (PSES), Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel. Email: yanrosen@gmail.com

*School of Mechanical Engineering, Faculty of Engineering, Tel Aviv University, Tel Aviv 69978, Israel
Email: hadasmg@tauex.tau.ac.il*

^c Department of Biology and Environment, Faculty of Natural Sciences, University of Haifa – Oranim, Tivon 3600600, Israel. Email: Gerchman.yoram@gmail.com

April 2018

Abstract

Municipal trimming wastes (lignocellulosic waste) are a promising sustainable feedstock for ethanol production, but require costly and polluting pretreatment, that often result in toxic byproducts. Ozonation is a nonpolluting, effective pretreatment method, but is not used commercially due to the high energy requirements of the assumingly high ozone doses needed. Results demonstrated that both ozonation time and enzyme dose (at optimal pH) impact conversion efficiency to glucose. Ozonation (15, 30 and 90 min, accumulated TOD =318, 435 and 1114 mg O₃/L) of water-submerged waste (at pH=5.5) prior to enzyme addition (×1.5 industrial enzyme dose) enabled high conversion of the cellulose fraction of the waste to glucose (31% and 42% respectively) compared to non-ozonated sample (with enzyme, 12%), suggesting ozonation could offer an effective and feasible pretreatment method. In these ozone doses, only 20% and 40% of the lignin was degraded showing that there is no need for delignification (as opposed to the common hypothesis) to obtain high sugar conversion. In addition, ozone process can be easily monitored by change in absorbance at 230, 280 and 436 nm, making it useful to use spectral scan in the field. Moreover, reduction in net calculated energy balance was obtained at higher ozone dose (90 min compared to 15 or 30 min), demonstrating increased process efficiency at lower ozone doses. Furthermore, ozonation can be generated on-site and on demand, enabling decentralized pretreatment operated near the feed source thus overcoming transportation costs.

Keywords

Lignocellulosic waste; Lignin; Cellulose; Ozone; Ethanol; Thermogravimetric analysis (TGA), municipal trimmings

1. Introduction

Lignocellulosic waste, i.e., waste plant material waste (biomass), such as found in municipal, agricultural and forest residues, is a promising feedstock for bioethanol production. Use of this such waste favors resource sustainability due to consequent reduction in dumping volumes (Saini et al., 2015) and the reduction in land, water and fertilizers used for production of specialized energy crops. Another major advantage is the ability to use components of first-generation biofuel infrastructure and technology (Naik et al., 2010). Nevertheless, much of this waste remains unused and is buried in landfills or burned in the field to save treatment costs (Ayalon et al., 2008; Gupta and Verma, 2015).

Lignocellulosic biomass is composed of cellulose, hemicellulose and lignin combined in an intricate structure (Menon and Rao, 2012; Mood et al., 2013). The cellulose can be hydrolyzed to glucose (saccharification) by specialized enzymes, i.e. cellulases, and the resulting sugar can then be fermented to ethanol (Menon and Rao, 2012). While effective, these enzymatic processes are hampered by the presence of lignin in the plant biomass, especially in woody stems (Yoshida et al., 2008; Ximenes et al., 2011) but also in other biomass (Abu Taye et al., 2016).

Lignin removal is a crucial pretreatment step in bioethanol production and one of the main economic costs in the process, reaching up to 20% of the cost (Alvira et al., 2010; Travaini et al., 2016). A large number of chemo-physical pretreatment approaches have been investigated on a wide variety of feedstock types (Gupta and Verma, 2015). An effective pretreatment should (i) suit a wide range of lignocellulosic wastes (multi-feed concept), (ii) result in insignificant sugar loss, (iii) allow for low enzyme load (enzymes are second in cost after pretreatment processes), (iv) allow for high sugar conversion from cellulose (>10%), (v) result in a minimal amount of toxic/inhibitory byproducts, (vi) require less than 10% of the energy content of the resulting biofuel, (vii) allow optimal recovery of hemicellulose and pentoses, and (viii) allow for minimization and simple disposal of resulting wastes and wastewater treatment (Alvira et al., 2010; Saini et al., 2015).

