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ELECTRONIC PEER-REVIEWED JOURNAL ON ALL TOPICS OF INDUSTRIAL AND MUNICIPAL ECOLOGY

RECENZOVANÝ ČASOPIS PRO VÝSLEDKY VÝZKUMU A VÝVOJE Z OBLASTI PRŮMYSLOVÉ A KOMUNÁLNÍ EKOLOGIE

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Ondřej Procházka

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Toluene oxidation by microwave assisted catalysis over alumina supported mixed cobalt-manganese oxide catalyst

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Abstract

This work is focused on the development suitable low cost catalyst for the microwave assisted catalytic oxidation of VOCs for future pilot technology. The series of nine single and mixed component cobalt and manganese oxides catalysts were prepared by impregnation of alumina with aqueous solutions of cobalt and manganese nitrates. These catalysts have been tested for the oxidation of toluene by innovative microwave heating, which can increase efficiency and reduce operating temperature. It has been observed a different heating rate of alumina or titanium oxide catalyst support and a different behaviour between single cobalt and manganese oxides on alumina support in microwave field. Mixed cobalt-manganese oxides are more reactive than a simple cobalt oxide. The addition manganese into precursor solution led to higher heating rate. Among the prepared catalysts, the mixed 10 wt% cobalt-manganese oxide catalyst in molar ratio 4:1 exhibited the best toluene conversion 70.4% at 240 °C.

Keywords: *Co_3O_4, MnO_x, Al_2O_3, VOCs, catalytic oxidation, microwave irradiation.*

Introduction

VOCs are significant contributors to air pollution. VOCs have toxic health effects even at very low concentrations and tends to cause the formation of a photochemical smog[1]. In chemical, pharmaceutical, machinery, electronic etc. industry, many hazardous organic compounds in not negligible concentrations are still emitted into the air through process ventilation systems in high volumes[2]. VOCs emissions are reduced using available efficient technologies such as thermal oxidation, adsorption, absorption or condensation, biofiltration, membrane separation or catalytic oxidation[3-5]. The catalytic oxidation is considered as the most effective and economical pathway to remove VOCs from dilute gaseous streams (< 0.5%) at much lower temperatures (typically 200 – 500 °C). As opposed to incomplete thermal oxidation, the catalytic oxidation allows to deep VOCs conversion into carbon dioxide and water without undesirable by-products[2,4,6]. The principle of catalytic oxidation is based on the interaction of organic molecules with oxygen on the surface of the catalyst. The diffusion and adsorption of the organic compounds onto catalyst surface from air stream must precede the reaction. The efficient VOCs conversion is driven mainly by temperature.

Supported noble metals (Pt, Pd, Rh etc.) or transition metal oxides (Co, Mn, Fe, Cu, Cr etc.) are used as the catalysts[4]. Supported noble metals catalysts exhibit high activity and stability at low temperature, but they are expensive and their sensitivity to poisoning by chlorine elements and sintering limit their wide use[4]. Current research is focused on developing of transition metal oxide catalysts such as efficient, low cost and available catalysts[7-10]. The catalytic performance is strongly dependent on the properties of the catalyst such as chemical structure (types of metals, and its dispersion) and stability, textural properties (surface area, porosity and pore size distribution), and their mechanical properties. Cobalt and manganese oxides are considered as the most active metal oxides for total oxidation[4,11].

Cobalt oxide catalysts are very efficient for the total oxidation of a large number of VOCs. Especially, Co_3O_4 with a spinel structure is considered like more active phase than CoO, in which cobalt is present in a lower oxidation state[11]. Likely, its catalytic activity is related to the presence of highly mobile oxygen in structure and the easy formation of highly active forms of oxygen[12]. Many researches are focused on the influence of the different morphology of unsupported catalysts (rods, sheets, plates, etc.)[13,14] and of the textural properties of supported catalysts to catalytic performance. However, the disadvantages of using cobalt oxide is the low stability at high temperatures, when the Co_3O_4 phase transforms to CoO phase at 700 °C, and sinters and agglomerates already at 500 °C[11,15].

There are several manganese oxides that are characterized by great catalytic activity, especially Mn_2O_3 and Mn_3O_4. MnO_x are able to shift between oxidation states and their structural properties contributes to high oxygen mobility and oxygen storage capacity[16,17]. The performance of manganese oxide depends also on the methods of preparation, surface area, and nature of the support material. Catalysts based on manganese oxides are resistant and non-toxicity, however, they are easily subject to chlorine poisoning[4].

Recently, microwave technology has been expanded to many industrial processes, including material engineering, industrial drying or chemical industry. Researchers also investigate the potential of microwave heterogeneous catalysis, where the heating of the catalyst via microwave irradiation can lead to the significantly higher efficiency of the process[18,19]. Microwave heating is characterized especially by selective and volumetric heating, and overheating of catalyst in surroundings media. Microwaves interact with different solids in complex specific mechanisms, and hot spot formation, where the temperature can be raised by up 200 °C than in the remaining parts of the catalyst[20-22]. Research results point to higher conversion and mineralization of toluene over nano-Co_3O_4 or MnO_x catalysts in the microwave field at lower temperature[23,24]. It is assumed that the activation energy of the catalytic reactions in the microwave field is reduced[24]. Metal oxides can be heated by the absorption of an electric or magnetic component of an electromagnetic field. Of the commonly used catalyst supports, Al_2O_3 interacts only with an electric component and the heating rate is 17.3 °C min^{-1} while TiO_2 heats up very slowly. The heating rate of the catalyst is influenced by the nature of support[25]. The use of microwave irradiation contributes to the rapid heating of the catalyst, the easy control of catalytic process, and the minimization of energy consumption[26], which can be advantageous as opposed to conventional heating.

In this study, we applied to apply the microwave assisted catalytic oxidation as innovative promising technique for the removal of toluene over cobalt, and mixed cobalt-manganese oxide catalyst on the support. The aim of the presented research project is to prepare an efficient low cost catalyst for microwave-assisted catalytic technology for toluene emission abatement and the optimization of operating conditions such as temperature, relative humidity and gas hourly space velocity (GHSV).

Experimental

Catalyst preparation

All catalysts were prepared by incipient wetness impregnation method. The impregnated samples were prepared by mixing calculated amount of γ-phase Al_2O_3 catalyst support (Alfa Aesar, high surface area, 1/8” pellets) with an aqueous solution of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, GPR Rectapur, in purity ≥ 98.0%), or/and manganese nitrate ($Mn(NO_3)_2 \cdot 4H_2O$, Acros organics, in purity ≥ 97.5%) to give 1, 3, 5, 10, and 15 wt% of Co/Al_2O_3, resp. Mn/Al_2O_3, $CoMn/Al_2O_3$. The volume of the used solution was necessary to completely wet the support. After impregnation, the water was allowed to evaporate. Impregnated samples were dried in air at 120 °C for 12 h and then calcined at 450 °C for 6 h under air atmosphere. Before tests, the catalyst was dried at 105 °C 2 h. Catalyst samples were denoted in accordance with the content of transition metals and their molar ratio.

The Co/TiO_2 sample was prepared in the same way from TiO_2 catalyst support (Alfa Aesar, 1/8” pellets) and cobalt nitrate using an amount corresponding to 5 wt% content of cobalt. The sample was dried and calcinated at the same condition. This sample was prepared for the comparison of the microwave heating of different catalyst support.

Catalyst characterization

The prepared catalysts were analysed using N_2 physisorption and X-ray fluorescence (XRF). The specific surface area (SSA) area was determined by N_2 physisorption isotherms at -196 °C with BET evaluation of surface using Coulter SA 3100. Before measurement, the samples were outgassed at 150 °C for 240 min. The chemical composition of catalysts was determined by XRF of powder materials using ARL 9400 XP (Thermo ARL). XRD was employed with the purpose of verifying the phase of chemical species using the powder method on D8 Advance ECO (Bruker) instrument applying CuKα radiation (λ = 1.5406 Å). The 2θ Bragg angles were scanned over a range from 5° to 70°, with a step of 0.02° and the integration time of 0.5 s.

The catalytic activity

The catalytic activity was evaluated in a laboratory microwave catalytic apparatus to provide basic knowledge about catalyst behaviour in microwave field. A schematic diagram of the experimental apparatus is shown in Figure 1.

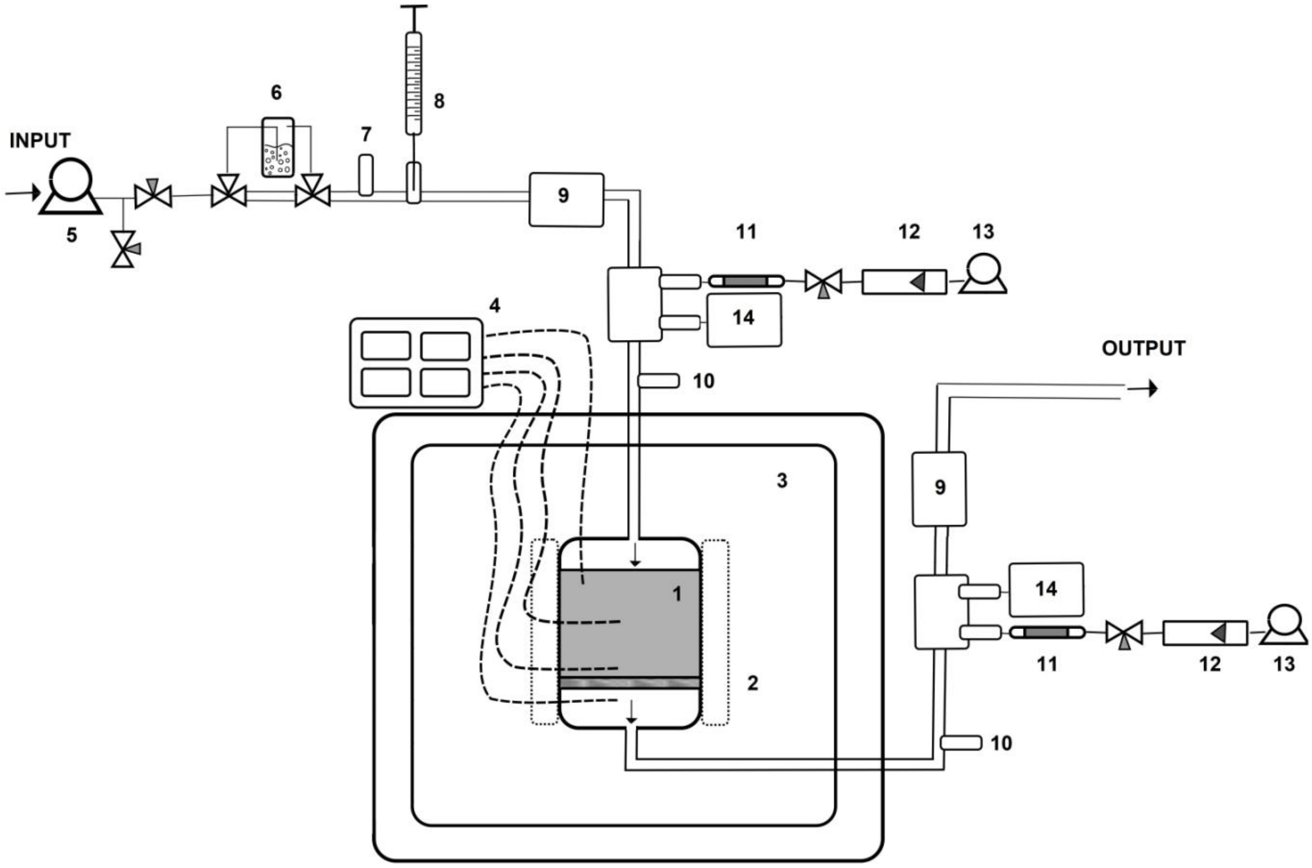

Figure 1: Scheme of microwave catalytic apparatus: 1 – catalyst bed, 2 – glass frit, 3 – microwave cavity, 4 – optical fibre probes and temperature measurement, 5 – air pump, 6 – bubble flask, 7 – relative humidity 8 – contamination point, 9 – flowmeter, 10 – pressure gauge, 11 – sorbent tube, 12 – rotameter, 13 - sampling pump, 14 – PID

The contaminated air stream was prepared by the injection of liquid contaminant into the stream using syringe pump. Toluene was selected as the model contaminant (in purity > 99%, Penta s.r.o.). Input air was pretreated using active carbon. The concentration of toluene was 800 mg m^{-3} (at 25 °C and 1 atm), which was controlled by the dosing rate of the liquid contaminant using syringe pump (New Era Pump Systems NE-1000) and by the air flow rate monitored by the air thermal mass flowmeters (Sensidyne Go-Cal Air-flow Calibrator). The doses were chosen to be easily evaporated in air flow while being constant at the various flow rates. The GHSV through the reactor was 2,000 h^{-1}. The bubble humidifier was included in air bypass behind the air pump. Humidity measuring unit (Greisinger GMH 3350) was behind the air bypass. Bypass was not always involved and humidification was used only in tests to examine the influence of air humidity on the catalytic activity. The air was guided through Tygon tubing directly into the reactor. The glass continuous-flow fixed bed reactor (cylinder, 3.5 cm diameter) was placed in microwave cavity of laboratory oven (Milestone Microsynth system, 2.45 GHz, resolution of 1 W up to 1000 W) under atmospheric pressure. The catalyst (50 mL) was placed on glass frit. The reactor was well sealed before the test and the pressure drop of the reactor was checked by two electronic pressure gauges (Greisinger GMH 3100). The optical fibres (Neoptix Reflex) for the temperature control was installed at upper layer, in the middle, and in last lower layer of the catalyst bed.

The input (c_{in}) and output (c_{out}) concentration of toluene were sampled simultaneously applying SKC sorbent tubes (CSC Anasorb, 50/100 mg coconut charcoal) according to standard procedure ČSN P CEN/TS 13649, 2015 (sample volume 0.5 L, flow rate 100 mL min^{-1}, elution with 1.5 mL of carbon disulphide (Honeywell, puriss. p.a., 99.9 %)). The extracts were analysed by gas chromatography with flame ionization detection (GC-FID, 6890N, Agilent) equipped with the capillary column TRV1 (Thermo Fisher Scientific, 30 m × 0.25 mm i.d.; film thickness 1.4 μm). Additionally, the output concentration of toluene was on-line monitored using photoionization detector (PID, RAE Systems, MiniRAE 2000) containing an internal pump with a flow rate of 0.5 L min^{-1} and a 10.6 eV lamp.

Temperature influence on toluene degradation efficiency was based on the sampling input and output air stream at various temperatures. Microwave heating was manually controlled using microwave power control system. The catalytic activity was evaluated by toluene conversion defined as follows:

Conversion [%] = (C_{in} – C_{out})/C_{in} x 100

Results and discussion

Table 1 summarizes the elementary chemical composition of the prepared catalysts measured by XRF and the specific surface area investigated by N_2 physisorption. A higher SSA is beneficial for the improvement of catalytic activity. The results show, with higher loading of the transition metals, SSA of the catalyst decreases slightly, which may negatively affect the adsorption of toluene on the catalyst surface. The SSA of used catalysts support Al_2O_3 and TiO_2 were 225.6 and 132.0 m^2 g^{-1}, respectively. Used alumina catalyst support has more than 1.7 times higher surface area than TiO_2 support. The crystalline phase composition of prepared catalysts was analyzed by XRD. The phase present in the samples are aluminum oxide γ–Al_2O_3 (PDF 79-1558) and manganese oxide MnO_2 (PDF 65-2821), or cobalt oxide Co_3O_4 (PDF 74-1657).

Table 1: Chemical composition and specific surface area of catalysts

	Mass fraction (%)							SSA (m^{2}g^{-1})
Catalyst	**Al**	**Co**	**Mn**	**Si**	**Cl**	**Fe**	**Ti**	
1 wt% Co/Al_2O_3	45.38	1.68		0.06	0.04	0.01		236.1
3 wt% Co/Al_2O_3	50.24	5.04		0.05	0.04	0.01		222.2
5 wt% Co/Al_2O_3	48.9	5.16		0.06	0.04	0.01		228.9
10 wt% Mn/Al_2O_3	47.1		8.29	0.05	0.04	0.01		195.6
10 wt% Co/Al_2O_3	54.77	15.83		0.03	0.02			195.8
15 wt% Co/Al_2O_3	54.27	23.03		0.03	0.02	0.02		190.6
5 wt% CoMn/Al_2O_3 1:4	47.78	1.76	6.13	2.21		0.02		213.6
5 wt% CoMn/Al_2O_3 4:1	49.36	6.89	1.50	2.21	0.01	0.02		220.6
10 wt% CoMn/Al_2O_3 4:1	51.62	12.98	2.72	2.15		0.02		189.3
5 wt% Co/TiO_2		4.88					55.8	80.4

The catalysts were tested for the oxidation of toluene. For all used catalysts, the main reaction product was probably CO_2 as no other products were observed by GC-FID. 50 mL of the catalyst was used, which corresponds to approximately 20 – 25 g. The contaminated air stream was prepared from the air at ambient relative humidity (averaged 37%). Toluene concentration in the artificially prepared input air stream fluctuated with RSD 5.5%. The microwave power was applied in the range of 100 to 250 W to heat the catalytic bed. The power was manually controlled and gradually increased to reach the required temperatures 180 to 240 °C at approximately a constant rate of heating of the catalytic bed during the experiment.

Figure 2a compares the conversion achieved at different temperatures for the alumina supported catalysts with different cobalt contents corresponding to 1, 3, 5, 10, and 15 wt%, respectively. The catalysts with higher cobalt content presented higher catalytic activity, nevertheless, only to some extent as the most active was the catalyst with 5 wt% cobalt loading. The activity follows the order 5 > 15 - 10 > 3 > 1 wt%. With further increases in content, significant improvement was not observed, probably too much loading affected the catalyst specific surface area that can be seen in Table 1. The comparison of the catalytic activity of cobalt and manganese oxide, shown in Figure 2b, indicates higher MnO_x activity for toluene oxidation versus Co_3O_4 impregnated on alumina. It shows that toluene conversion 76.4, and 59.7% over MnO_x/Al_2O_3, and Co_3O_4/Al_2O_3 was achieved at 240 °C. This observation led to the use of mixed cobalt-manganese oxide catalyst in followed experimental series.