Pretreatment methods used today suffer from many disadvantages (Table 1). To solve this, the combination of pretreatment process is investigated, including alkaline immersion followed by diluted acid, alkaline immersion followed by ionic liquid and diluted acid–high-pressure steam explosion. (Taherzadeh and Karimi, 2008; Mood et al., 2013). Nevertheless, due to the complex expensive infrastructure needed, none of these methods allow for decentralized, small-scale, local pretreatments, resulting in the requirement for shipment of large amounts of agricultural waste and hazardous materials, such as acids, alkali or organic solvents. Thus, use of the waste as feedstock becomes less energetically and economically feasible (Gnansounou and Dauriat, 2010; Greenhot, 2015).

Ozonation can be done on-demand (making transport of dangerous chemicals redundant) in small-scale decentralized systems, allowing for local pretreatment and even portable facilities, an great economic importance (Balan, 2014). Ozone (O_3) is a powerful oxidizing species ($E^0 = 2.07 \text{ V}$, $25 \text{ }^\circ\text{C}$) with high affinity for phenol ($1300 \text{ M}^{-1} \text{ s}^{-1}$) and polyphenols (e.g. lignin and tannic acid) (Hoigné and Bader, 1983; Balat, 2011; Peretz et al., 2017), and low affinity for ethanol and glucose (0.37 and $0.45 \text{ M}^{-1} \text{ s}^{-1}$, respectively) (Hoigné and Bader, 1983; Mvula and von Sonntag, 2003). In addition, ozone dissolved in water (up to 110 mg L^{-1} , $25 \text{ }^\circ\text{C}$) has a short life span of 20 min (von Gunten, 2003; Zucker et al., 2016), resulting in the absence of residual ozone that would need to be treated or could interfere

with subsequent hydrolysis or fermentation (García-Cubero et al., 2009). Ozonation processes carried out at room temperature were found to effectively degraded lignin and somewhat hemicellulose (Vidal and Molinier, 1988; Shi et al., 2015; Travaini et al., 2016) while avoiding the formation of the inhibitory compounds known to be formed by acid pretreatment (e.g., furfural and Hydroxymethyl furfural) (Jönsson et al., 2013).

Table 1: Current industrial pretreatment methods and their drawbacks^a,

Pretreatment	Disadvantages
Low temperature/ concentrated acid	Toxicity, corrosiveness, acid recovery, degradation of glucose and production of fermentation inhibitors (furans, HMF)
High temperature/diluted acid (DA) (mainly diluted sulfuric acid)	Heating power demands, production of fermentation inhibitors and low glucose yield
High-pressure steam explosion (SExp)	High water demands for the process and washing the formed fermentation inhibitors
Ammonia fiber explosion (AFExp)	High cost of ammonia, environmental issues and inefficient ammonia recovery and recycling
Alkaline immersion (ALK)	Long residence time, formation of harmful slurry and the need for its neutralization
Ionic liquid (IL)	Damage to cellulose enzymes and formation of side reactions
Organosolv (dseolution of lignin in organic solvents)	Solvents' low boiling point and flammability, expensive solvent recycling and inhibitory effects on enzymes and yeast
Ozonation (Travaini et al., 2016)	High ozone-dosage requirements and high energy demand for ozone production
^a Data from Taherzadeh and Karimi, 2008; Menon and Rao, 2012; Mood et al., 2013.	

Although ozone-based pretreatment technologies have high potential, they are rarely used because the dose needed for full mineralization of the lignin requires too much energy (Neely, 1984; Ozonok et al., 1997). Nevertheless, a recent study by Peretz et al. (2017) demonstrated that very short ozonation of a tannic acid dissolved in water (a lignin model and cellulase inhibitor) resulted in recovery of activity with considerably lower ozone dose than previously thought. These results, and the results of Sugimoto et al. (2009), suggest that if done properly, short ozonation could serve as energetically effective pretreatment. The goal of the current study was to determine conditions for short ozonation of water-submerged agriculture waste (here, municipal trimmings) to enable high conversion rate of the cellulose fraction of the waste to glucose.

2. Proposed methodology

- Investigate the chemical/physiological properties of the biomass wastes. Composition and structure.
- Establishing a method for tracking the degradation of the harmful lignin.
- Optimizing the ozonation procedure for the lignin degradation
- Verifying non-inhibition to saccharification enzymes by ozonated by-products of lignin degradation.
- Verifying non-inhibition and non-toxicity to fermenting yeasts by the lysate.
- Calculation of optimized ozone dose vs. energetic balance

3. preliminary results

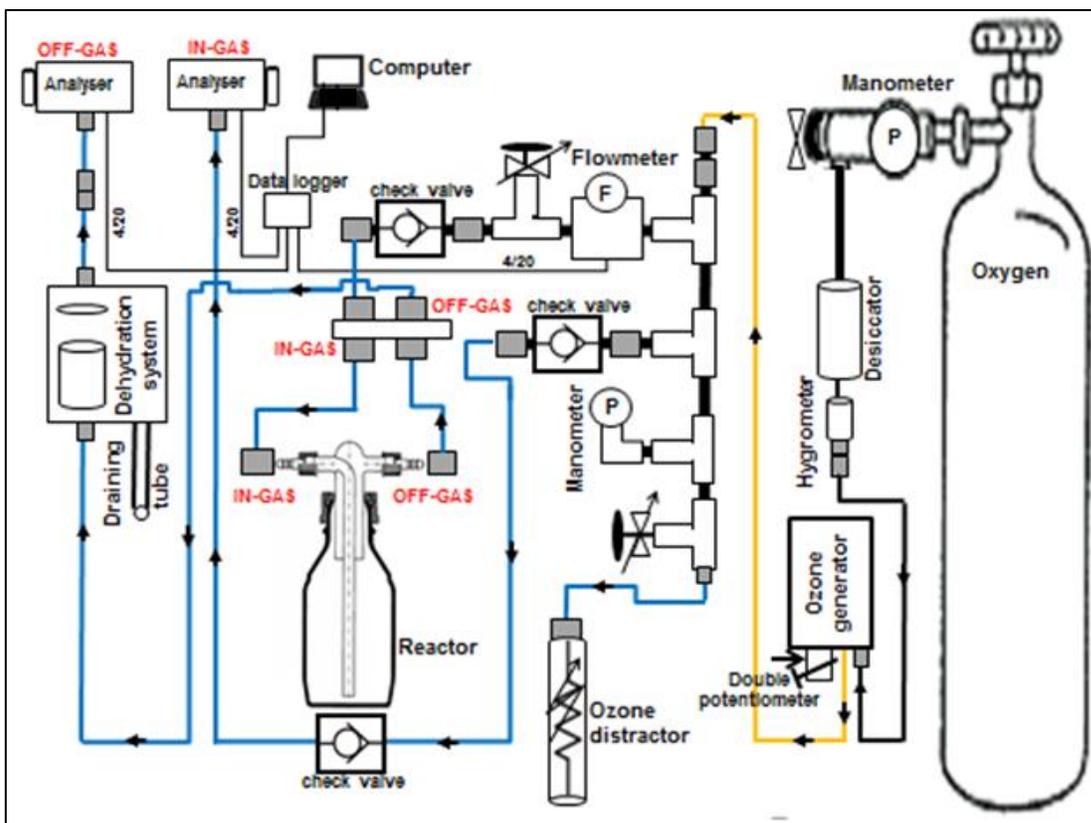


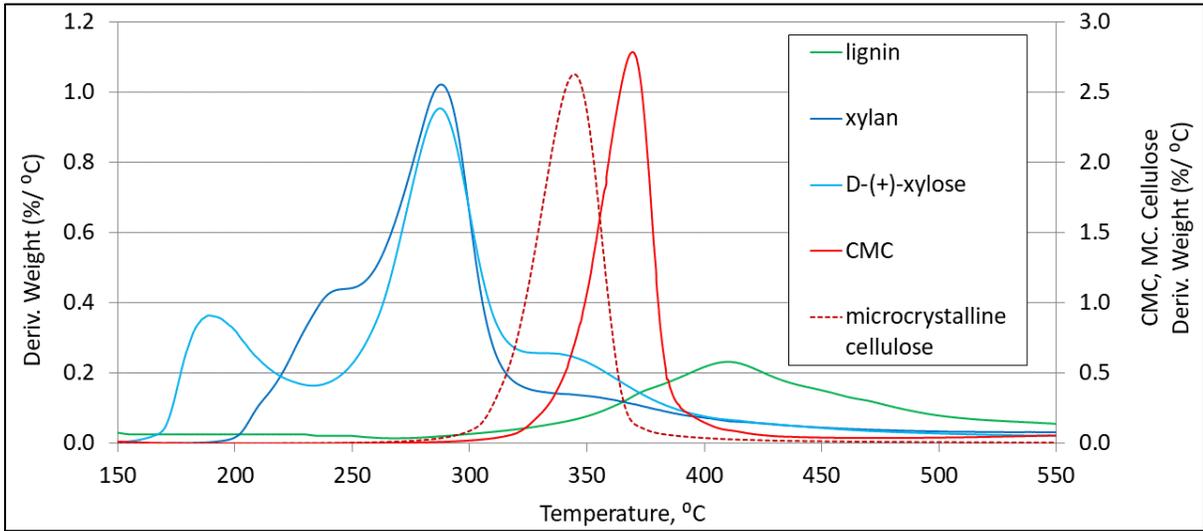
Fig.1: Scheme of the ozonation system. Analyzers measuring in-gas and off-gas for calculation of transferred ozone dose (TOD).