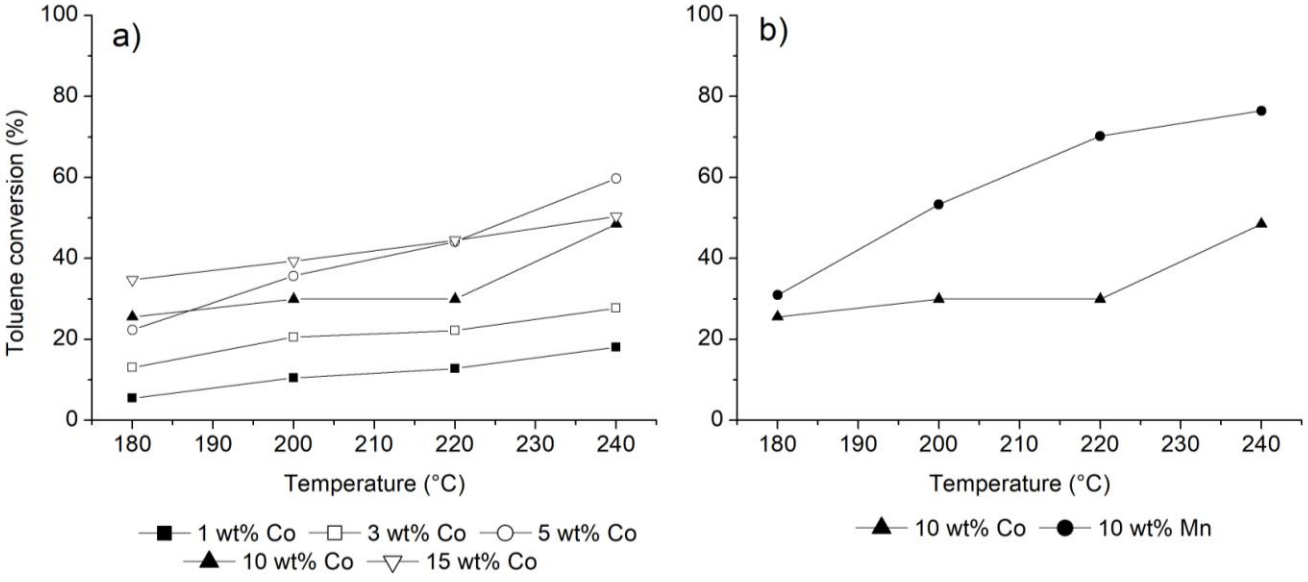

Figure 2: The effect of a) cobalt loading, and b) the comparison of the catalytic activity of cobalt and manganese oxide

However, cobalt and manganese oxides have different behaviour in the microwave field. To explore this phenomenon, the catalysts were heated at constant power and GHSV 2,000 h^{-1} and the heating rates were compared. As shown in Figure 3a, the temperature of the Co/Al_2O_3 stabilized on value 122 °C at 200 W after 15 minutes, but MnO_x/Al_2O_3 showed very intense heating at 200 W (230 °C in 6 minutes; not included in Figure 3a). The temperature of MnO_x/Al_2O_3 catalyst showed a growing tendency above 220 °C at power 150 W even after 15 minutes (Figure 3a). MnO_x interacts with microwave irradiation much more intensively. The temperature difference inside the catalyst bed was higher for Co_3O_4 (5 °C) than for MnO_x (11 °C), which can lead to uneven heating of the whole bed. Therefore, the addition of MnO_x to the Co_3O_4 could lead to faster microwave heating and energy saving, but to higher variation of temperatures inside the bed at the same time. The microwave heating depends even on the catalyst support (Figure 3b). Generally, both alumina and titanium dioxide are low-interaction materials with microwave irradiation and significant differences were observed for the different supports employed. Applying power 80 to 200 W, alumina is heated faster with minor temperature differences inside the bed (8 °C). The lower absorption of microwave is required for further upscale of technology while to appropriate technology capacity in terms of air flowrate, it is necessary to penetrate microwaves uniformly across relatively high volume of bulk catalyst bed. In general, Mn and Co oxides interact with microwave strongly, that could lead to the penetration of microwaves only through thin surface layer of catalyst bed. That is the reason for the necessary application of catalyst carrier from material of low dielectric losses during microwave irradiation, as alumina and titania are. Moreover, the applied power must not be considered as energy consumption of 25 g catalysts heating in applied test setup, as only few percent of applied energy is dissipated in this scale, nevertheless, the microwave system was not equipped by reflected power measurements. The transfer of energy consumption data from laboratory to pilot scale is almost impossible due to specific character of microwave heating.

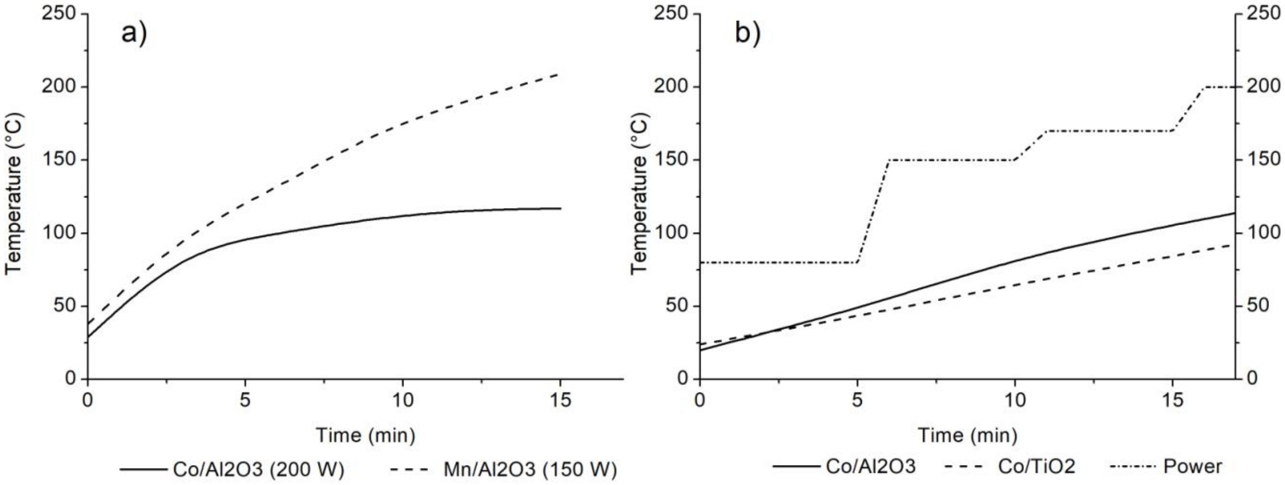

Figure 3: The comparison of microwave heating of a) cobalt and manganese catalyst at different power, and b) cobalt catalyst supported with Al_2O_3 or TiO_2

Figure 4 shows the dependence of the toluene conversion on the temperature of mixed cobalt-manganese oxide catalysts. A similar behaviour was observed for the catalysts 5 wt% Co,Mn in molar ratios 1:4 and 4:1 at temperatures above 200 °C. As can be seen, the most active mixed catalyst was 10 wt% Co,Mn/Al_2O_3 in molar ratio 4:1, that reached toluene conversion of 51.3 and 70.4% at 200 °C and 240 °C respectively. The temperature differences inside the bed were averaged 3.6 °C. In the comparison with results of microwave assisted catalytic oxidation of cobalt catalysts presented in Figure 2a, as recent results indicated, the doping with manganese increases the catalytic activity and this depends on the active component introduction onto the catalyst surface.

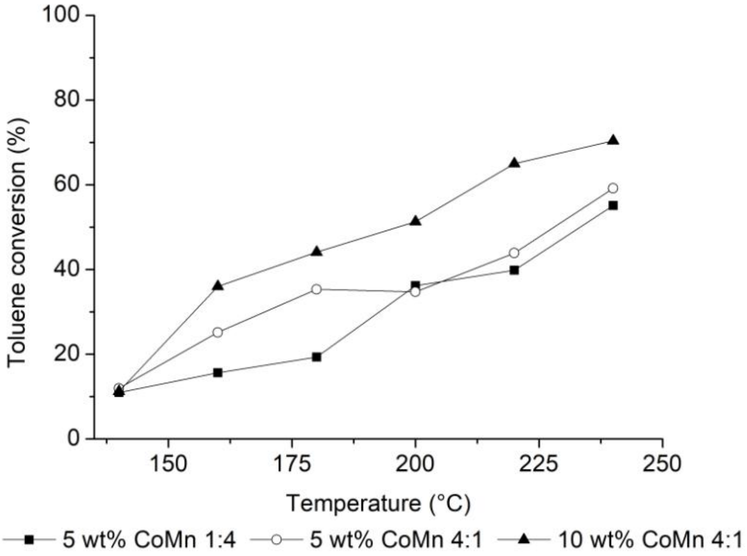

Figure 4: The comparison of mixed Co, Mn catalysts

The effect of water vapour on catalytic activity was examined and input airflow was saturated by water. The results are shown in Table 2. Water molecules inhibited a part of the active sites and the toluene conversion decreased in all tests. This deactivation is mostly reversible. A smaller difference between toluene conversion at 240 ° C without or with air humidification was observed for catalysts with increasing cobalt loads. High relative humidity could change the efficiency of contaminant removal in some cases of varying air quality. Also, the catalytic activity may be affected by GHSV (see Table 3). The experiment was performed at the different flow rates of the gas mixture through the reactor, specifically 1,000 – 6,000 h^{-1} GHSV. The constant input toluene concentration was adjusted by different dosing rates. As expected, the activity of all examined catalyst decreases at elevated GHSV values. However, it is obvious, the process of catalytic oxidation in our experiments was not fully covered by our tests at 240 °C and it is necessary to focus on GHSV over a wider temperature range. GHSV is a variable processing parameter and its optimization is necessary to reach best technology performance.

Table 2: The influence of the relative humidity of air stream on toluene conversion at 240 °C

	Toluene conversion (%)	
Catalyst RH (%)	**37**	**93**
5 wt% Co/Al_2O_3	59.7	43.1
10 wt% Co/Al_2O_3	48.5	38.3
15 wt% Co/Al_2O_3	50.4	43.5
5 wt% CoMn/Al_2O_3 1:4	55.1	52.9
5 wt% CoMn/Al_2O_3 4:1	59.2	39.5
10 wt% CoMn/Al_2O_3 4:1	70.4	61.7

Table 3: The effect of GHSV on toluene conversion at 240 °C

	GHSV (h^{-1})			
Catalyst	**1,000**	**2,000**	**3,000**	**6,000**
5 wt% Co/Al_2O_3	73.8	59.7	59.1	39.0
5 wt% CoMn/Al_2O_3 1:4	64.1	55.1	38.8	31.2
5 wt% CoMn/Al_2O_3 4:1	60.7		40.2	
10 wt% CoMn/Al_2O_3 4:1	85.9	70.4	44.0	34.1

We examined catalytic activity of cobalt and manganese catalysts in microwave field due to the necessity to find the suitable and low cost catalyst for scaled-up pilot microwave-assisted catalytic technology for toluene emission abatement. The further research should focus to better structure of of mixed cobalt-manganese oxide catalyst. Impregnation wetness method applied in this research for the preparation of catalysts are characterized by the distribution of catalytic species over bulk catalyst pellet, whereas the contaminant is oxidised particularly directly in the surface layer. Therefore, the catalytic material could be prepared with improved method toward thinner catalytic layer where the catalytically active sites are more concentrated and so more effective, so called egg-shell structured catalyst. Moreover, precipitation methods for better material crystallinity on the pellet surface could be applied in the future that could help further synergy between microwaves and mixed cobalt-manganese catalysts.

Conclusion

In this work, supported single component cobalt and manganese and mixed cobalt-manganese oxide catalysts were prepared using the impregnation method, characterized and tested as catalysts for the oxidation of toluene via microwave heating. Although these types of catalyst did not exhibit comparable efficiency like noble metal-based catalyst, their preparation was much less expensive due to the application of cheaper precursors and one of the simplest preparation methods. The use of microwave irradiation was tested as innovative and fast way of catalyst heating which can lead to the significantly higher efficiency of the toluene oxidation. The cobalt catalyst supported on the alumina presented the higher specific surface area and better interaction of microwaves than catalyst supported on titanium oxide. The addition manganese into precursor solution led to higher heating rate. The alumina was shown to be the most favourable support for a future pilot scale. Satisfactory catalytic activity results (70.4% toluene conversion at 240 °C) have been obtained for the mixed 10 wt% cobalt-manganese oxide catalyst in molar ratio 4:1 that has achieved higher activity than a simple cobalt oxide at the relatively low reaction temperatures. In catalyst activity tests, toluene conversion increased with increasing temperature of catalyst and decreased with increasing water vapour saturation of air and airflow through the catalyst. The microwave enhancement was able to decrease efficient operation temperature while the application of catalyst like Co and Mn oxides impregnated on alumina decreases significantly material costs and makes process more robust.

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References

1. Amann M., Lutz M.: Journal of Hazardous Materials *78*, 41 (2000).
2. He C., Cheng J., Zhang X., Douthwaite M., Pattisson S., Hao Z.: Chemical Reviews *119*, 4471 (2019).
3. Krishnamurthy A., Adebayo B., Gelles T., Rownaghi A., Rezaei F.: Catalysis Today *350*, 100 (2020).
4. Kamal M. S., Razzak S. A., Hossain M. M.: Atmospheric Environment *140*, 117 (2016).
5. Khan F. I., Kr. Ghoshal A.: Journal of Loss Prevention in the Process Industries *13*, 527 (2000).
6. Ojala S. a X spoluautorů: Topics in Catalysis *54*, 1224 (2011).
7. Gaur V., Sharma A., Verma N.: Carbon *43*, 3041 (2005).
8. Li W., Wang J., Gong H.: Catalysis Today *148*, 81 (2009).
9. Li T.-Y., Chiang S.-J., Liaw B.-J., Chen Y.-Z.: Applied Catalysis B: Environmental *103*, 143 (2011).
10. Wyrwalski F., Lamonier J.-F., Siffert S., Gengembre L., Aboukaïs A.: Catalysis today *119*, 332 (2007).
11. Liotta L. F., Di Carlo G., Pantaleo G., Venezia A. M., Deganello G.: Applied Catalysis B: Environmental *66*, 217 (2006).
12. de Rivas B., López-Fonseca R., Jiménez-González C., Gutiérrez-Ortiz J. I.: Journal of Catalysis *281*, 88 (2011).
13. Wang Y., Arandiyan H., Liu Y., Liang Y., Peng Y., Bartlett S., Dai H., Rostamnia S., Li J.: ChemCatChem *10*, 3429 (2018).

14. Ren Q., Mo S., Peng R., Feng Z., Zhang M., Chen L., Fu M., Wu J., Ye D.: Journal of Materials Chemistry A *6*, 498 (2018).
15. Solsona B., Davies T. E., Garcia T., Vázquez I., Dejoz A., Taylor S. H.: Applied Catalysis B: Environmental *84*, 176 (2008).
16. Huang H., Xu Y., Feng Q., Leung D. Y.: Catalysis Science & Technology *5*, 2649 (2015).
17. Santos V., Pereira M., Órfão J., Figueiredo J.: Applied Catalysis B: Environmental *99*, 353 (2010).
18. Durka T., Van Gerven T., Stankiewicz A.: Chemical Engineering & Technology *32*, 1301 (2009).
19. Horikoshi S., Serpone N.: *Microwaves in catalysis: methodology and applications*. John Wiley & Sons, 2015.
20. Yang Z. a X spoluautorů: Chemical Engineering Journal *319*, 191 (2017).
21. Meredith R. J.: *Engineers' handbook of industrial microwave heating*. Iet, 1998.
22. Stiegman A. E., v knize: *Microwaves in Catalysis: Methodology and Applications* (Horikoshi S., Serpone N., ed.). John Wiley & Sons, 2015.
23. Yi H. a X spoluautorů: Chemical Engineering Journal *333*, 554 (2018).
24. Yi H., Song L., Tang X., Zhao S., Yang Z., Xie X., Ma C., Zhang Y., Zhang X.: Ceramics International *46*, 3166 (2020).
25. Sobek J.: *Mikrovlnná chemie - interakce materiálu s elektromagnetickým polem, (n.d).*
26. Hirano T., v knize: *Microwaves in Catalysis: Methodology and Applications* (Horikoshi S., Serpone N., ed.). John Wiley & Sons, 2015.

Mikrovlnná katalytická oxidace toluenu na katalyzátoru na bázi směsného oxidu kobaltu a manganu na alumině

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Souhrn

Tato práce je zaměřena na vývoj vhodného a nízkonákladového katalyzátoru pro mikrovlnnou katalytickou oxidaci VOCs pro budoucí poloprovozní technologii. Série devíti jednosložkových a směsných katalyzátorů na bázi oxidů kobaltu a manganu byla připravena impregnací aluminy vodnými roztoky dusičnanů kobaltu a manganu. Tyto katalyzátory byly testovány pro oxidaci toluenu při inovativním mikrovlnném ohřevu, který může zvýšit účinnost a snížit provozní teploty. Bylo pozorováno odlišné chování mezi jednotlivými oxidy kobaltu a manganu v mikrovlnném poli. Směsné oxidy kobaltu a manganu jsou reaktivnější než jednoduchý oxid kobaltu. Přidání manganu do prekurzorového roztoku vedlo k vyšší rychlosti ohřevu. Mezi připravenými katalyzátory vykazoval nejlepší konverzi toluenu 70,4 % při 240 °C katalyzátor s obsahem 10 hm. % na bázi směsného oxidu kobaltu a manganu v molárním poměru 4:1.

Klíčová slova: *Co_3O_4, MnO_x, Al_2O_3, VOCs, katalytická oxidace, mikrovlnné záření.*

Sludge dewatering reed beds and their performance in terms of sludge quality improvement at small wastewater treatment plants

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Abstract

Wastewater treatment sludge presents a significant problem for small wastewater treatment plants due to both the high costs of the final handling process and the need to solve the various technological problems involved. However, several technologically simple and low-cost solutions are currently being introduced into practice. To date, the Czech Republic has very little experience of Reed Bed technology (RBs, or STRBs) that is commonly employed in European countries such as Denmark, Spain, Austria or Poland. This study focused on the testing of two pilot RB systems of different construction installed at two small wastewater treatment plants – a constructed wetland in the Southern Moravia region for 800 PE and an activated sludge treatment plant in the Central Bohemian region for 1900 PE. The two pilot reed beds were filled with liquid sludge containing between 2 to 13 % of total solids (TS), depending on the origin of the sludge, using different loading schemes for the studied period 2017-2018. Both of the pilot units evinced very promising results in terms of the extensive dewatering of the sludge by up to 30 – 34 % of the TS in average at the end of each campaign. At the end of the study period, it was observed that the content of pathogenic microorganisms and other monitored harmful substances did not exceed Czech limits for agricultural use, thus allowing the use of the material as fertilizer.

Keywords: *Sludge, sludge dewatering, sludge stabilization, constructed wetlands, Reed Beds, Sludge Treatment Reed Beds*

Introduction

Wastewater treatment sludge represents a significant environmental and economic problem for most wastewater treatment plants (WWTP) due to its dangerous properties and limited options in terms of final treatment. Moreover, it also represents a significant component of the costs of the wastewater treatment process, especially for small WWTPs.

Although such sludge is a carbon- and nutrient-rich material that might be further used in the agricultural sector as a fertilizer, the main problem lies in its potential for also containing a wide spectrum of harmful toxic substances such as heavy metals, polycyclic aromatic hydrocarbons (PAHs), other persistent organic pollutants, pharmaceuticals, personal care products, endogenous hormones, synthetic steroids and others (Singh and Agrawal 2008; Smith 2009; Fijalkowski et al. 2017). The use of sludge for agricultural purposes is, therefore, seriously limited by the content of such harmful substances. Czech limits have been standardized via domestic legislation based on European standards (see Hudcová et al. (2019); for example, conditions governing the use of treated sludge on agricultural land are set out in Decree No. 437/2016 Coll., which defines the technical and organizational conditions for application and the qualitative indicators concerning sludge. Adherence to these conditions is essential to eliminating the negative impacts of sludge due to the presence of contaminants, especially concentrations of certain risk elements, hazardous organic substances, and pathogenic microorganisms.

In general, sludge is characterized by considerable variability in terms of its nutrient content, which depends on the source of the wastewater and the treatment process (Moss et al. 2002). Organic carbon may constitute as much as 40 % of the total mass (Uggetti et al., 2010), and organic nitrogen and inorganic phosphorus constitute the majority of the total nitrogen (TN) and total phosphorus (TP) contents respectively in sewage sludge (Singh and Agrawal 2008). Uggetti et al. (2010) published the percentage ratio of three nutrients in the sewage sludge of a WWTP for a 1500 population equivalent (PE): total nitrogen 9.8 %, total phosphorus 2.7 %, and potassium (K) 0.3 % of total solids. Svoboda (2015) presented the content of nutrients (N, P, K and other 8 elements) in dry matter (DM) of sludges from different countries, including the Czech Republic. The range of values is following: N 2.2–4.8 %, P 0.8–2.5 %, K 0.2–0.6 %. Rozkošný et al. (2015) published results of a survey of sludge characteristics and contamination by selected hazardous pollutants and heavy metals of different types of small WWTP in the Czech Republic and Slovakia. Results of the survey showed that small WWTP sludges contamination by heavy metals, PAHs, PCBs fulfill given legislation limits for agricultural applications in general and the main problem is appropriate hygienization in many cases.

Currently, most EU countries prohibit the disposal of untreated sludge on agricultural land and some Member States require the special treatment of such sludge before its reuse (biological or chemical stabilization), which, naturally, incurs additional operational costs for WWTPs. Such costs are then reflected in the charges paid by users. To decrease these costs, low-cost technologies have been widely introduced especially at smaller WWTPs that reduce both the technical and financial demands of wastewater treatment.

So-called sludge dewatering Reed Beds (RBs) or Sludge Treatment Reed Beds (STRBs) provide a low-cost solution for such WWTPs. STRBs have been used in Europe for sludge dewatering and stabilization since the late 1980s. The largest experience comes from Denmark (Nielsen, 2007; Nielsen, Larsen, 2016) and, today, they are in operation practically worldwide. STRB is based on constructed wetlands, which are being used for wastewater treatment (Caselles-Osorio et al., 2007). RBs consist of sealed space for sludge dewatering with drainage layers composed of different fractions of sand and gravel that are planted with wetland plant species, particularly common reed (*Phragmites australis*). RBs are commonly designed in the form of basins with plastic liners or as concrete tanks (Fig. 1 and 2) positioned beneath the level of the local terrain. The capacity of RBs is dimensioned with the expectation that space will serve for several (up to ten) years depending on the design volume.

The role of the wetland vegetation is to ensure the more rapid dewatering of the deposited sludge principally via the evapotranspiration (ET) process. Following the end of the growing season, the plants decay and decompose within the sludge layer, which serves to enrich the final dewatered matrix with carbon-rich vegetation residues. Liquid sludge is regularly pumped into the RB system via distribution pipes which, over time, leads to changes in its properties, mainly in terms of the total solids (TS) concentration (DM content) as well as that of various organic substances and the number of pathogenic bacteria present.

The basic RB treatment process consists of dewatering via the gravitational percolation of the water from the sludge into the drainage layer and the evapotranspiration of water via wetland vegetation (Stefanakis and Tsihrintzis, 2011). The draining of excess water by means of gravity commences immediately following the pumping of the sludge into the RB. The drying process itself via evaporation/evapotranspiration subsequently continues for a longer time period. The processes occurring with the sludge filled into drainage RB units with wetland plant vegetation are more precisely described by Peruzzi (2017). The main operating principles, design and operation errors as well as recommendations for the subsequent management of drained matter are summarized in a study by Brix (2017).

Although RB treatment technology has proved to be both efficient and economically advantageous in small decentralized areas across Europe. The closest such facilities are located in Austria (Fig. 1) and Poland (Obarska-Pempkowiak et al., 2003) they have not yet been generally introduced in the Czech Republic. Thus, this paper aims to present the results of the research of two experimental RB installations established for the dewatering and stabilization of sludge at two small wastewater treatment plants of the category 500–2000 PE in the Czech Republic. The general objective of the paper is to demonstrate the potential for the use of this technology under the climate conditions pertaining in Central Europe, with the eventual aim of producing a final added-value material, i.e. organic fertilizer.

Figure 1: Examples of RB units operated as part of a small WWTP in the Waldviertel region of Austria (Autumn 2017)

Experimental part

Experimental locations

Two pilot-scale RB units were installed for the purposes of the study at two WWTPs in the Czech Republic. The first one consists of an Imhoff tank as the WW mechanical pre-treatment, three constructed wetlands, and a final purification pond. The WWTP is located in the village of Dražovice (D1) in the South Moravia region. This WWTP is connected to a combined sewerage system and it was built with a projected capacity of 780 PE. More information on the Dražovice WWTP provides Rozkošný et al. (2011). The second one is the activated sludge WWTP at a location in the Central Bohemia region (K2). This WWTP has a designed capacity of 1,900 PE.

RB units at the D1 location

The reed bed units at the Dražovice WWTP (hereinafter referred to as RB1) were constructed at the location in the form of concrete tanks with drainage systems at the bottom. The RBs receive a primary sludge pumped from the mechanical pre-treatment of the WWTP. Each experimental RBs has a surface area of 9.5 m^2. The drainage pipes inside the fields were covered with a 300 mm thick sand filter layer (grain size 2–4 mm). Czech technical guidance ČSN EN 12255-8 recommended the sand filter layer between 50 and 100 mm, combined with a gravel layer between 300 and 400 mm. Both units were planted with the common reed in 2011. To investigate the influence of climatic conditions on the vegetation drainage and evapotranspiration process, one of the units was covered with a greenhouse-type shelter (hereinafter referred to as RB1-GH). The second RB was left uncovered (RB1-O). The states of both units, especially with concern to the development of the planted vegetation, in the year of completion (2011) and 2017 (after 6 years of trial operation) are documented in Fig. 2 and Fig. 3.

Figure 2: The RB units at Dražovice – RB1-GH on the left and RB1-O on the right in 2011

Figure 3: The RB units at Dražovice – RB1-GH on the left and RB1-O on the right in 2017

Mobile RB at the K2 location

The second pilot unit (hereinafter referred to as RB2) was constructed in the form of a mobile unit in a container at the K2 location in Central Bohemia (Fig. 4). The surface area is 9.84 m^2. The total volume of the unit is approximately 12 m^3 with a 300 mm thick drainage layer (volume 3 m^3) composed of two fractions (4-8 mm and 8-16 mm) of fine gravel and an available sludge dewatering volume of approximately 9 m^3. The sludge dosing distribution pipes are connected to the WWTP's extensive activated sludge storage facility.

Figure 4: Mobile RB unit at the beginning of the operation on the left and during the excavation of dewatered and stabilized sludge on the right

Operation characteristics

Both RB systems have been intermittently loaded with sludge and old reed vegetation planted at the RBs since the commencement of their operation. The main difference between the two locations in terms of the sludge filling regime is determined by the specific requirements set out concerning sludge disposal by the respective type of the WWTP. The sludge produced via mechanical pre-treatment process in a WWTP based on constructed wetland technology usually needs to be pumped out every three months or between 3 and 8 times per year, in general (Obarska-Pempkowiak et al., 2003). The frequency of the disposal of sludge at the D1 RB units following the interval. Information about the RB1 filling is summarized in Table 1. Sludge disposal of an activated sludge WWTP is provided on daily basis. The loading frequency at the second locality was one week.

The RB1-O unit was filled 4 times per year in the study period, each filling consisting of 1.2 m^3 of sludge mixture on average. The filling was performed during the disposal of the total volume of sludge from the Imhoff tank. The sludge that was not used to fill the RBs was transported to a larger WWTP. Each of the RB filling campaigns increased in the RB mixture layer of 15 cm of new liquid sludge. The same filling was done for the RB1-GH unit in 2018. Total sludge load per area and a year was similar to the values of Spanish operated full-scale RB units (55 and 51 kg TS/m^2 and year, Uggetti et al., 2009). These sludge loading rates are within the range suggested in the literature (50-60 kg TS/m^2 and year) Nielsen (2007), Brix (2017), etc.

During campaigns 1 (40 weeks in 2017-2018) and 2 (92 weeks in 2018-2019), the RB2 sludge dose was set at 10 cm. The application regime is presented in Table 2. Sludge filling took place for 15 and 23 weeks, respectively, in a given campaign (Table 2). A total load of sludge per area to the RB2 unit was thus about half in each campaign compared to the recommended value of 50 kg of TS/m^2/year (Brix, 2007). The reason was the lower available height for sludge filling at the mobile unit, the need to allow the disposal of dewatered sludge, and to ensure access inside the unit. Reducing the load with respect to the design and operation of this type of RB unit led to the possibility of testing the process of dewatering (up to 20-25 weeks) and stabilization (about 20-25 weeks) in one campaign (year). In practice, therefore, the simultaneous use of two units to use the recommended annual sludge load per area is assumed.

All the material was excavated in 2018 after campaign 1 of operation prior to the second filling campaign so as to provide the necessary space in the RB2 unit. Moreover, the climatic conditions during both filling campaigns resulted in the complete drying and maturation of the sludge.

Table 1: The RB1 loading scheme

Year	Number of loadings	Average loading interval	Average load (m^3)	Average inlet TS (%)	Total weight of sludge (kg of TS)	Total load per area (kg_{TS}/m^2)
2017	4	2.2 months	1.2	11.5	552.0	58.1
2018	4	2.5 months	1.2	10.8	518.4	54.6

Table 2: The RB2 loading scheme

Year	Number of loadings	Average loading interval	Average load (m^3)	Average inlet TS (%)	Total weight of sludge (kg of TS)	Total load per area (kg_{TS}/m^2)
2017	13	1 week	0.3	5.3	205.2	20.8
2018	18	1 week	0.28	3.6	179.2	18.2

RB monitoring, sampling and biosolid analysis

Both RB1 and RB2 were sampled regularly following each of the filling campaigns to determine the Total Solids concentration (TS) and combustible substances (Volatile Solids – VS), for microbiological (MBI) analysis purposes and to determine the presence of selected elements including nutrients, heavy metals and organic compounds (PAHs, PCBs, AOX). All the sampling and analysis methods were applied based on procedures set out in Czech technical guidelines as harmonized with the ISO system. The TS concentration of the sludge was determined gravimetrically under laboratory conditions. The following MBI parameters were monitored: *Salmonella*, faecal coliform bacteria and enterococci.

The TS and the VS of the dewatered mixtures at the RB1 site were monitored 1 or 2 days following each of the filling campaigns, followed by monitoring one week later and then every two weeks until the next filling campaign. Samples were taken from the top layer 0–2 cm (the “crust” in Tables 3–5) and the layer at 5–15 cm (the “profile” in Tables 3–5). Each sample consisted of a mixture of samples extracted from three randomly-selected locations (10 x 10 cm areas) in the respective RB. The samples were stored in PP boxes and transported to the WRI laboratory in cooled transportation box.

With respect to RB2, sludge samples were taken at three locations at which hygrometers were positioned. Each sample was extracted from at least two differently-spaced points to obtain representative sludge samples. Moreover, sampling was conducted in two layers – upper 5 cm, the crust (see in Fig. 7) and 20 – 40 cm beneath the surface (the “profile” layer in Fig. 7 and 8). In addition, sampling was performed every third week for the purposes of the microbial and hazardous substances analyses.

Both pilot units were equipped with continuous monitoring systems that measured the basic meteorological variables (air temperature and humidity). In addition, one soil temperature sensor and three soil moisture sensors were connected to the data logger for the monitoring of the RB2 sludge moisture content.

All results of the raw sludges and RB mixtures content analyses were compared with limit values given by the Czech legislation (Decree No. 437/2016 Coll.) focused on the wastewater treatment sludge use in agriculture. The Decree specifies values similar to other EU countries' legislation requirements (Hudcová et al., 2019).

Results and discussion

RB1 at the D1 location

The sludge pumped into RB1 had an average TS concentration of 11 % and a VS of 78 %. TS and VS measured at the end of the filling campaigns, i.e., before new filling are mentioned in Tables 3–5. The progress of the TS concentration and VS losses via the annealing of the dewatered layer for RB1-O were depended on the part of the year. The best values, up to 49 % of TS in 2017 and up to 24 % in 2018 were reached during the summer. In the autumn weather and during winter, where is no ET by plant biomass, we observed stagnation of TS concentration by the time. The maximum measured TS concentration was about 25 %. Precipitations also dilute the upper layer of the dewatered sludge in an open RB. Uggetti et al. (2011) measured the highest TS concentration during the summer season (25 % of TS) and lower (around 16 %) during the rest of the year. In general, the long-term average TS concentration value was observed 34 % for the “profile” layer, which means the layer of sludge pumped in the particular year without the crust, usually a few cm thick. A systematic increase in the TS concentration from 1–3 % in the influent (raw) sludge to 20–30 % in the dewatered material was measured by Uggetti et al. (2009) for three full-scale RB systems operated for the WWTP 400, 600, and 1500 PE. Nielsen and Bruun (2015) published the efficiency of few Danish Reed Bed systems operated 10–20 years. Inflow sludges with TS concentration 0.5–3 % achieved TS concentration up to 26 % (average value 22 %) after dewatering, reduction and mineralization. Mineralization removed up to 27 % of the organic solids in the sludge to the average value of the VS 46 %. Obarska-Pempkowiak et al. (2003) reported TS values of the dewatered sludge up to 58 %, which might be a result of a higher TS concentration in filled sludge (up to 10 %) and the origin of sludge, it was from an Imhoff tank. The same origin as the sludge at D1 locality.

Higher dewatering can be achieved by covering the RB surface area. We tested a greenhouse covering (RB1-GH) made from polycarbonate sheets mounted on a galvanized profile structure. In the case of RB1-GH the maximum TS concentration after sludge drying was measured usually about 55 %, with a peak value up to 80 % in summer 2018.

VS values decreased in course of the campaigns from values between 70 and 85 in 2017 to the range 48–57% in the “profile” layer of the RB1-O. In the year 2018, the decrease was from the range 76–82% of VS in raw pumped sludge to the range 39-59% in the “profile” layer. Uggetti et al. (2009) observed the decrease of VS concentration from 52–67% to 31–49%. The higher decrease was during summer periods, which correspond with the limiting factors like the environment temperature for microbial processes. In the case of the RB1-GH unit, the final VS values at the end of each campaign were stable during a year (Table 5).

The TS and the VS of the final materials, after a longer resting period, were 49% and 30% respectively for the RB1-GH material and 38% and 34% respectively for the open-surface RB1-O material.

Table 3: Changes in TS and VS of the sludge in RB1-O unit during campaigns in 2017

RB1 unit	**Sampling point**	**Campaign 1 23. 3.–11. 6.**		**Campaign 2 12. 6.–13. 8.**		**Campaign 3 14. 8.–21. 9.**		**Campaign 4 22. 9.–27. 11.**	
		TS (%)	**VS (%)**	**TS (%)**	**VS (%)**	**TS (%)**	**VS (%)**	**TS (%)**	**VS (%)**
RB1-O	Inflow (raw sludge)	11	73	12	85	13	70	10	78
	Final - crust	76	51	83	32	32	50	19	62
	Final - profile	**31**	**48**	**49**	**57**	**30**	**49**	**24**	**48**

Table 4: Changes in TS and VS of the sludge in RB1-O unit during campaigns in 2018

RB1 unit	**Sampling point**	**Campaign 5 1. 2.–30. 5.**		**Campaign 6 31. 5.–30. 8.**		**Campaign 7 31. 8.–18. 10.**		**Campaign 8 19. 10.–9. 12.**	
		TS (%)	**VS (%)**	**TS (%)**	**VS (%)**	**TS (%)**	**VS (%)**	**TS (%)**	**VS (%)**
RB1-O	Inflow (raw sludge)	12	81	13	82	11	77	7	76
	Final - crust	92	59	68	56	55	57	28	60
	Final - profile	**34**	**41**	**35**	**39**	**42**	**44**	**27**	**59**

Table 5: Changes in TS and VS of the sludge in RB1-GH unit during campaigns in 2018

RB1 unit	**Sampling point**	**Campaign 1 1. 2.–30. 5.**		**Campaign 2 31. 5.–30.8.**		**Campaign 3 31. 8.–18.10.**		**Campaign 4 19. 10–9. 12.**	
		TS (%)	**VS (%)**	**TS (%)**	**VS (%)**	**TS (%)**	**VS (%)**	**TS (%)**	**VS (%)**
RB1-GH	Inflow (raw sludge)	9	75	13	82	11	77	7	76
	Final - crust	42	55	88	28	56	60	53	27
	Final - profile	**55**	**22**	**80**	**21**	**51**	**34**	**56**	**24**