TOD (accumulated amount of ozone transferred) was calculated using the formula (Buffle et al., 2006):

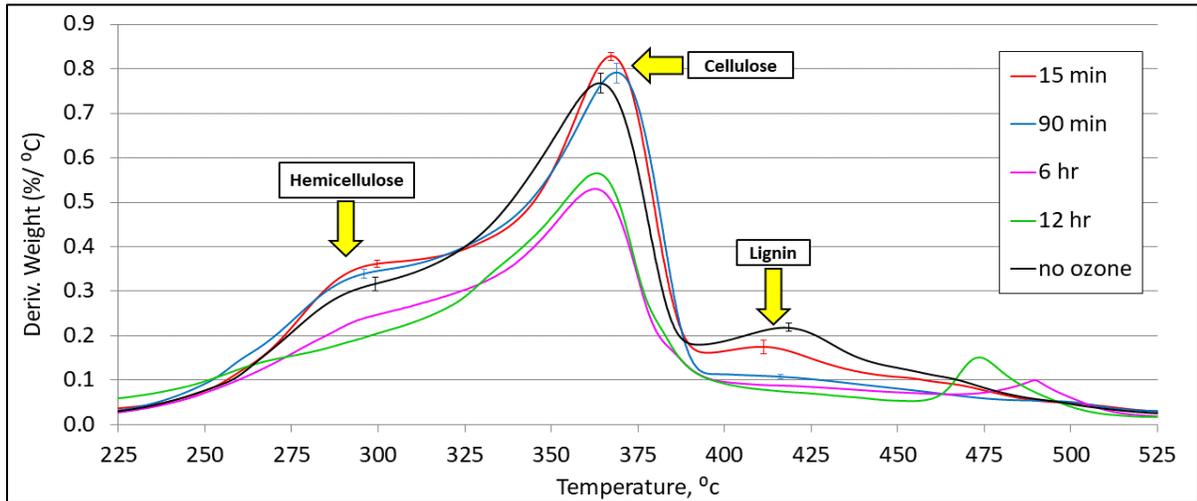
$$\text{TOD} \left(\frac{\text{mg}}{\text{L}} \right) = \frac{\sum (C_{\text{O}_3, \text{in}} - C_{\text{O}_3, \text{out}})_{\text{mg/L}} \times \text{gas flow rate}_L \times t_{\text{min}}}{\text{volume}_L}$$

where $C_{\text{O}_3, \text{in}}$ = ozone concentration in the inlet gas, $C_{\text{O}_3, \text{out}}$ = ozone concentration in the outlet gas, representing the unreacted ozone exiting the reactor, and volume_L = water volume in the reactor.

Fig. 2.(a)



(b)



(c)