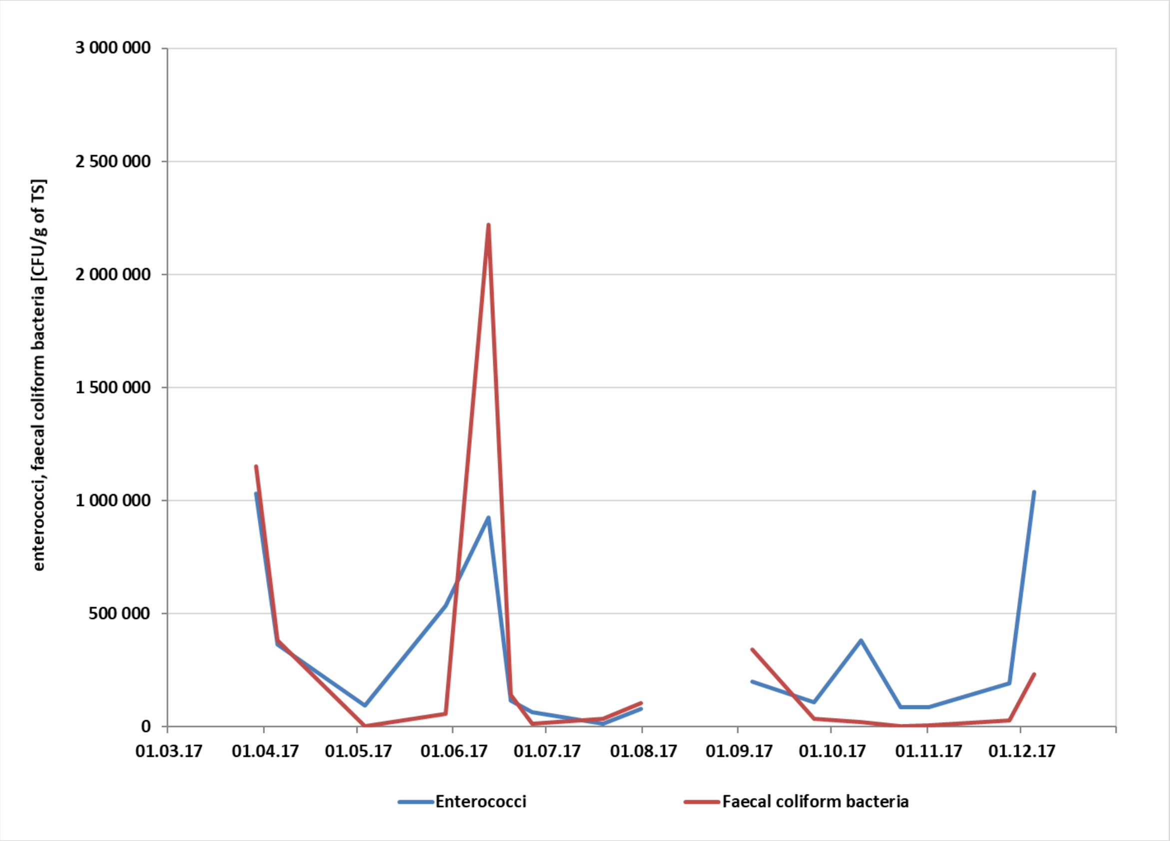

Figure 5: Development of the MBI contamination of the RB1-O mixture in 2017

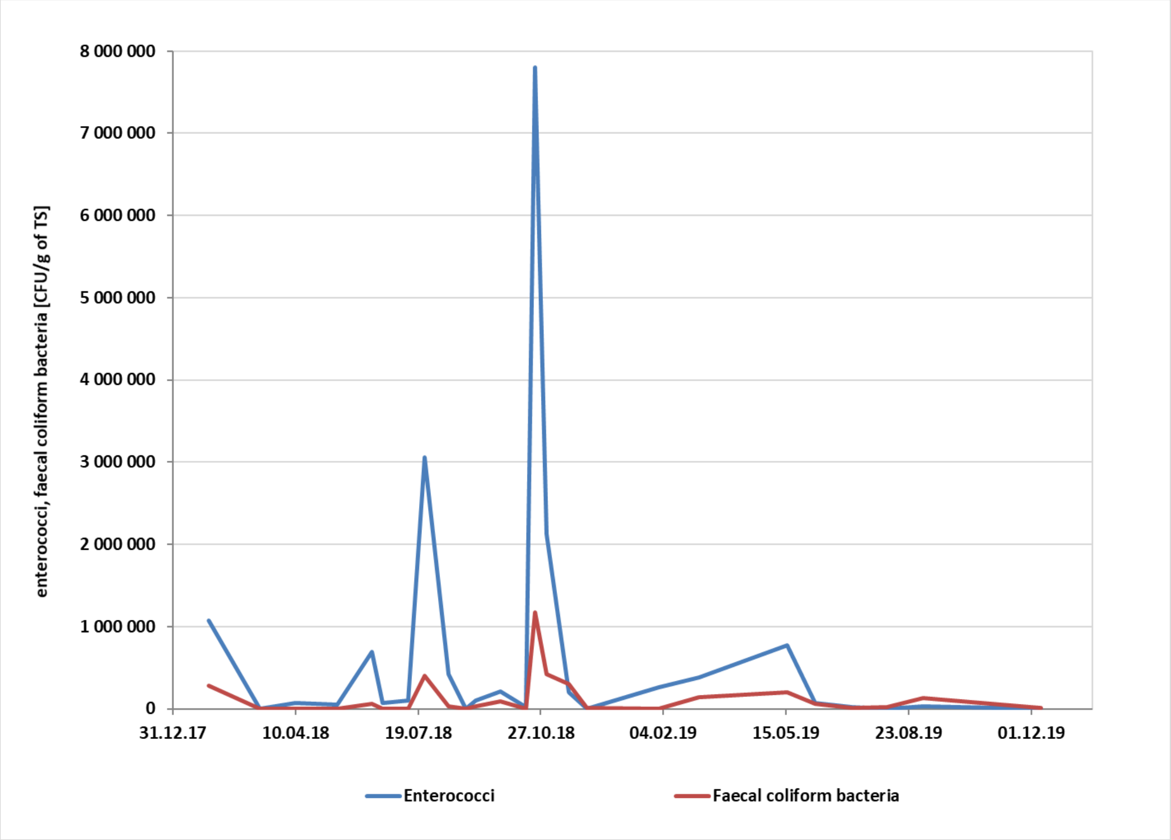

Figure 6: Development of the MBI contamination of the RB1-O mixture in 2018 – 2019

The microbial contamination of used Dražovice WWTP mechanical pre-treatment raw sludge reached peak values between approx. 400 000 CFU/g of TS and 3 000 000 CFU/g of TS showed in Fig. 5 and Fig. 6 during the whole study period, with one exception, a peak up to 8 000 000 CFU/g of TS in case of enterococci. The sludge does not contain any Salmonella. The microbial contamination of the dewatered sludge in RB1-O remained at a level of thousands of CFU/g of TS in case of enterococci, although gradual decreases were observed of up to three orders of magnitude compared to the level of the fresh sludge (Fig. 5 and 6). In the case of faecal coliform bacteria, their amount decreased during campaigns to the level of hundreds or tens CFU/g of TS. The number of enterococci CFU/g of TS in RB1-GH decreased by 3 orders of magnitude during each campaign, to thousands of CFU. In the case of the number of faecal coliform bacteria CFU, a decrease of two orders of magnitude was found, from hundreds of thousands of CFU to thousands of units. Samples from both of the RBs had evinced microbial contamination at levels that met the limits for the agricultural use of sludge (Decree No. 437/2016 Coll., Hudcová et al., 2019) by the end of the resting period, i.e. 4–6 months following the final filling campaign. There was no occurrence of Salmonella.

The contents of metals and arsenic complied with legislative requirements. A comparison of the content of elements in the raw sludge and both RB1 units final mixtures are provided in Table 6. Each value is the average from three values measured in sludge samples from the year 2019 after the end of filling (final mixtures). Predominant heavy metals in the Dražovice sludge are Zn, Cu, Cr and Ni. This is influenced by the connection of the WWTP to the combined sewerage system. Zn, Cu and Cr are also predominant elements in the sludge of RB2 locality (Fig. 9). Nielsen and Bruun (2015) find Zn, Ni and Pb as predominant heavy metals in the sludge. The difference in terms of changes in the content of elements between the raw sludge pumped into the RBs and the final RB mixtures of dewatered sludge and reed biomass tissue indicate a higher amount in final mixtures due to concentrating the content of the elements. Such findings were published e.g. Uggetti et al. (2011). Higher values of monitored elements were measured in the final mixture of greenhouse RB (RB1-GH), thanks to the higher decreasing of organic content (VS) and volume reduction. But all monitored elements content was lower than limit values given by the Decree no. 437/2016 Coll. Similar results of the analysis were obtained Uggetti et al. (2009) for Spanish RB units. Heavy metals remained below law threshold concentrations.

Table 6: The average content of elements (mg/kg of dry matter) in the raw sludge and the RB1 final mixtures

Element	Raw sludge	RB1-O mixture	Average change (%)	RB1-GH mixture	Average change (%)	Limit value (Decree No. 437/2016 Coll.)
As	4.5	3.8	- 16	6.5	+ 44	30
Cd	0.5	0.6	+ 20	0.94	+ 88	5
Co	7.6	5.1	- 33	7.3	- 4	
Cr	20	31	+ 55	47	+ 135	200
Cu	99	131	+ 32	210	+ 112	500
Hg	0.28	0.44	+ 57	0.78	+ 179	4
Mo	1.8	2.3	+ 28	3.1	+ 72	
Ni	15	22	+ 47	30	+ 100	100
Pb	12	30	+ 150	39	+ 225	200
V	14	21	+ 50	40	+ 186	
Zn	550	675	+ 23	1100	+ 100	2500

The aboveground biomass of common reed growing in the RB1 units was harvested at the end of the vegetation season in 2017 and 2018. The average weight of the biomass was calculated at 2336 g per m^2 for RB1-O and 2928 g per m^2 for RB1-GH, which means 22192 g for the total RB1-O unit area and 27816 g for the total RB1-GH area per a year. Vymazal and Kröpfelová (2005) studied the growth of common reed at constructed wetlands for wastewater treatment of the 13 Czech villages. Common reed aboveground biomass varied widely between 1652 and 5070 g/m^2 with an average value of 3266 g/m^2.In our case, the biomass weight represents approx. 4% of all material added to the RB units per year.

The elements analysis of the biomass was not provided, because of the plants' uptake elements, including heavy metals, from the sludge mixture only. To compare the potential content of elements in biomass from RB units, we can use the results of the analysis of common reed biomass from the Czech WWTPs based on constructed wetlands, published by Vymazal et al. (2009): As 0.17 mg/kg of TS, Cd 0.01, Co 0.12, Cr 0.16, Cu 7, Hg 0.02, Mo 1.5, Ni 1.3, Pb 0.17, V 0.06 and Zn 24 mg/kg of TS. Similar results were published Bonanno (2011) for a biomonitoring study including common reed plants.

RB-2 at the K2 location

Fig. 7 illustrates the results of the TS concentration in RB2. The end of the filling was at the 14th week of the first campaign (2017 – 2018) and the 23rd week of the second campaign (2018 – 2019). It is evident that although the average inlet TS concentration was just 5.3 % and 3.6 % in the first and second campaign, respectively, in the dewatered layer, the TS concentration ranged between 10% and 15% during the filling periods in both campaigns. The TS concentration gradually increased towards the end of the first campaign, to reach values in the range 30% to 35%, which corresponded to the average calculated values for RB1-O (Tables 3 and 4). At the end of the second campaign, the TS concentration reached approx. 20% only.

While the content of enterococci decreased by one order of magnitude even during the filling period (Fig. 8), in the case of faecal coliform bacteria, a decrease was observed only in the maturation phase (Fig. 8). The material excavated from the mobile RB in May 2018 no longer contained any *Salmonella*, and the amount of CFU per gram of the material was below 50 CFU/g of TS for both faecal coliforms and enterococci. The same results for *Salmonella* and faecal coliform bacteria were measured for the second campaign. The number of enterococci was higher, about 600 CFU/g of TS. Following 12 months of sludge deposit resting and stabilization helped to decrease the number of enterococci to the values of about 100 CFU/g of TS. It was discovered that a resting period is necessary following the filling of RBs so at to ensure the hygienization of the deposited material thus fulfilling legislative requirements for further agricultural use. Other studies in RB have shown that the number of monitored bacteria was reduced to less than 10 CFU/g (enterococci) and up to 6-7 orders for faecal coliform bacteria during a period of 3–4 months after the last loading (Brix, 2017).

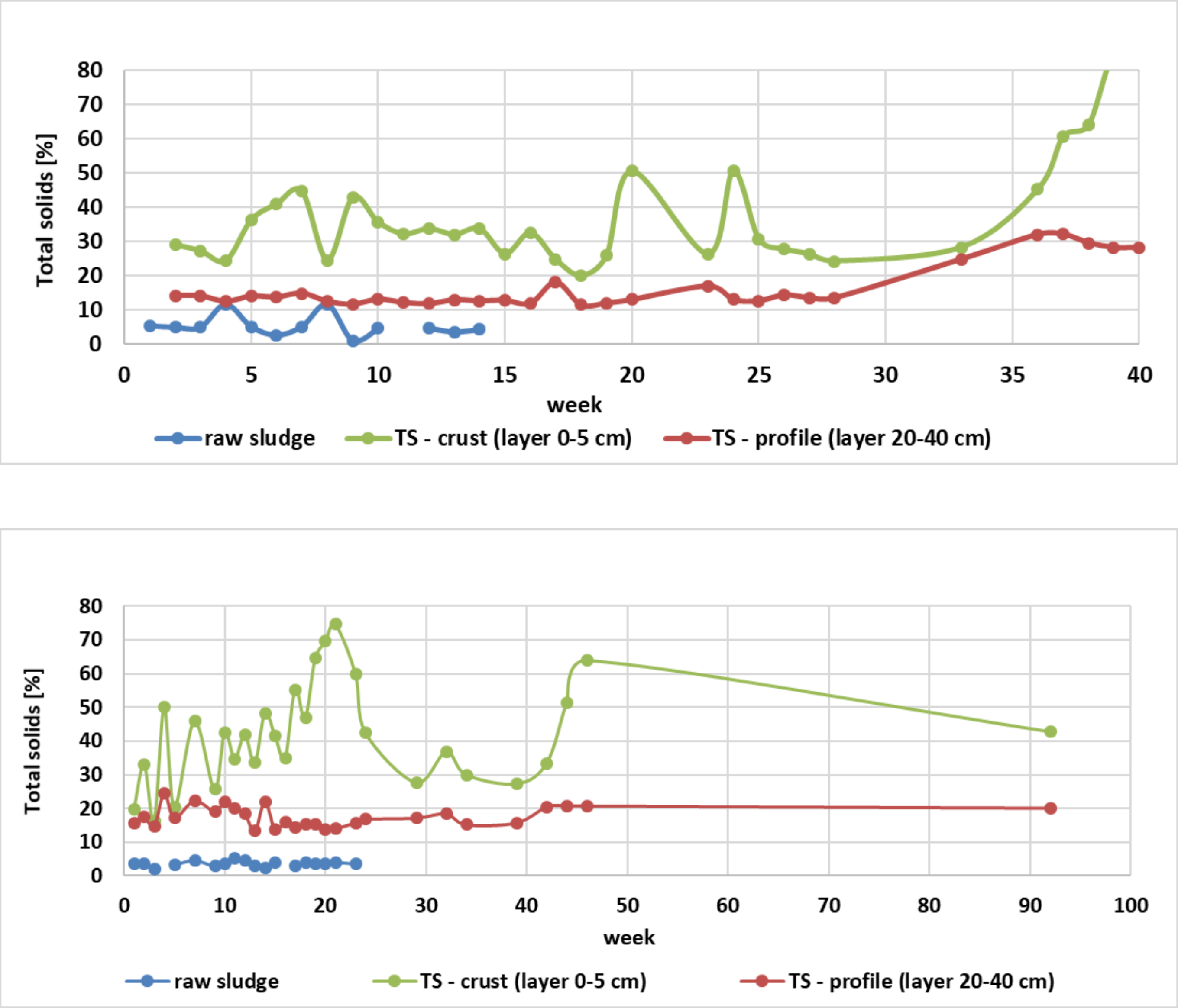

Figure 7: Development of the TS concentration in sludge following the filling of the mobile RB2 unit in campaign 1 (upper graph) and in campaign 2 (bottom graph)

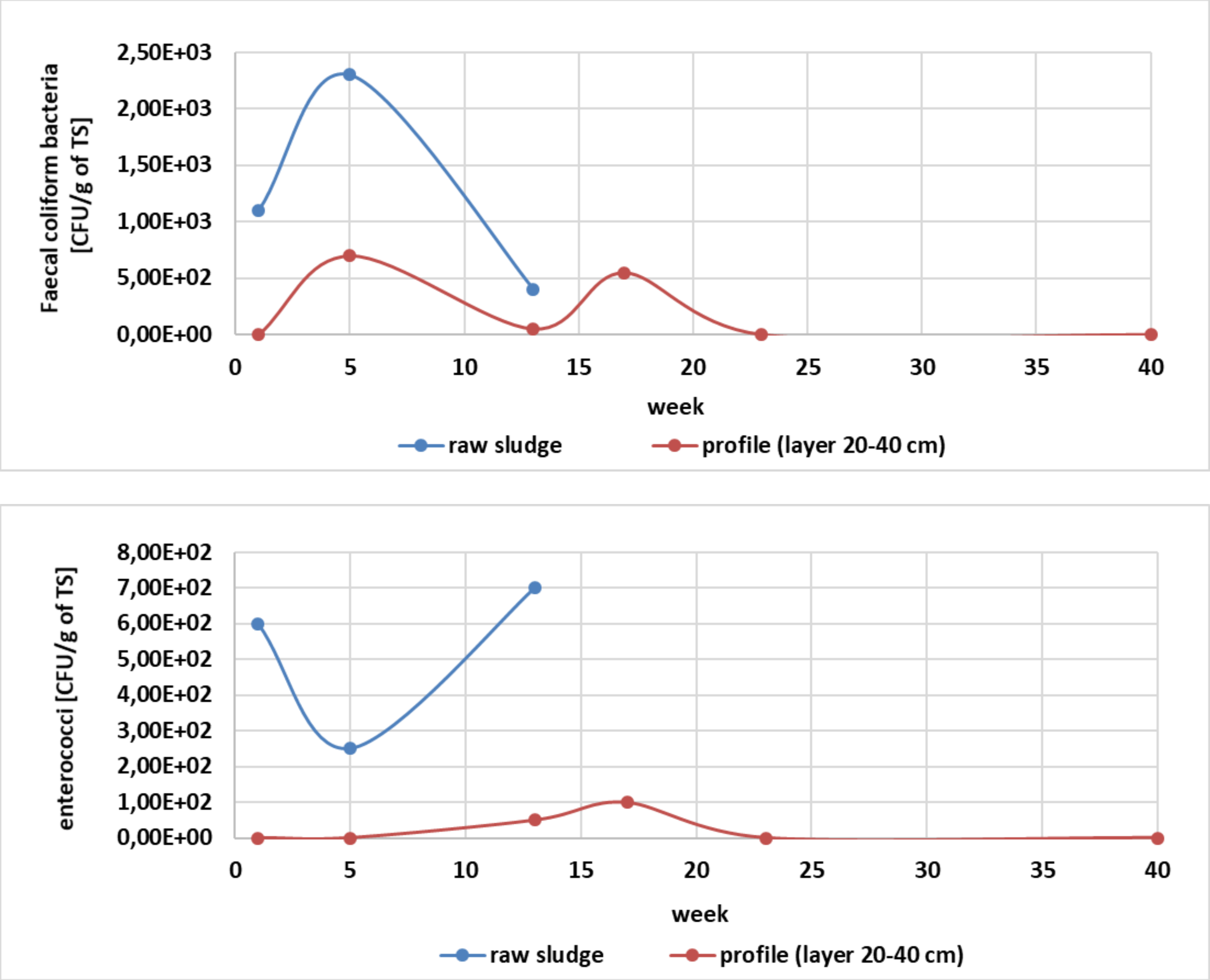

Figure 8: Changes in the microbial contamination of the sludge in the RB2 during campaign 1

The progress of the concentrations of selected metals and arsenic in the sludge in RB2 is shown in Fig. 9. With respect to the content of Zn, Cu, and Cr, an increase was apparent from the end of the filling campaign up to the removal of the dewatered material from the unit, the reason for which may have been the loss of the organic fraction (VS values decreasing) and a subsequent increase in the concentration of these metals in the remaining mass. Nevertheless, the concentrations were below the limits set by Czech legislation (Decree No. 437/2016 Coll., Hudcová et al., 2019). The extracted material also complied with all the limit values for the sum of PAH (content in the material of approximately 2.5 mg/kg) and the sum of PCB (content in the material of below 0.05 mg/kg).

When designing RB units for a certain area with given climatic conditions, it is necessary to determine the optimal interval between, and the duration of, the filling and drying periods. For constructed wetland WWTPs, it would be advisable to determine filling times only at those times in the year at which it is necessary to remove sludge from their mechanical pre-treatment facilities in connection with filling to a level about 10 to 20 cm in the filling interval between 1.5 and 3 months depending on the part of a year and actual climate conditions.

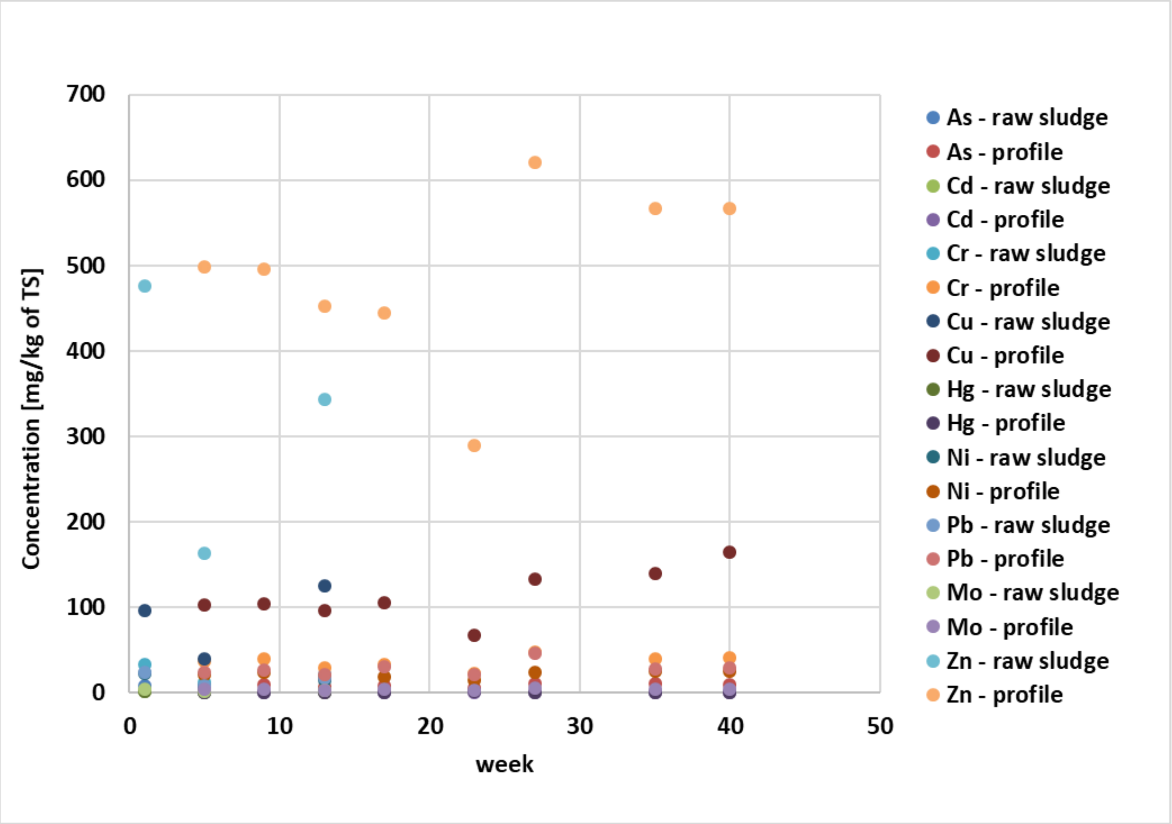

Figure 9: Changes in the content of selected elements in the sludge in the RB2 during campaign 1

Concerning activated sludge WWTPs, the filling and drying periods can be shorter and correspond to the experience gained with the mobile RB2 unit.

Both variants must leave the material in the RBs following filling and drying for a recommended period, preferably including the summer (Brix, 2017; Kolecka, 2017), thus allowing for the mineralization and hygienization of the material. Recommended is at least 6 months, based on the presented experiment results. The resulting matrix should exhibit a composition and properties that are comparable to compost produced from sludge (Kannepalli, 2016), as is also demonstrated in the results of this study.

The sludge of an activated sludge WWTP, built for approx. 1200 PE and located in the same region as the Dražovice WWTP, was sampled during the studied period. The sludge is dewatered by centrifuge equipment. Measured range of TS concentration after dewatering was between 12.2% and 45.6% with an average value of 23.7%. For the VS, we measured a range of values between 50% and 96% with an average value of 86%. The comparison of these values with the measurement of dewatered sludge from RB1 units show that dewatering was similar during the period of monitoring. The reduction of organic matter is higher in the Reed Beds thank the longer time of dewatering and stabilization. Other experiences show that sludge dewatered on centrifuges or belt presses typically reach a dry solid content of 15–20% and 15–24% (Nielsen and Larsen, 2016). Covering by a greenhouse can enhance the VS decreasing to the values between 20% and 45%.

The Reed Bed technology can be useful for small WWTP between a few hundred PE and 2000 PE (our calculation and also Uggetti et al., 2011). We estimated the necessary area of an RB for 100 PE WWTP is 32–78 m^2, for 500 PE WWTP it is 160–388 m^2, for larger WWTP (1000–2000 PE) up to the range 640–1560 m^2 under the Czech local conditions.

Conclusions

Wastewater treatment sludge presents a significant problem for small wastewater treatment plants due to both the high costs of the final handling process and the need to solve the various technological problems involved. However, some technologically simple and low-cost solutions are currently being introduced into practice. To date, the Czech Republic has very little experience with the Reed Bed technology. This study proved a possible use of the technology for Czech small WWTP both, constructed wetland and activated sludge WWTPs. The two pilot reed beds were filled with liquid sludge with the TS between 2 to 13%, depending on the origin of the sludge, using different loading schemes for the studied period 2017–2019. Both of the pilot units evinced very promising results in terms of the extensive dewatering of the sludge by up to 30–40% of the TS at the end of each campaign. In the case of the greenhouse covered RB unit, the sludge dewatering reached values of TS concentration between 51% and 80% based on the year season and climate conditions. Tested intervals between, and the duration of, the filling and drying periods for both types of WWTPs seems to be usable for the full-scale RB units under the Czech Republic climate conditions.

At the end of the study period, after resting and stabilization period, it was observed that the content of pathogenic microorganisms and other monitored harmful substances did not exceed Czech limits for agricultural use, thus allowing the possible use of the material as fertilizer. The final material should be further investigated for example by toxicity tests, weed seed content evaluation and germination inhibition test. For example, toxicity tests, weed seed content evaluation, and germination inhibition test. However, these tests and trials have not been studied.

Acknowledgments

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References

1. Bonanno, G. Trace element accumulation and distribution in the organs of *Phragmites australis* (common reed) and biomonitoring applications. Ecotoxicology and Environmental Safety, 74: 1057 – 1064 (2011).
2. Brix, H. Sludge Dewatering and Mineralization in Sludge Treatment Reed Beds. Water, 9, 160 (2017).
3. Caselles-Osorio, A., Puigagut, J., Segú, E., Vaello, N., Granés, F., García, D., García, J. Solids accumulation in five full-scale subsurface flow constructed wetlands. Water Research, 41 (6): 1388 – 1398 (2007).
4. ČSN EN 12255-8 (Czech technical guidance). Wastewater treatment plants – Part 8: Sludge treatment and storage. ČNI, 2002.
5. Fijalkowski, K., Rorat A., Grobelak A., Kacprzak M.J. The presence of contamination in sewage sludge – the current situation. Journal of Environmental Management, 203: 1126 – 1136 (2017).
6. Hudcová, H., Vymazal J., Rozkošný M. Present restrictions of sewage sludge application in agriculture within the European Union. Soil and Water Research, 14: 104 – 120 (2019).
7. Kannepalli, S. et al. Composting of Aged Reed Bed Biosolids for Beneficial Reuse: A Case Study in New Jersey, USA. Compost Science and Utilization, 24 (4): 281 – 290 (2016).
8. Kolecka, K., et al. Integrated dewatering and stabilization system as an environmentally friendly technology in sewage sludge management in Poland. Ecol. Eng. 98: 346 – 353 (2017).
9. MoE, 2016. Decree No. 437/2016 Coll. on conditions for the use of treated sludge on agricultural soil (In Czech). (https://www.psp.cz/sqw/sbirka.sqw?cz=437&r=2016)

10. Moss, L.H., Epstein E., Logan T. Evaluating Risks and Benefits of Soil Amendments Used in Agriculture. Alexandria, International Water Association and Water Environmental Research Foundation (2002).
11. Nielsen, S. Sludge treatment and drying reed bed systems. Ecohydrol. Hydrobiol., 7: 223 – 234 (2007).
12. Nielsen, S.; Larsen J.D. Operational strategy, economic and environmental performance of sludge treatment reed bed systems-based on 28 years of experience. Water Sci. Technol. 74: 1793 – 1799 (2016).
13. Nielsen, S., Bruun, E.W. Sludge quality after 10-20 years of treatment in reed bed systems. Environ.Sci.Pollut.Res., 22: 12885 – 12891 (2015).
14. Obarska-Pempkowiak, H., Tuszynska, A., Sobocinski, Z. Polish experience with sewage sludge dewatering in reed systems. Water Science and Technology, 48 (5): 111 – 117 (2003).
15. Peruzzi, E, et al. Stabilization process in reed bed systems for sludge treatment. Ecol. Eng. 102: 381 – 389 (2017).
16. Rozkošný, M., Hudcová, H., Plotěný, M., Novotný, R., Matysíková, J. Kvalita kalů a odpadů z domovních a malých ČOV a možnosti jejich využití v zemědělství. VTEI, 57 (6): 44 – 49 (2015).
17. Rozkošný, M., Sedláček, P., Sova, J., Funková, R. Dražovice reed beds and stabilisation pond wastewater treatment system: long-term operation and monitoring results. Water Practice & Technology, 6 (3): 1 – 8 (2011).
18. Singh, R.P., Agrawal M. Potential benefits and risks of land application of sewage sludge. Waste Management, 28: 347 – 358 (2008).
19. Smith, S.R. Organic Contaminants in Sewage Sludge (Biosolids) and Their Significance for Agricultural Recycling. Philosophycal Transactions, Series A, Mathematical, Physical and Engineering Sciences, 367: 4005 – 4041 (2009).
20. Stefanakis, A.I., Tsihrintzis, V.A. Dewatering mechanisms in pilot-scale Sludge Drying Reed Beds: Effect of design and operational parameters. Chemical engineering Journal, 172: 430 – 443 (2011).
21. Svoboda, J. Upravené kaly a jejich využití v zemědělství. Ekomonitor (2015). (http://www.ekomonitor.cz/sites/default/files/filepath/prezentace/23__svoboda.pdf).
22. Uggetti, E., Ferrer I., Llorens E., Güell D., García J. Properties of biosolids from sludge treatment wetlands for land application. In: Vymazal J. (ed.): Water and Nutrient Management in Natural and Constructed Wetlands. Springer: 9 – 20 (2010).
23. Uggetti, E., Ferrer, I., Molist, J., García, J. Technical, economic and environmental assessment of sludge treatment wetlands. Water Research, 45: 573 – 582 (2011).
24. Uggetti, E., Llorens, E., Pedescoll, A., Ferrer, I., Castellnou, R., García, J. Sludge dewatering and stabilization in drying reed beds: Characterization of three full-scale systems in Catalonia, Spain. Bioresource Technology, 100: 3882 – 3890 (2009).
25. Vymazal, J., Kröpfelová, L. Growth of *Phragmites australis* and *Phalaris arundinacea* in constructed wetlands for wastewater treatment in the Czech Republic. Ecological Engineering, 25: 606 – 621 (2005).
26. Vymazal, J., Kröpfelová, L., Švehla, J., Chrastný, V., Štíchová, J. Trace elements in *Phragmites australis* growing in constructed wetlands for treatment of municipal wastewater. Ecological Engineering, 35: 303 – 309 (2009).

Posouzení „Reed Bed“ jednotek k odvodnění a zlepšení kvality kalu malých ČOV

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Abstrakt

Nakládání s kalem z čištění odpadních vod představuje pro malé čistírny odpadních vod významnou součást celého procesu, a to jak z důvodu vysokých nákladů na konečný manipulační proces, tak z potřeby řešit různé technologické problémy. V současné době se proto do praxe zavádí řada technologicky jednoduchých a levných řešení. Česká republika má dosud velmi málo zkušeností s variantou odvodňovacích kalových polí, takzvanou technologií rákosových polí („Reed Bed“, RB, STRB), běžně používanou v jiných evropských zemích, jako je Dánsko, Španělsko, Rakousko nebo Polsko.

Tato studie se zaměřila na testování pilotních systémů instalovaných ve dvou malých čistírnách odpadních vod různého typu, tzv. kořenovou čistírnu na jižní Moravě pro cca 800 EO a aktivační ČOV ve Středočeském kraji pro cca 1900 EO. Dvě pilotní rákosová pole různé konstrukce byla plněna tekutým kalem obsahujícím 2 až 13 % sušiny (v závislosti na původu kalu) pomocí různých schémat nakládání pro sledované období 2017 – 2018. Obě otevřené pilotní jednotky vykázaly velmi slibné výsledky odvodnění kalu na 20 až 49 % sušiny podle podmínek dané kampaně, s průměry okolo 34 %, respektive 30 %. V případě zastřešení RB jednotky bylo možné dosáhnout odvodnění kalu průměrně až 60 % sušiny. Na konci celého sledovaného období bylo zjištěno, že obsah patogenních mikroorganismů a dalších sledovaných škodlivých látek nepřekročil české limity pro zemědělské použití takto odvodněných a stabilizovaných kalů, což znamená potenciál použití materiálu i jako hnojiva po další úpravě.

***Klíčová slova:** kaly, ČOV, odvodnění, kalová pole, rákosová pole*

Proposal of processing chicken by-products tissues into food-grade collagen

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Abstract

The consumption of poultry has been on rise and shows no signs of diminishing; hence greater importance is placed on subsequently treating animal by-products, which are divided into 3 categories. Such materials are produced in large quantities, and with respect to its biological nature, needs to be handled in a way that prevents polluting the environment. Finding an effective use for this by-products, for example, as a raw material which could be processed into other products, would constitute an ideal way to address the issue. Indeed, it contains large amounts of protein, especially collagen, as widely applied in the food sector and other industries. By-products that boast a high proportion of collagen include the skin of poultry, which can be obtained by a procedure involving controlled isolation of any undesirable components, i.e. fats, soluble non-collagenous proteins and pigments. Hence, what was once considered waste is turned into a valuable raw material rich in collagen, and further transformation of the latter translates into soluble collagen and collagen hydrolysate. As an example, chicken skin, which is high in fats (84%), can be effectively defatted by shaking of grinded raw material in a mixture of solvents for a certain period of time, the result being collagen with the residual fats content of approximately 14% using mixture of solvents petroleum ether and ethanol. The use of acetone brought a similar effect (18%). However, the use of $NaHCO_3$ *solution did not lead to the acceptable result (81%). The shaking of the raw material in water solution with lipolytic enzymes was also tested. Three types of enzymes in different concentrations were used for this purpose, but the residual fats content was also much higher compared to chemical solvents (48 – 69%). Possibilities for further processing of the raw material into products with potential applications in industry were also proposed.*

Keywords: *category III material; by-products; chicken; collagen; hydrolysate; lipolytic enzyme; processing; skin*

Introduction

It is estimated that 20 to 100 million tons of food waste is produced globally every year. In the EU, the production of fish results in 5.2 million tons of waste, while the figure for the meat-processing industry stands at 16.5 million tons[1]. These materials are defined as a by-products of animal origin and are divided into 3 categories according to Regulation (EC) No. 1069/2009 of the European Parliament and of the Council. Category 1 materials are, for example, animal bodies or their parts suspected or confirmed of TSE (Transmissible Spongiform Encephatolaphaties) infection, bodies of non-farmed and wild animals, experimental animals and others suspected of being infected with a disease communicable to humans or animals containing specified risk material. Category 2 materials includes, for example, manure, unmineralised guano and digestive tract content; animal by-products collected during waste water treatment, animal by-products containing residues of permissible substances or contaminants in excess of permitted levels, products of animal origin which have been declared unfit for human consumption due to the presence of impurities in these products. Category 3 materials are, for example, bodies and parts of slaughtered animals which are suitable for human consumption but are not intended for human consumption for commercial reasons, bodies of animals slaughtered in a slaughterhouse and found suitable for human consumption, poultry heads, skins, horns and limbs and feathers, or poultry by-products slaughtered on a farm which did not show signs of a disease portable to humans[2]. This study deals with category 3 materials.

By-products from the meat-processing sector include blood, bones, meat scraps, skin, fat, horns, hooves, limbs and guts. The cost of disposal can be compensated by raising the price of end products, thus increasing their profitability. Nevertheless, a large quantity of these by-products contain important nutrients such as proteins, fats, minerals and vitamins, which potentially could increase the revenues of meat-processing businesses[3].

More than seven million tons of by-products bones per year are generated through slaughtering mammals. For centuries, these surplus bones have been used to prepare soup and stock. Moreover, efforts currently exist to develop techniques to raise the percentage of meat obtained during processing by slaughterhouses. In many countries, meat that is mechanically separated is added into meat products, but the quantity of this tends to be capped[4]. As mentioned above, blood represents an important by-product of the meat industry. In healthy animals, blood is a sterile material and comprises 2.4 to 8.0% of the live weight of an animal. Blood is used in foodstuffs, for instance, as an emulsifier, stabilizer, coloring agent or nutritional ingredient. The greatest proportion of such blood is destined for producing blood-based foodstuffs in the animal feed industry. Other applications include medical and pharmaceutical products. One of the most sought-after by-products is the skin of mammals, which comprises 4 to 11% of the live weight of the animal. Collagen sourced from bovine and porcine skin is used in the primary packaging of food products, in particular the casings or skins of meat-based items (sausages, etc.), as well as an ingredient in cosmetics. Moreover, the skin of the pig is similar in composition to that of humans; thus it has been utilized medically to cover burns or ulcers or in skin transplantation surgery. Additionally, the guts of animals are high in nutritional value and are deemed fit for human consumption, particularly in Southeast Asian cuisine. In China, Japan and India, guts form an ingredient in traditional medicine. Animal fat is also considered an important by-product, traditionally in the preparation of meals, but it is applied in margarines and hydrogenated vegetable fats as well. Lard is added to goods such as sausages, processed meat-based items and emulsified products[5,6].

The poultry industry is one of the fastest growing agri-food industries in the world, with an annual production of over 100 million tonnes of chicken meat worldwide. (FAO, 2019).[7] The meat of poultry represents 5.5% of total agricultural production, and 12.7% of the output of the meat-processing industry in the EU. In 2014, the EU produced 13 million tons of meat from poultry, 9% more than in 2007. The largest producers are Poland (13.9%) and France (12.9%), closely followed by the U.K. (12.6%) and Germany (11.8%). Of this, chicken (79.8%) and turkey (14.8%) make up the largest proportion of such meat; while duck only stands at 3.6% of total production of poultry meat. Waste from the manufacture of meat, poultry, cattle and porcine products causes excessive pollution if the process is carried out through inadequate methods. Otherwise, serious environmental complications could occur that lead to degradation of the soil, surface water and groundwater. A major problem also arises in animals through the presence of pathogenic micro-organisms. Repurposing such waste is the only option for reducing the environmental impact of inappropriate disposal[8]. By-products of the poultry industry account for approximately 22 to 30% of total production of poultry, and include edible tissues, blood, guts and other materials. Animal by-products from farming are bedding litter and manure, which can be recycled into feed or fertilizers, as well as those from hatcheries, particularly egg shells, unhatched eggs and dead/discarded chickens, which can be added to feedstuffs in the form of meal to the extent of 3 to 5%[5].