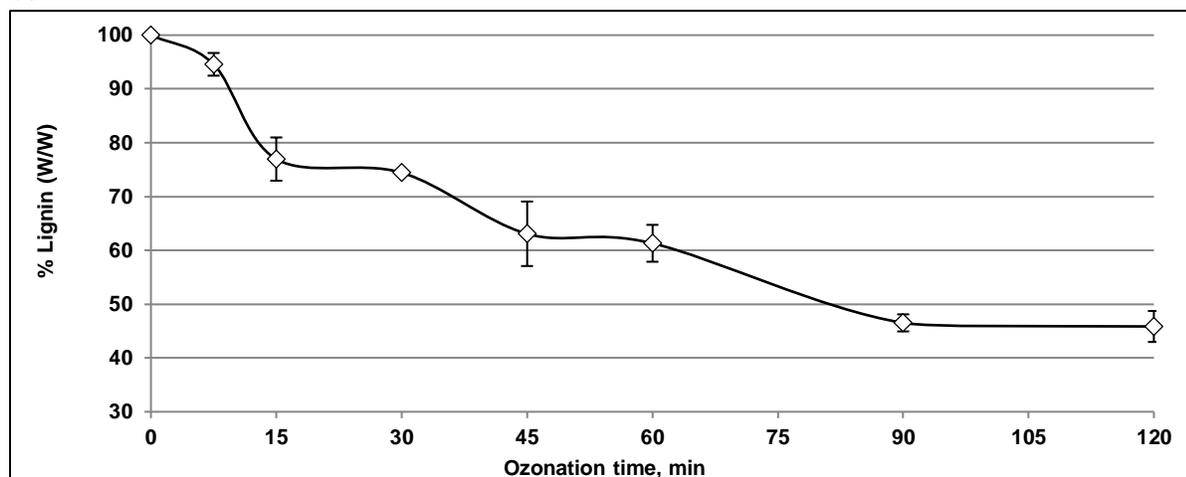


Fig. 2: TGA - Thermogravimetric analysis (Carrier et al., 2011), used for determination of specific lignocellulose composition, showed differential curves of: (a) standards; (b) dehydrated solids from the slurry taken after different ozonation times; (c) lignin percentage of those samples, calculated from the TGA differential curves. data points are average of three treatments and error bars are 1 SD.

Table 2: Net energy balance

Ozonation time	0 min	15 min	90 min	
Transferred ozone dose (TOD)	0	343	1135	mgO ₃ L ⁻¹
KgO ₃ per Ton biomass	0	8.58	28.38	Kg
Energy, per Ton biomass	0	85.8	283.8	kW×hr
Energy, per Ton biomass	0	309	1,022	MJ
Liter ethanol from 1 Ton biomass	31	80.1	108.5	L
Energy as ethanol (MJ/ton biomass)	734.4	1,897.20	2,570.40	MJ
Net energy balance (MJ/metric ton)	734	1,611	1,567	MJ

Reduction in net calculated energy balance was obtained at higher ozone dose (90 min compared to 15), demonstrating increased process efficiency at lower ozone doses. These results suggest that contrary to common belief, long ozonation is unnecessary, making ozonation pretreatment more economical and energy favored.

4. Acknowledgements

This research was conducted in the framework of the Israeli Ministry of National Infrastructure, Energy and Water Resources grant number 214-11-006, the Israeli Ministry of Environmental Protection grant number 132-3-4, and a scholarship from the Israeli Ministry of Science and Technology. We would also like to thank Dr. Alex Golberg, Tel Aviv University, for his enormous help in the HPIC data analysis, and for his advice. We also wish to thank Du-Pont company for their donation of enzymes.

E-supplementary data of this work can be provided by yanrosen@gmail.com.

5. References

1. Abu Tayeh, H., Levy-Shalev, O., Azaizeh, H., Dosoretz, C.G., 2016. Subcritical hydrothermal pretreatment of olive mill solid waste for biofuel production. *Biores. Technol.* 199, 164-172
2. Alvira, P., Tomás-Pejó, E., Ballesteros, M., Negro, M.J., 2010. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis. *Bioresour. Technol.* 101, 4851-4861.
3. Ayalon, O., Elimelech, E., Spenser, J., Zaban, H., Lev-On, M., Lev-On, P., 2008. *Bioethanol in Israel: Global Context, Research, Planning and Policy*. Samuel Neaman Institute, Haifa, Israel.
4. Balan, V., 2014. Current challenges in commercially producing biofuels from lignocellulosic biomass. *ISRN Biotech.* 2014, 463074
5. Buffle, M.O., Schumacher, J., Meylan, S., Jekel, M., von Gunten, U., 2006. Ozonation and advanced oxidation of wastewater: effect of O₃ dose, pH, DOM and HO• scavengers on ozone decomposition and HO• generation. *Ozone Sci. Engineer.* 28, 247-259.
6. Carrier, M., Loppinet-Serani, A., Denux, D., Lasnier, J.M., Ham-Pichavant, F., Cansell, F., Aymonier, C., 2011. Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass. *Biomass Bioenergy* 35, 298-307.
7. García-Cubero, M.T., González-Benito, G., Indacochea, I., Coca, M., Bolado, S., 2009. Effect of ozonolysis pretreatment on enzymatic digestibility of wheat and rye straw. *Bioresour. Technol.* 100, 1608-1613.
8. Gnansounou, E., Dauriat, A., 2010. Techno-economic analysis of lignocellulosic ethanol: a review. *Bioresour. Technol.* 101, 4980-4991.
9. Greenhot, Z., 2015. *Agriculture Byproducts in Israel*. Report. Ministry of Environmental Protection, Israel.
10. Gupta, A., Verma, J.P., 2015. Sustainable bio-ethanol production from agro-residues: a review. *Renewable Sustainable Energy Rev.* 41, 550-567.
11. Hoigné, J., Bader, H., 1983. Rate constants of reactions of ozone with organic and inorganic compounds in water—I: non-dissociating organic compounds. *Water Res.* 17 (2), 173-183.
12. Jönsson, L.J., Alriksson, B., Nilvebrant, N., 2013. Bioconversion of lignocellulose: inhibitors and detoxification. *Biotechnol. Biofuels* 6 (16), 1-10.
13. Menon, V., Rao, M., 2012. Trends in bioconversion of lignocellulose: biofuels, platform chemicals & biorefinery concept. *Prog. Energy Combust. Sci.* 38, 522-550.
14. Mood, S.H., Golfeshan, A.H., Tabatabaei, M., Jouzani, G.S., Najafi, G.H., Gholami, M., Ardjmand, M., 2013. Lignocellulosic biomass to bioethanol, a comprehensive review with a focus on pretreatment. *Renewable Sustainable Energy Rev.* 27, 77-93.
15. Mvula, E., von Sonntag, C., 2003. Ozonolysis of phenols in aqueous solution. *Org. Biomol. Chem.* 1, 1749-1756.
16. Naik, S.N., Goud, V.V., Rout, P.K., Dalai, A.K., 2010. Production of first and second generation biofuels: a comprehensive review. *Renewable Sustainable Energy Rev.* 14, 578-597.