The literature mentions the possibilities of using the feet of poultry, skin and heads as raw materials for preparing soluble collagen. For example, Almeida et al. researched the effect of treating chicken feet with 4% acetic acid for 16 h[9]. Kim et al. reported the process of preparation (0.1 mol/L HCl for 48 h at room temperature) and characterization of duck feet gelatin[10]. Yeo et al. conducted similar experiments; used 0.1 mol/L HCl as well, although the duration of processing equaled 5 days[11]. Rafieian et al. utilized 1% NaCl for treating remnants from mechanically processed chicken for 30 minutes, in addition to 3 – 7% HCl for 24 h at room temperature[12]. In case of chicken skin, Sarbon et al. investigated 0.15% NaOH for 120 minutes, and 0.15% H_2SO_4 or 0.7% citric acid for 120 minutes[13]. Du et al. looked into treating poultry heads with 0.015 mol/L $NaHCO_3$ solution for 3 hours, 0.1 mol/L NaOH for 6 hours and 0.05 mol/L acetic acid for 18 h at 4 °C[14].

The university department of the authors has previously been active in finding applications for poultry paws processed by means of microbial proteases under moderate reaction conditions (i.e. neutral pH, temperature not exceeding 75 °C, and atmospheric pressure); experiments resulting in preparation of collagen hydrolysate[15]. Poultry feathers are a significant source of keratin, a chemically and mechanically highly durable protein due to the presence of disulphide bridges. Hydrolytic cleavage of disulphide (–S–S–) and peptide (–CO–NH–) bonds in keratin facilitates soluble products of varying molecular weight[16,17,18]. Processing poultry feathers into keratin hydrolysates, under alkaline conditions with proteolytic enzymes, is also something the authors have engaged in previously[19,20]. In the food industry, hydrolysed keratins have been employed variously, e.g. in nutritional supplements, as a means to adjust the viscosity of dairy products, in energy drinks, and as a stabilizing agent for emulsions. Furthermore, the cosmetic sector has witnessed major adoption of keratin hydrolysates. Adding them into cosmetics emulsions for the skin improves barrier and moisturizing properties, while in hair cosmetics (shampoos or conditioners) keratin hydrolysates enhance the structure and characteristics of the hair[21,22].

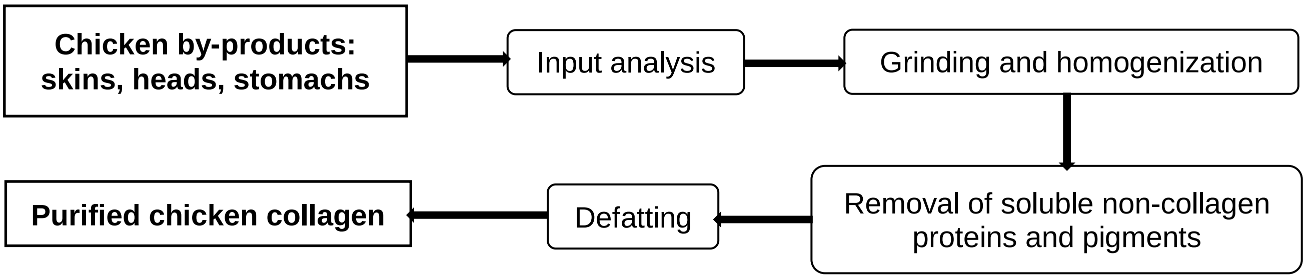
Interestingly, little information is available on turning of some poultry by-products into a raw material for generating collagen; probably due to the complexities involved in cleaning raw materials, e.g. undigested remnants of food, digestive enzymes and the extremely sensitive nature of the tissues. Consequently, the authors decided to dedicate research to this type of by-products.

The aims of the paper

The objectives of this paper are as follows, to: 1*)* select appropriate by-products high in collagen from a slaughter house for chickens; 2*)* analyze the composition of selected tissues (especially with regard to protein content and the proportion of collagen); 3*)* propose a suitable method for the preparation of tissues for further processing; in particular, by focusing on temperature and the grinding technique during homogenization; 4*)* process tissues high in collagen and devise a simple procedure to facilitate controlled removal of undesirable constituents in studied tissues (fats, soluble non-collagenous proteins and pigments) with a view to generating collagen; and to focus on the effective removal of fats, which are an important component of biological tissues; 5*)* assess the possibilities of processing collagen into a soluble collagen or other products.

Materials and methods

A general process layout of the procedure for processing chicken by-products from slaughter into purified collagen is shown in Scheme 1.



Scheme 1: The flow chart of preparation of purified chicken-sourced collagen

Appliances, tools and chemicals

The equipment utilized in the laboratory comprised the following: SPAR Mixer SP-100AD-B industrial meat cutting machine with four-arm knife (TH Industry RD, Taiwan), Memmert ULP 400 dryer (Memmert GmbH + Co. KG, Germany), LT 3 shaker (Nedform, Czech Republic), desiccator, , metal filtering screen (mesh size 1 mm), PA cloth (mesh size 200 µm), muffle furnace (Nabertherm GmbH, Germany), and Parnas-Wagner distillation apparatus (Fisher Scientific, Czech Republic). The list of chemicals was as follows: NaCl, NaOH, $NaHCO_3$, petroleum ether, ethanol, chloroform (Verkon, Czech Republic); all chemicals were of analytical grade.

Additionally, the authors utilized enzymes delivered by Novozymes, Denmark. Lipozyme TL - an enzyme produced through immobilizing microbial lipase from *Thermomyces lanuginous* onto a granulated silica carrier; the lipase is produced through submersion fermentation of *Aspergillus oryzae*, a genetically modified organism with the declared activity of 100 KLU/g, the optimal operating values of which stand at 70 °C and pH 6.0 – 9.0. Lipex 100 L - a lipase produced through submersion fermentation of a genetically modified strain of *Aspergillus* with the declared activity of 100 KLU/g, the optimal operating values of which stand at 30 °C and pH 7.0. Lipolase 100 T - a lipase with *Thermomyces lanuginosus* produced through submersion fermentation of a genetically modified micro-organism *Aspergillus oryzae* with the declared activity of 100 KLU/g, the optimal operating values stand at 30 °C and pH 11.0. Polarzyme 6.0 T - a protease produced through fermentation of a micro-organism not present in the final product, its declared activity equals 100 KPPU/g, and the optimal operating values stand at 10 – 60 °C and pH 7.0 – 11.0.

Raw Materials and Input Analysis

Skins, heads and stomachs were chosen as prospective by-products from the slaughter of chickens since they were deemed suitable for generating collagen; they were supplied by Raciola Uherský Brod, Ltd. (Czech Republic). Analysis was subsequently carried out to determine the composition of the raw materials. Further to this, the content of dry matter, protein, collagen, fats and minerals was determined. Each analysis was repeated three times and mean values were calculated.

Determining the content of dry matter involved applying an indirect method to determination of moisture (AOAC, 2000)[23], wherein the sample was dried at 103.0 ±2.0 °C until constant weight was reached. The amount of protein present was arrived at by the Kjeldahl method, through mineralization in concentrated H_2SO_4 for around 1.5 h, followed by extraction of ammonia released from boric acid solution via distillation apparatus. Subsequently, titration was carried out with a solution of hydrochloric acid, and the proportion of protein content in the total amount of nitrogen was calculated[24].

The principle process to determine the extent of collagen is as follows: a portion of the tissue was mixed with 0.1 mol/L NaOH, at the ratio 1:30 (w/v), and the mixture was heated for 45 minutes at 95.0 ±2.0 °C. Then filtration and drying of any solid matter occurred at 103.0 ±2.0 °C until constant weight was reached. The figure for loss of collagen was identified by a calculation; since collagen is soluble in NaOH, the observed loss of material represents the proportion of collagen in the raw material[25,26]. The fats content was discerned by weighing out 10.0 g of the sample, putting it into a thimble and placing into extraction apparatus, in accordance with Soxhlet. The extraction process took place in two cycles: in the first, fats were extracted with chloroform, whereas ethanol was applied in the other; the combined duration of both lasted 6–8 h. The amount of residual extracted fats were identified by gravimetry. The content of mineral substances was determined as follows: a portion of the dried sample (1.0 g) was placed in a platinum ashing crucible and incinerated above a pilot flame (about 30 minutes); this was followed by annealing the sample at 650.0 ±5.0 °C in a muffle furnace for 2 hours. The quantity of mineral substances present was identified using gravimetry[27]. The results from analyses of studied tissues are shown in Table 1 (see below).

Isolation of Chicken Collagen

Process of isolation of collagen from the slaughter-house chicken by-products comprises three main technological steps:

1. Grinding and homogenization of the raw material. After sampling, the raw material was rinsed with water in the transport pipeline system, where it was also cooled off. Any excess water was left to drain away before the raw material was placed in collection containers. These containers were located in a cooler plant to prevent microbial contamination of the raw material; they were stored at 0 – 5.0 °C for a maximum of 36 hours. Prior to grinding and homogenizing the raw material, it was chilled or frozen to a low temperature, i.e. –6.0 to –4.0 °C, which varied in accordance with the given material. Grinding was carried out swiftly to prevent the temperature exceeding 12.0 °C. An industrial meat cutter was utilized for this purpose, which had been fitted with a four-arm knife unit; various holes of different shape and size on the cutting plate were tested, depending upon the type of raw material, along with assessment of the optimum number of grinding cycles. This technique brought about a rise in temperature to a maximum of 3.0 °C. Subsequently, the raw material was put into a Polyethylene packaging material with a wall thickness of 100 μm, and then frozen to –36.0 ±2.0 °C and stored in the freezer at –20.0 ±2.0 °C. Prior to the steps described below, the raw material was placed in a cooler box and defrosted at 10.0 ±2.0 °C for 12 hours.

2. Removal of soluble non-collagenous proteins and unwanted pigments. Extraction took place in two phases by applying two different solutions. The crude tissue was mixed with 1 mol/L solution of NaCl in an Erlenmeyer flask, at the ratio 1:10 (w/v); then the flask was placed on a shaker in an incubator at 5.0 ±2.0 °C. Shaking lasted 6 hours in total; after the initial period of 3 hours the raw material was filtered on a filtering screen fitted with one layer of Polyamid cloth and rinsed with water. Afterwards, the raw material was again treated for the remaining three hours with 1 mol/L solution of NaCl. After further filtration, the raw material was mixed with 0.5% NaOH solution, at the ratio 1:10 (w/v), the sample undergoing such treatment for a period of 18 hours; the temperature was the same as in the preceding period of treatment, i.e. 5.0 ±2.0 °C. Finally, the raw material was filtered through the screen with a layer of PA cloth.

3. Defatting. This was required due to the high amount of fats (84 %) in the raw material. Four possible methods were tested for the purpose, utilizing: a*)* diluted $NaHCO_3$; *b)* lipolytic enzymes; c*)* solvents; and *d)* combination of enzyme + solvent and $NaHCO_3$ + enzyme.

a) During defatting with $NaHCO_3$, steps were taken according to the slightly modified method devised by Du et al., who had tested this procedure using chicken heads[14]. Immediately after removing unwanted proteins and pigments, the raw material was mixed with 0.1 mol/L $NaHCO_3$ in an Erlenmeyer flask, at the ratio 1:4, placed on a shaker and treated for one hour at 5.0 ±2.0 °C. This was followed by filtration through a layer of PA cloth. This sequence was repeated in triplicate. Finally, the raw material was dried in a drying oven with forced convection at 35.0 ±2.0 °C.

b) As part of the enzyme defatting technique, three types of lipolytic enzymes were investigated. The process proceeded thus: the raw materials were first mixed with distilled water in an Erlenmayer flask, the ratio being 1:10 (w/v), and an enzyme was added, at the amounts (related to the weight of the raw material, w/w) of 2% for Lipex 100 L, 4% (w/w) for Lipozyme TL and 5% (w/w) for Lipolase 100 T. The level of pH was adjusted to 7.0 ±0.3 (Lipex 100 L and Lipozyme TL) or 11.0 ±0.3 (Lipolase 100 T) in order to achieve optimum enzymatic activity. The Erlenmayer flask was fixed on a shaker and shaken at room temperature. Treatment with the enzyme lasted 72 hours; twice per day the mixture was filtered through a PA cloth and the mixture was supplemented with a fresh dose of the enzyme. The level of pH was monitored and adjustments to adhere to the specified level were made when necessary. Finally, the raw material was dried in a drying oven with forced convection at 35.0 ±2.0 °C.

c) For the solvent method, the poultry skins were initially dried at 35.0 ±2.0 °C for approximately one day in a drying oven with air circulation. The Petroleum ether and Ethanol solvent system was selected by the authors since its effectiveness had been proved previously in the processing of chicken paws[15]. The mixture of solvents was prepared so that the volume ratio stood at 1:1. The raw material was combined with the solvent in an Erlenmeyer flask, the ratio of this equaling 1:10 (w/v), and shaken on a shaker at 23.0 ±2.0 °C in three cycles (to allow for testing in triplicate) for 72 hours in total. After 24 and 48 hours of such shaking, the solvents that had been applied were filtered out and a fresh mixture of solvents were used. The defatted material was left in a fume hood for any remaining solvent to evaporate (about 30 minutes in duration).

d) Regarding the combined method, two systems were tested: As part of combination of enzyme + solvent, the chicken skins were treated in an Erlenmeyer flask with 2% (w/w) Lipex 100 L in distilled water, at the ratio 1:10 (w/v); the mixture was shaken for 72 hours at room temperature; twice per day the mixture was filtered through a PA cloth and a new dose of mixture was prepared with a fresh enzyme. The level of pH was regulated and adjusted to 7.0 ±0.3 when necessary. After filtration, the skins were mixed with acetone in an Erlenmeyer flask, at the ratio 1:10 (w/v), and shaken for 32 hours in three cycles at room temperature. After 8 and 24 hours, the solvent was filtered out and a fresh dose of solvent added. Afterwards, the solvent was filtered out using a filter screen, and the defatted material was left in a fume hood for any remaining solvent to evaporate (about 30 minutes in duration). As part of combination of $NaHCO_3$ + enzyme, the poultry skins were first defatted in an Erlenmeyer flask (in triplicate for 1 hour each) by applying 0.1 mol/L solution of $NaHCO_3$, at the ratio 1:4 (w/v) at room temperature. After filtration, the skins were mixed with distilled water, Lipolase 100 T was added at the amount of 1% (w/v), and the mixture was shaken for 72 hours at room temperature; twice per day, the mixture was filtered through a PA cloth and a new dose of mixture was prepared with the fresh enzyme. The level of pH was regulated and adjusted to 11.0 ±0.3 when necessary. Finally, the raw material was dried in a drying oven with forced convection at 35.0 ±2.0 °C.

For the defatted raw material, the content of remaining fats were determined via the Soxhlet method of two extraction steps. Firstly, the fats were extracted for eight hours from the raw material by chloroform; the same extraction time was then applied for ethanol extraction after the chloroform had been distilled out. The residual content of fats were calculated by gravimetry. The determination was carried out three times; the results are presented as an arithmetic mean.

Results and discussion

Input Analysis

Table 1 shows the composition of the chicken skins, heads and stomachs.

Table 1: Composition of the chicken skins, heads and stomachs

Chicken:	**Dry matter** [%]	**Proteins** [%] *	**Collagen** [%] *#	**Fat** [%] *	**Minerals** [%] *
Skins	53.6 ±1.51	15.5 ±1.32	92.6 ±0.11	84.0 ±2.41	0.91 ±0.31
Heads	23.0 ±0.10	50.3 ±0.51	88.8 ±1.01	32.9 ±0.44	16.8 ±0.13
Stomachs	19.1 ±0.50	74.6 ±0.84	98.5 ±0.14	21.7 ±0.10	3.92 ±0.10

**based on the dry weight of the raw material, #from total protein content, n=3*

Upon analyses of the composition discerned of the sampled tissues, the authors decided to use skin to isolate collagen, as it contains a high proportion of collagen (≈ 93% of total protein) and a low content of mineral substances (< 1%), see Table 1; the limited extent of inter-molecular netting of collagen can also be assumed to simplify any further processing of collagen.

Grinding and Homogenization

A two-step procedure was devised for grinding and homogenizing raw materials. When processing the skins, the raw material is to be frozen to –4.0 to –2.0 °C; for the initial grinding phase, a cutting plate with kidney-shaped elements is recommended, while a circular plate with elements 3 mm in diameter should be used in the second phase. When processing the heads, the raw material is frozen to –6.0 to

–4.0 °C; for the first stage of grinding, the kidney-shaped cutting plate is applicable, whereas the circular plate with elements of 3-mm diameter is most suitable for the second stage. For processing stomachs, it is sufficient to freeze the material to –2.0 to 0°C, since grinding them does not generate warmth as it does for the heads. Again, the initial grind should be carried out with the kidney-shaped cutting plate, while a circular plate with elements of 5-mm diameter is optimum in the second stage. Alternatively, a single grinding cycle is possible for processing the stomachs, which requires the circular cutting plate with elements of 5-mm diameter; the temperature of the stomachs has to range between –6.0 to –4.0 °C.

Deffating

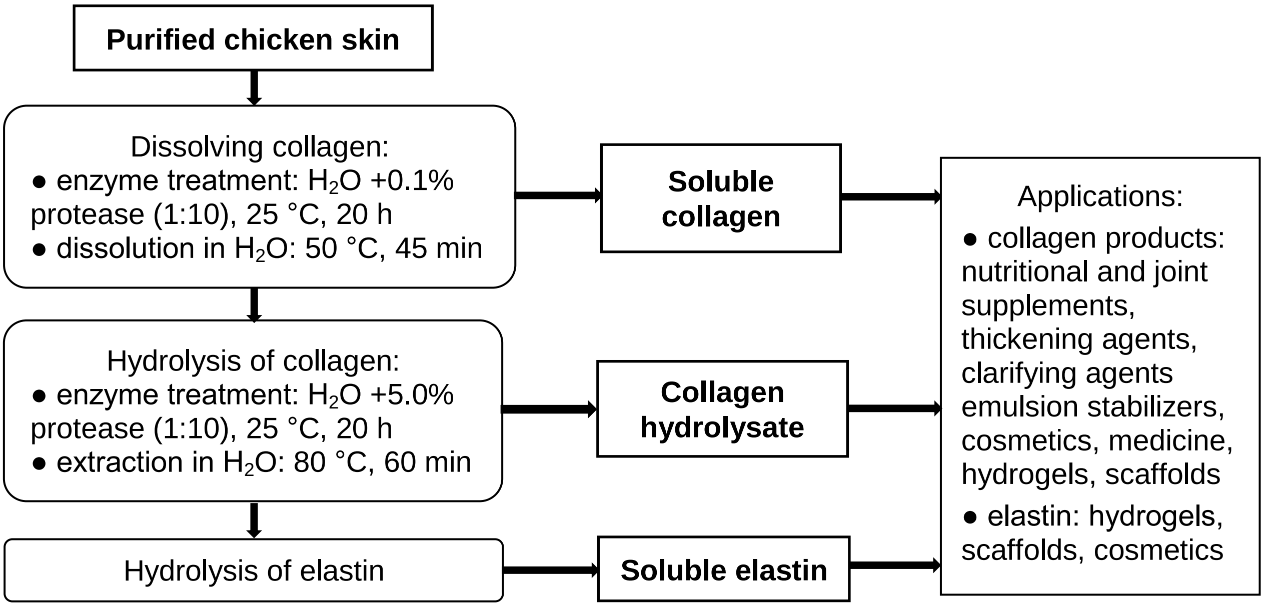
Results from the defatting of skins are detailed in Table 2. The first method investigated herein involved defatting with 0.1 mol/L solution of $NaHCO_3$. Findings showed that this method was not suitable for this form of tissue (i.e. skin) since the residual content of fats exceeded 80.0 %. This method was used by Du et al. (2013) as well for defatting of turkey and chicken heads, but the result of defatting was not reported[14].The second defatting method required three types of lipolytic enzymes. Therein, the effect of defatting was extremely low as this method reduced the fats content from the initial figure of approx. 84.0 % to levels of 68.7 % (Lipozyme TL), 62.0 % (Lipex 100 L) and 48.3 % (Lipolase 100 T). The enzyme Lipolase 100 T showed the highest activity of the tested enzymes, probably due to the highest enzyme concentration used. Lipex 100L was found more effective than Lipozyme TL, despite the enzyme concentration was half. If the residual content of fat in the raw material is low, then this method would be advantageous in reality. Indeed, compared with methods necessitating chemicals, it would represent an option for carrying out the process free of solvents. Defatting by solvents was another method under test. In this case, defatting with a mix of petroleum ether and ethanol was investigated. In fact, this method demonstrated the greatest defatting effect. The content of residual fats equaled 14.5%, which is an acceptable value for the further processing of collagen. The systems of combined methods were researched last. Of these, the initial one pertained to a combination of enzyme (Lipex 100 L) and solvent (acetone), for which residual fats stood at 18.1%, while the combination of $NaHCO_3$ solution and an enzyme (Lipolase 100 T) exhibited the figure of 70.3% for residual fats. Nadalian et al. (2013) performed defatting of chicken skin by shaking the tissue in acetone three times for 1 h, but did not report the result of defatting efficiency[28]. Acetone defatting has already been tested in the previous study of the authors (Mrázek et al. 2018)[29] for defatting chicken paws with a result of 7.74% residual fat; a combination of petroleum ether and ethanol with a result of defatting 4.97% was tested as well. Low values of residual fat in chicken paws compared to chicken skins are probably due to much lower fat content in chicken paws (34.8%)[29].