17. Neely, W.C., 1984. Factors affecting the pretreatment of biomass with gaseous ozone. *Biotechnol. Bioengineer.* 26, 59–65.
18. Ozonek, J., Fijalkowski, S., Polio, I., 1997. Exergy identification of energy utilization efficiency in an industrial process of ozone generation. *Ozone Sci. Engineer.* 19, 201–226.
19. Peretz, R., Gerchman, Y., Mamane, H., 2017. Ozonation of tannic acid to model biomass pretreatment for bioethanol production. *Bioresour. Technol.* 241, 1060–1066.
20. Saini, J.K., Saini, R., Tewari, L., 2015. Lignocellulosic agriculture wastes as biomass feedstocks for second-generation bioethanol production: concepts and recent developments. *3Biotech* 5, 337–353.
21. Shi, F., Xiang, H., Li, Y., 2015. Combined pretreatment using ozonolysis and ball milling to improve enzymatic saccharification of corn straw. *Bioresour. Technol.* 179, 444–451.
22. Sugimoto, T., Magara, K., Hosoya, S., Oosawa, S., Shimoda, T., Nishibori, K., 2009. Ozone pretreatment of lignocellulosic materials for ethanol production: improvement of enzymatic susceptibility of softwood. *Holzforschung*, 63, 537-543
23. Taherzadeh, M.J., Karimi, K., 2008. Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review. *Int. J. Mol. Sci.* 9, 1621–1651.
24. Travaini, R., Martín-Juárez, J., Lorenzo-Hernando, A., Bolado-Rodríguez, S., 2016. Ozonolysis. An advantageous pretreatment for lignocellulosic biomass revisited. *Bioresour. Technol.* 199, 2–12.
25. Vidal, P.F., Molinier, J., 1988. Ozonolysis of lignin – improvement of in vitro digestibility of poplar sawdust. *Biomass* 16, 1–17.
26. von Gunten, U., 2003. Ozonation of drinking water. Part I. Oxidation kinetics and product formation. *Water Res.* 37, 1443–1467.
27. Ximenes, E., Kim, Y., Mosier, N., Dien, B., Ladisch, M., 2011. Deactivation of cellulases by phenols. *Enzyme Microb. Technol.* 48, 54–60.
28. Yoshida, M., Liu, Y., Uchida, S., Kawarada, K., Ukagami, Y., Ichinose, H., Kaneko, S., Fukuda, K., 2008. Effects of cellulose crystallinity, hemicellulose, and lignin on the enzymatic hydrolysis of *Miscanthus sinensis* to monosaccharides. *Biosci. Biotechnol. Biochem.* 72 (3), 805–810.
29. Zucker, I., Avisar, D., Mamane, H., Jekel, M., Hübne, U., 2016. Determination of oxidant exposure during ozonation of secondary effluent to predict contaminant removal. *Water Res.* 100, 508–516.