Table 2: The residual fats content in chicken skins for the various defatting methods investigated

Defatting method	Residual fats (% ±SD)
0.1 mol/L $NaHCO_3$	81.2 ±3.3
Lipozyme TL (4%, w/w)	68.7 ±4.1
Lipex 100 L (2%, w/w)	62.0 ±2.9
Lipolase 100 T (5%, w/w)	48.3 ±4.7
Petroleum ether and Ethanol	14.5 ±3.8
Lipex 100 L (2%, w/w) + acetone	18.1 ±3.5
0.1 mol/L $NaHCO_3$ + Lipolase 100 T (1%, w/w)	70.3 ±4.3

The Proposal of Processing of Purified Chicken Skin

Purified chicken-sourced collagenous materials can be further processed in several steps to obtain soluble collagen, collagen hydrolysate and (soluble) elastin by utilizing technology intended for zero-waste. Authors of this study suggest the following possibilities of procedures as is depicted in Scheme 2.



Scheme 2: General example layout for processing purified chicken skin collagen into collagenous (and elastin) products and examples of their utilization.

Under moderate reaction conditions (temperature not exceeding 50.0 °C, potentially with the slight addition of a proteolytic enzyme, the collagen was first treated in distilled water, at the ratio 1:10 (w/v), and supplemented with 0.1 % (w/w) Polarzyme 6.0 T (a proteolytic enzyme), this treatment occurred at 25.0 ±2.0 °C over a period of 20 hours. Once filtered and rinsed with water, dissolution of the collagen followed for 45 minutes with distilled water at 50.0 ±2.0 °C. Any soluble collagen was filtered out, and the non-degraded part (residual collagen and elastin) was further treated for 20 hours at 25.0 ±2.0 °C by water supplemented with the same proteolytic enzyme (5.0 %, w/w). After filtering and rinsing the same with water, extraction in distilled water took place for 60 minutes at 80.0 ±2.0 °C in order to prepare collagen hydrolysate, which was separated out by filtration. Any elastin that remains at this stage has the capacity to be further hydrolysed to obtain elastin hydrolysate.

Conclusion

Three by-products from the slaughter of chickens were sampled - skins, heads and stomachs. After cleaning and cooling them, identification was made as to the composition of studied by-products. Chicken skin was selected for further processing since it was high in collagen and contained minimal mineral substances; subsequently, collagen was isolated from the skin by gradually removing any undesirable constituents from the material. The process of grinding and homogenizing was optimized with regard to temperature and the size of the holes in the cutting plate. Unwanted soluble non-collagen proteins and pigments were also removed from the skins. Additionally, several methods were tested as regards defatting the raw material, out of which the combination of solvents (petroleum ether and ethanol) was most effective at defatting the skins, which contained approximately 14.5% residual fat. Isolated chicken collagen was subjected to sequential processing in water alone, then water that had been supplemented with a proteolytic enzyme. As part of this first phase, soluble collagen was obtained, the approximate yield being 24%; afterwards, (low-molecular) collagen hydrolysate was prepared, resulting in a yield of around 74%. Such products could be used, for example in the food industry as nutritional supplements and agents to thicken milk products, stabilize emulsions and clarify beverages (beer/wine); further applications includes cosmetics (humectants) or pharmacy (e.g. joints nutrition supplements)[30,31]. Out of the part left non-degraded, 2% pertains to elastin that can be further processed into soluble elastin, an additive in cosmetics, which is also utilized to create scaffolds in human medicine[32,33]. From the work reported in this manuscript following patent resulted: Patent CZ 307665 - Biotechnology-based production of food gelatine from poultry by-products (2019).

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References

1. Ferraro, V., Anton, M., Santé-Lhoutellier, V.: *The “Sisters” A-Helices of Collagen, Elastin and Keratin Recovered from Animal By-Products: Functionality, Bioactivity and Trends of Application*. Trends Food Sci. Technol. 51, 65 – 75 (2006).
2. Regulation (EC) No 1069/2009 of the European Parliament and of the Council of 21 October 2009 Laying Down Health Rules as Regards Animal By-Products and Derived Products not Intended for Human Consumption and Repealing Regulation (EC) No 1774/2002 (Animal by-products Regulation) OJ L 300, 14.11.2009, 1 – 33. Available online: http://data.europa.eu/eli/reg/2009/1069/oj downloaded 17. 6. 2020
3. Toldrá, F., Mora, L., Reig, M.: *New Insights Into Meat By-Product Utilization*. Meat Sci. 120, 54 – 59 (2016).
4. Roupas, P., De Silva, K., Smithers, G., Ferguson, A.: *Waste Management and Co-Product Recovery in Red And White Meat Processing. In Handbook of Waste Management and Co-Product Recovery in Food Processing*, 1st ed.; Waldron, K., Ed.; Woodhead Publishing: Cambridge, United Kingdom, 13, 305 – 331 (2007).
5. Jayathilakan, K., Sultana, K., Radhakrishna, K., Bawa, A.S.: *Utilization of Byproducts and Waste Materials from Meat, Poultry and Fish Processing Industries: A Review*. J. Food Sci. Technol. 49, 278 – 293 (2012).
6. Gómez-Juárez, C., Castellanos, R., Ponce-Noyola, T., Calderón, V., Figueroa, J.: *Protein Recovery from Slaughterhouse Wastes*. Bioresour. Technol. 70, 129 – 133 (1999).
7. FAOSTAT (Food and Agricultural Organization: Livestock statistics. Available online: http://www.fao.org/faostat/en/#data/QL. downloaded 14. 3. 2019.
8. Almeida, P.F., da Silva Lannes, S.C.: *Extraction and Physicochemical Characterization of Gelatin from Chicken By-Product.* J. Food Process Eng. 36, 824 – 833 (2013).
9. Almeida, P.F., Calarge, F.A., Santana, J.C.C.: *Production of a Product Similar to Gelatin from Chicken Feet Collagen. Engenharia Agrícola*, 33, 1289 – 1300 (2013).
10. Kim, H.W., Park, J.H., Yeo, E.J., Hwang, K.E., Song, D.H., Kim, Y.J., Ham, Y.K., Jeong, T.J., Choi, Y.S., Kim, C.J.: *Effect of Duck Feet Gelatin Concentration on Physicochemical, Textural, and Sensory Properties of Duck Meat Jellies*. Korean J. Food Sci. Anim. Resour. *34*, 387 – 394 (2014).
11. Yeo, E.J., Kim, H.W., Hwang, K.E., Song, D.H., Kim, Y.J., Ham, Y.K., He, F.Y., Park, J.H., Kim, C.J.: *Effect of Duck Feet Gelatin on Physicochemical, Textural, and Sensory Properties of Low-Fat Frankfurters.* Korean J. Food Sci. Anim. Resour. 34, 415 – 422 (2014).
12. Rafieian, F., Keramat, J., Kadivar, M.: *Optimization of Gelatin Extraction from Chicken Deboner Residue Using RSM Method.* J. Food Sci. Technol. 50, 374 – 380 (2011).
13. Sarbon, Mhd.N., Badii, F., Howell, K.N.: *Preparation and Characterisation of Chicken Skin Gelatin as an Alternative to Mammalian Gelatin.* Food Hydrocoll. 30, 143 – 151 (2011).

14. Du, L., Khiari, Z., Pietrasik, Z., Betti, M. *Physicochemical and Functional Properties of Gelatins Extracted from Turkey and Chicken Heads.* Poult. Sci. 92, 2463 – 2474 (2013).
15. Mokrejš, P., Gál, R., Janáčová, D., Plšková, M., Brychtová, M: *Chicken Paws By-Products as an Alternative Source of Proteins.* Oriental J. Chem. 33, 2209 – 2216 (2017).
16. Schrooyen, P.M., Dijkstra, P.J., Oberthür, R.C., Bantjes, A., Feijen, J.: *Stabilization of Solutions of Feather Keratins by Sodium Dodecyl Sulfate.* J. Colloid Interface Sci. 240, 30 – 39 (2001).
17. Grazziotin, A., Pimentel, F.A., Sangali, S., de Jong, E.V., Brandelli, A.: *Production of Feather Protein Hydrolysate by Keratinolytic Bacterium Vibrio Sp. Kr2.* Bioresour. Technol. 98, 3172 – 3175 (2007).
18. Gupta, R., Ramnani, P.: *Microbial Keratinases and Their Prospective Applications: And Overview.* Appl. Microbiol. Biotechnol. 70, 21 – 33 (2006).
19. Mokrejš, P., Svoboda, P., Hrnčiřík, J., Janáčová, D., Vašek, V. *Processing Poultry Feathers into Keratin Hydrolysate through Alkaline-Enzymatic Hydrolysis.* Waste Manag. Res. 29, 260 – 267 (2011).
20. Mokrejš, P., Hrnčiřík, J., Janáčová, D., Svoboda, P.: *Processing of Keratin Waste of Meat Industry.* Asian J. Chem. 24, 1489 – 1494 (2012).
21. Mokrejš, P., Huťťa, M., Pavlačková, J., Egner, P.: *Preparation of Keratin Hydrolysate from Chicken Feathers and its Application in Cosmetics.* J. Vis. Exp. 129 (2017).
22. Mokrejš, P., Huťťa, M., Pavlačková, J., Egner, P., Beníček, L. *The Cosmetic and Dermatological Potential of Keratin Hydrolysate.* J. Cosmet. Dermatol. 16, E21 – E27 (2017).
23. AOAC Assn. of Official Analytical Chemists. 2000. *Determination of moisture content*. In: Official methods of analysis. 17th ed. Gaithersburg, Md.: AOAC
24. ISO 937:1978. *Meat and meat products - Determination of nitrogen content*.
25. Nadalian, M., Yusop, S.M., Mustapha, W.A.*W. Extraction and Characterization of Elastin from Poultry Skin*. *In: AIP Conference Proceedings 1571*, Proceedings of the Universiti Kebangsaan Malaysia: Kuala Lumpur, Malaysia, 692 – 695 (2013).
26. Neuman, R., E., Logan, M., A.: *The Determination of Collagen and Elastin in Tissues*. J. Biol. Chem. 2, 186, 549 – 556 (1950).
27. Nollet, L.M.L., Toldrá, F. *Handbook of Food Analysis*, 3rd ed.; CRC Press: Boca Raton, USA, 357 – 754 (2015).
28. Nadalian, M., Yusop, S.M., Mustapha, W.A.W., Azman, M.A., Babji, A.S.: *Extraction and Characterization of Elastin from Poultry Skin*, AIP Conference proceedings, 1571, 692 (2013).
29. Mrázek, P., Mokrejš, P., Gál, R., Krejčí, O. *Preparation of Collagen Concentrate from Chicken Feet*, Waste Forum, 4, 441 – 451 (2018).
30. Phillips, G.O., Williams, P.A.: *Handbook of Food Proteins*, 1st ed.; Woodhead Publishing: Philadelphia, USA, 92 – 115 (2011).
31. Schrieber, R., Gareis, H: *Gelatine Handbook - Theory and Industrial Practice*, 1st ed.; Wiley-VCH: Weinheim, Germany, 93 – 95, 155 – 162 (2007).
32. Nivison-Smith, L., Weiss, A. *Elastin Based Constructs.* In *Regenerative Medicine and Tissue Engineering - Cells and Biomaterials*, 1st ed.; Eberli, D. Ed.; InTech: London, United Kingdom, Chapter 15 (2011).
33. Daamen, W.F., van Moerkerk, H.T., Hafmans, T., Buttafoco, L., Poot, A.A., Veerkamp, J.H., van Kuppevelt, T.H. *Preparation and Evaluation of Molecularly-Defined Collagen-Elastin-Glycosaminoglycan Scaffolds for Tissue Engineering*. Biomaterials, 24, 4001 – 4009 (2003).

Návrh zpracování vedlejších kuřecích produktů na potravinářský kolagen

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Souhrn

Celosvětová spotřeba drůbežího masa neustále roste. Z tohoto důvodu je v současnosti kladen velký důraz na následné zpracování vedlejších produktů, které vznikají při zpracování masa a jsou rozděleny do 3 kategorií. Vzhledem k tomu, že jsou produkovány ve velkém množství a s ohledem na svou biologickou povahu je třeba s nimi zacházet způsobem, který je šetrnný k životnímu prostředí. Nalezení účinného využití těchto vedlejších produktů, např. jako suroviny, která by mohla být zpracována na další výrobky, by představovalo ideální způsob řešení tohoto problému. Vedlejší produkty mohou obsahovat velké množství bílkovin, zejména kolagenu, které jsou široce využívány v potravinářství a dalších průmyslových odvětvích. Mezi vedlejší produkty, které obahují vysoký podíl kolagenu, patří např. drůbeží kůže, kterou lze zpracovat postupem zahrnujícím kontrolované odbourávání nežádoucích složek, konkrétně tuků, rozpustných nekolagenních proteinů a pigmentů. To, co bylo dříve považováno za odpad, se tak změní v cennou surovinu bohatou na kolagen a další zpracováním na rozpustný kolagen a hydrolyzát kolagenu. Například kuřecí kůže obsahuje vysoký podíl tuků (84 %), avšak může být účinně odtučněna třepáním rozemleté suroviny ve směsi rozpouštědel po určitou dobu; výsledkem je surovina s obsahem zbytkového tuku přibližně 14 %, pokud se použije směs petroletheru a ethanolu. Použití acetonu znamená podobný výsledek (18 %). Naopak použití roztoku $NaHCO_3$ však nevede k přijatelnému výsledku (více jak 80 %). Bylo také testováno třepání suroviny ve vodném roztoku s lipolytickými enzymy. Pro tento účel byly použity tři typy enzymů v různých koncentracích, ale obsah zbytkových tuků byl také mnohem vyšší ve srovnání s chemickými rozpouštědly (48 – 69 % zbytkového tuku).Výsledkem studie bylo rovněž navržení možností dalšího zpracování suroviny na výrobky s potenciálem využití např. v potravinářském, nebo jiném průmyslu.

Klíčová slova: *hydrolyzát; kolagen; kuře; kůže; lipolytický enzym, materiály III. kategorie, vedlejší produkty; zpracování*

An example of increasing biogas and methane production by supplying anaerobic digester with biochar prepared from solid digestate

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Summary

This paper presents biogas and methane production results attained from biochar-supported single-stage mesophilic anaerobic digestion tests. Chicken droppings were selected to be the substrate, although it is a moderately suitable nitrogen-rich material. Biochar, which added as support material for anaerobic digestion, was prepared at three different pyrolysis temperatures, namely 300, 400 and 500 °C. Comparison of the actual and expected CH_4 *production, which was calculated as the weighted sum of the individual digestion of substrate and biochar, indicated that biochar prepared at 500 °C had only limited or no supporting effect on chicken droppings anaerobic digestion. On the other hand, addition of biochar prepared at 400 °C resulted in 6% higher specific* CH_4 *production than the expected by theoretical calculations. The best digestion performance was attained by the mixture of chicken droppings and biochar prepared at 300°C, which showed 30% higher* CH_4 *production than the theoretical value.*

Keywords: *anaerobic digestion, BMP, chicken droppings, nitrogen, biochar*

Introduction

Anaerobic digestion as means of treatment of biomass is currently widely used for energy recovery. Anaerobic digestion is a biochemical process in which complex organic substrates are converted under non-air conditions to biogas via a series of heterogeneous reactions performed by multiple groups of microorganisms such as *Pseudomonas, Micrococcus, Mycobacterium, Flavobacterium, Methanosarcina, Methanobacterium*[1]. The organic part of substrate is partly converted to biogas, whilst the rest remains in digestate forming a residue with characteristics similar to biomass. This type of residual biomass is used as fertilizer, however it presents varying fertilizing capacity due to its different composition and quality. The gaseous product of anaerobic digestion is an excellent energy carrier. At large-capacity plants, raw biogas is used for production of heat for buildings and greenhouses, operating industrial equipment such as driers, and production of electricity supplied to grid. Cleaned biogas, which is produced after moisture, CO_2 and minor components removal, is referred as biomethane and can be used for production of mechanical energy in power vehicles alone or together with compressed natural gas (CNG)[2].

Nitrogen-rich materials such as chicken droppings present problematic behavior and low biogas generation performance when treated under anaerobic digestion conditions mainly due to accumulation of ammonia and volatile fatty acids (VFA) caused by the excess of ammonia nitrogen. Biochar generated by thermal decomposition of biomass can potentially be supporting material for anaerobic digestion of nitrogenous substrates[3]. Due to its adsorption properties, biochar can effectively retain at low levels the concentration in reacting sludge of substances such as ammonia nitrogen, free ammonia, and VFA, which inhibit anaerobic digestion. Thus, biochar potentially increases the efficiency of anaerobic digestion by absorbing a great amount of substances like ammonia and hydrogen sulphide released by nitrogenous substrates during digestion[4]. It has also been reported that even problematic wastewater streams deriving from pyrolytic processes can be easily digested when biochar is used as supporting material in anaerobic digestion system[4]. Furthermore, biochar is composed of well-developed porous structure and contains high surface area providing space for growth, enrichment and colonization of microorganism communities, thereby promoting digestion efficiency[5]. Besides, biochar materials present enhanced pH buffering capacity[6] that can potentially contribute in maintaining the system under balanced conditions, eventually supporting biogas production.

In the current study, the solid effluent of biogas plant was subjected to pyrolysis and the generated biochar was used as additive in the anaerobic digestion of chicken droppings. The main purpose was to define the influence of biochar on biogas and biomethane production potential of a nitrogen-rich substrate and to assess the role of biochar generation conditions on anaerobic digestion efficiency.

Experimental part

Inoculum and substrate

Inoculum was digestate material collected from the first digester of a mesophilic (40 °C) agricultural biogas plant (Pustějov II, Zemspol Studénka, a.s., Moravian-Silesian Region) operating on wet mode with feedstock consisting of corn silage and cattle slurry. Inoculum was merely pre-treated using a screw mill forcing the material to pass through a matrix with 2 mm openings. Chicken droppings were the single substrate used for anaerobic digestion tests. It was solid, brown-grey slurry containing visible feather impurities, while characterized by the absence of fibrous bedding material, Figure 1. Another characteristic of chicken droppings was the strong smell of ammonia and organic acids. Before testing, the substrate was stored at 1 – 4 °C. All sample quantity was homogenized by agitation without water addition.

Figure 1: Chicken droppings without bedding material

Biochar preparation

Biochars were generated in a bench-scale reactor consisted of a vertical steel tube (50 mm internal diameter) placed inside an electrically heated furnace. A thermocouple was submerged into solid sample, continuously measuring pyrolysis temperature during process evolution. The furnace was connected to an external control system responsible to conduct the desired temperature program. A second thermocouple attached to reactor’s wall was the reference thermo-element for system to maintain temperature to the set level. Inert gas inserted the system from a port at the top of tube reactor. The gas flow rate was regulated by providing an inlet flow and measuring the exact rate at reactor´s outflow. Pyrolysis gases escaped the system from a port located at the upper section of reactor, and directed to an inclining tube equipped with a water cooling system. The condensable mixtures were obtained by cooling down the gaseous effluent stream at around 30°C. Condensates were collected in a container connected at the lower end of the inclining tube. Any non-condensable gases, after passing through an acetone and water trap, were measured for their volume.

Biochar was prepared from solid digestate collected from the first stage of the agricultural biogas plant, from which inoculum was obtained. Moisture excess was removed by drying digestate under inert conditions (continuous N_2 flow) for about seven days, which provided sufficient time for moisture removal to an end value lower than 2%wt. Before pyrolysis, the reactor system was purged by supplying 2 lt/min of N_2 for 10 minutes. Three biochars were generated by isothermal pyrolysis tests, where the dried digestate was firstly heated from atmospheric temperature to 300, 400 and 500 °C with a heating rate of 10 °C/min, and then remained at this temperature for the chosen constant pyrolysis time of 180 min. Pure nitrogen (50 ml/min) was used for all tests. Before being loaded in BMP reactor, biochars were milled (IKA Tube Mill Control) for 2 min to obtain a particle size fraction between 50-400 μm, Figure 2.

(a) ***(b)***

Figure 2: Digestate (a) after drying and milling, and (b) after pyrolysis at 300 °C (biochar)

Analyses

The pH of samples was determined potentiometrically using a WTW 340i pH-meter with SenTix 41 probe[7]. Total solids (TS) were determined by drying approximately 10 g of material at 105 °C and oxygen atmosphere to constant weight (relative stable weight <2.0 %wt) in a KERN DLB 160 3A moisture analyzer with halogen lamp[8]. A thermogravimetric analyser (LECO TGA 701) was used for the determination of volatile solids (VS) by heating the sample at 550 °C in O_2 atmosphere to constant weight (relative stable weight >5,0%wt)[9]. To increase measurements accuracy both TS and VS determination were repeated for five times. The density of samples was assessed using a Thermo Fisher Scientific Pycnomatic ATC semi-automatic gas pycnometer with helium at 50 kPa[10,11]. Elemental composition (CHNSO) was determined by the LECO Truspec CHN 628+ S628 elemental analyzer[12].

Biochemical methane potential tests

Mesophilic anaerobic digestion tests were performed in 16 glass bioreactors (volume 1,0 dm^3) operating in parallel. Bottle-reactors were tightly closed with glass burettes (volume 1,4 dm^3), Figure 3. Experiments were performed by following the ČSN EN ISO 11734[13] and VDI 4630[14] standard methods.

The endogenous potential of inoculum and of biochars to produce biogas and methane was examined by adding in bottle-reactor 500 g of inoculum (liquid) for the first case, and 500 g of inoculum (liquid) and 10 g of each biochar (solid) for the latter case. The biogas generation performance of substrate with the presence of biochar was examined by mixing in reactor an amount of 500 g of inoculum, 10 g of substrate, and 10 g of biochar. Bottle-reactors were placed in a water bath, which steadily operated at 40 ± 0.5 °C, while gas burettes maintained at atmospheric temperature, Figure 3. The reacting mixtures were continuously agitated by magnetic stirrers operating at 200 rpm. All tests were duplicated to increase accuracy of measurements. The BMP tests lasted for 40 days.

The temperature of water bath was continuously checked, whereas biogas volume and barometric pressure were continuously measured on a daily basis. Biogas composition was recorded for 40 days using a “Biogas5000” analyzer (Geotechnical Instruments Ltd.) equipped with dual infrared sensors for

CH_4 (0 – 70% ± 0,5%) and CO_2 (0 – 60% ± 0,5%) and electrochemical sensors for O_2 (0 – 25% ± 1,0%), H_2 (0 – 2000 ppm ± 2,0% FS) and H_2S (0 – 5000 ppm ± 2,0% FS). The H_2 content measurement was mainly used to avoid inoculum overloading. TS, VS_{TS} and pH, were also measured for digestates obtained after tests ending.

Figure 3: Experimental unit for BMP tests

Results and discussion

The physicochemical characteristics of chicken droppings, biochar and their mixtures used for the anaerobic digestion tests are listed in Table 1.

Table 1: Physicochemical characteristics of primary digestate used for biochar production, inoculum, and substrates

Substrate	Term	**Acidity**	**Total solids**	**Loss of dry matter ignition**		**Density**		**C**	**H**	**N**	**S**	**O**	**C:N ratio**
		pH	**TS**	**VS**	**VS**	**ρ**	**ρ**						
		-	**%**	**%**	**$\%_{TS}$**	**kg m_{TS}^{-3}**	**kg m^{-3}**	**$\%_{TS}$**					**-**
	Pristine digestate	-	95.87	72.31	75.43	1548	1526	40.90	4.93	5.11	0.67	29.42	8.00
	Inoculum	7.43	7.26	5.39	74.20	1560	1041	41.05	4.93	3.59	0.64	27.60	11.42
S1	Chicken droppings	5.90	23.70	17.55	74.06	1563	1133	34.98	4.38	5.11	0.85	30.39	6.85
S2	Biochar 1 (500°C)	11.46	96.25	57.66	59.91	1793	1763	49.15	2.40	1.07	0.02	9.99	46.14
S3	Biochar 2 (400°C)	11.74	98.66	64.55	65.43	1660	1651	49.48	3.50	1.53	0.08	12.56	32.28
S4	Biochar 3 (300°C)	10.42	98.73	70.21	71.11	1580	1572	51.94	4.47	3.12	0.45	12.99	16.67
S5	Droppings 50%-Biochar 1 50%	10.36	59.98	37.61	62.71	1747	1448	46.35	2.79	1.86	0.19	14.02	24.86
S6	Droppings 50%-Biochar 2 50%	10.61	61.18	41.05	67.10	1641	1392	46.67	3.67	2.23	0.23	16.01	20.97
S7	Droppings 50%-Biochar 3 50%	9.55	61.22	43.88	71.68	1576	1353	48.66	4.45	3.50	0.53	16.36	13.89

The analysis for the primary digestate used for production of biochars is also included. For chicken droppings, the C:N ratio was significantly low at 5.90, which, however, is not surprizing for a nitrogen-rich substrate. It has been reported[15] that C:N ratio between 20 – 30 is of assistance for anaerobic digestion, and 25 is the optimum C:N value that promotes bacterial growth and methane production in anaerobic digestion systems. Therefore, the low C:N ratio of chicken droppings is expected to have an adverse effect on proper evolution of digestion. Concerning sulphur, the content of substrate at $0.67\%_{TS}$ is considered relatively low. Comparison of characteristics for the primary digestate and the three biochars indicates that TS increased with pyrolysis. This is likely due to the inorganic components that retained inside the sample after pyrolysis and the removal of volatile compounds. Contrary to TS, VS content for biochars was lower than that of the parent digestate. Moreover, VS decreased as the pyrolysis temperature increased. These findings are also attributed to volatile matter removal occurring during pyrolysis process. As temperature increase, greater quantities of complex organic structures dissociate, thereby higher proportions of VS are released. VS structures remaining in biochars, however, are likely partly or fully modified due to the temperature treatment, which is expected to affect their biodegradability.

Table 2 presents raw biogas and methane generation results for primary materials and their mixtures. For biochars, biogas and methane production ranged between 4.7 – 4.9 and 2.9 – 3.1 L respectively. The very small differences in both biogas and biomethane production indicate that potentially a similar amount of organic material is converted to biogas regardless of biochar production temperature. Comparison of biogas volume (L) released from sixteen bioreactors, and in particular comparison of reactors containing droppings with or without biochar, indicates that the mixture of droppings and biochar 1 (500 °C) provided 2% less biogas, but 3% more methane than chicken droppings alone, Table 2. The two most promising mixtures seem to be chicken droppings with biochar 2 (400 °C) and biochar 3 (300 °C). In these cases, methane release increased by 15 and 12%, respectively, in comparison with the gas volume produced by anaerobic digestion of chicken droppings without biochar addition, Table 2.

Table 2: Total volume of biogas and methane released at BMP tests

Reactor	Material	Biogas	Relative production (baseline: chicken droppings)	Methane	Relative production (baseline: chicken droppings)
		L	**%**	**L**	**%**
1	Inoculum	4.7	87	2.7	86
2					
3	Inoculum + Chicken droppings	5.4	100	3.2	100
4					
5	Biochar 1 (500°C)	4.7	86	2.9	89
6					
7	Biochar 2 (400 °C)	4.8	88	3.1	96
8					
9	Biochar 3 (300°C)	4.9	90	2.9	91
10					
11	Chicken droppings 50% - Biochar 1 (500°C) 50%	5.3	98	3.3	103
12					
13	Chicken droppings 50% - Biochar 2 (400°C) 50%	5.7	104	3.7	115
14					
15	Chicken droppings 50% - Biochar 3 (300°C) 50%	5.9	108	3.6	112
16					

Specific biogas and methane production on TS-basis for anaerobic digestion of chicken droppings are listed in Table 3. For the nitrogen-rich substrate, the actually achieved biogas and methane yields of 0.3068 and 0.1990 $m_N^3 kg_{TS}^{-1}$, respectively are considered significantly high. Chicken droppings, therefore, constitute a highly efficient substrate in terms of biogas and biomethane production, whereas, concurrently, it represents a low quality feedstock in terms of environmental risk due to its nitrogenous nature.

Table 3: Theoretical and experimental specific gas production (TS-basis)

Material	**Biogas**			**Methane**			**Methane in biogas**	
	Theoretical	**Test**	Diff. Index	Theoretical	**Test**	Diff. Index	Theoretical	**Test**
	B_t	**B**	**η_B**	**M_t**	**M**	**η_M**		
	$m_N^3kg_{TS}^{-1}$	**$m_N^3kg_{TS}^{-1}$**	**%**	**$m_N^3kg_{TS}^{-1}$**	**$m_N^3kg_{TS}^{-1}$**	**%**	**%v/v**	
Inoculum	0.7742	**0.1305**	16.9	0.4048	**0.0757**	18.7	52.3	58.0
Chicken droppings	0.6597	**0.3068**	46.5	0.3125	**0.1990**	63.7	47.4	64.9
Biochar 1 (500°C)	0.9269	**0.0227**	2.5	0.4895	**0.0174**	3.6	52.8	76.6
Biochar 2 (400°C)	0.9331	**0.0294**	3.2	0.5116	**0.0258**	7.0	54.8	87.7
Biochar 3 (300°C)	0.9795	**0.0219**	2.2	0.5459	**0.0193**	3.5	55.7	88.3

B_t = Theoretical biogas production, B = Experimental biogas production, M_t = Theoretical methane production, M = Experimental methane production, n_B, n_M = Theoretical and experimental difference indexes

Figures 4 and 5 present cumulative biogas and methane generation curves on TS-basis, respectively. It is seen that biochars prepared at different temperatures (300, 400 and 500 °C) exhibited very similar biogas production, Figure 4. Table 3, which presents the corresponding biogas and methane production data, confirms that biogas generated from the three biochars was within a notably narrow interval of 0.0219-0.0294 $Nm^3\ kg_{TS}^{-1}$. This finding suggests that for each of the three biochars, a similar amount of TS is converted to biogas. It is also interesting to note that the cumulative methane production was minimal for all biochars compared not only to methane generation from chicken droppings but also to that of inoculum. This indicates a significantly small biomethane production for the three biochars, confirming that most of TS contained in the pyrolysed material are persistent and non-easily digestible complexes. The great difference between the calculated and the experimental methane production for all biochars, Table 3, further confirms the low biodegradability characterizing the organic material contained in biochars after pyrolysis.

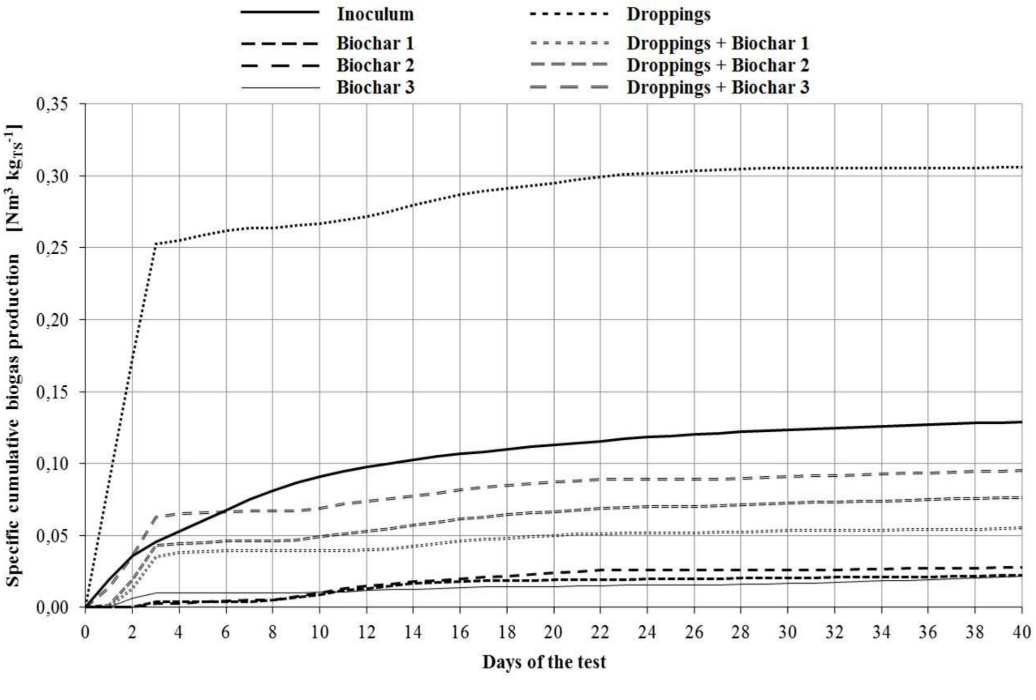

Figure 4: Cumulative biogas production

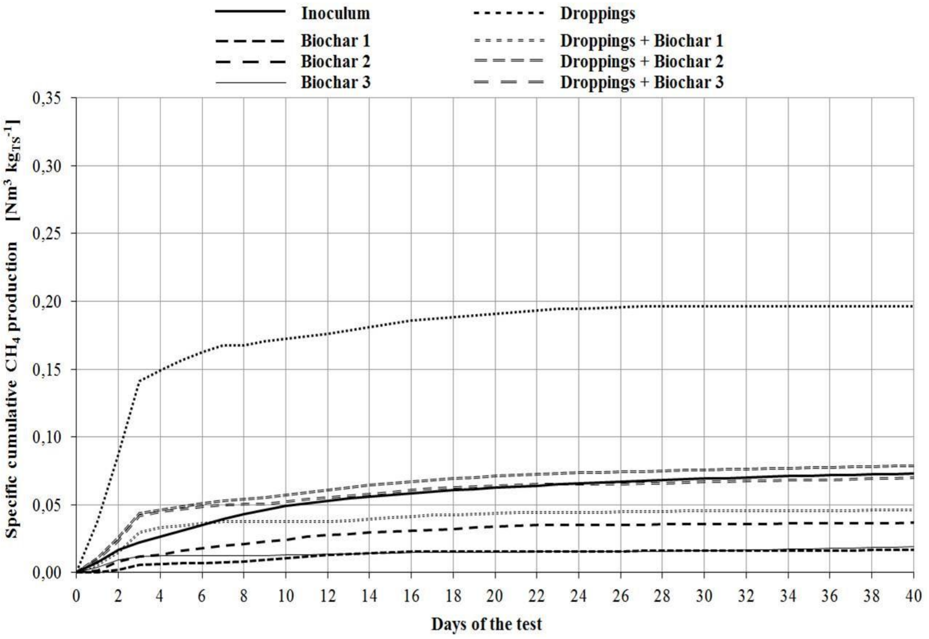

Figure 5: Cumulative methane production

Richards et al.[16] developed a method for calculating the theoretical methane potential based on the chemical composition of substrate. A principal assumption of the method is that each generated mole of ammonia is retained in the reacting solution and balanced by bicarbonate, which derived from the produced carbon dioxide. The final equation is:

$$C_nH_aO_bN_c + (n - 0{,}25a - 0{,}5b + 1{,}75c)H_2O \Rightarrow (0{,}5n - 0{,}125a + 0{,}25b - 0{,}625c)CO_2 + (0{,}5n + 0{,}125a - 0{,}25b - 0{,}375c)CH_4 + cNH_4^+ + cHCO_3^-$$

The theoretical biogas and methane generation potential computed according to Richards formula for inoculum, substrate and three biochars on TS-basis are included in Table 3. For inoculum, theoretical production was significantly high (0.7742 and 0.4048 $m_N^3kg_{TS}^{-1}$ for biogas and methane, respectively) due to its great proportion of contained carbon, Table 1. Nevertheless, real gas yields attained by digestion of inoculum in assays were comparably low (0.1305 and 0.0757 $m_N^3kg_{TS}^{-1}$ for biogas and methane, respectively), Table 3. This is explained by the fact that the inoculum is a digestion product, and therefore substantial portion of digestible organic compounds have already been partially or completely degraded during the preceding biogas production process. For chicken droppings, methane yield achieved after 40 days of digestion was about 64% of the expected methane according to formula. This can be considered sufficient biomethane generation potential, especially if it is taken into account that whole digestion process was performed without being supported by stirring of reacting mixture, which promotes methane generation. For all three biochar samples, the extremely high theoretical methane production is only due to mathematical calculations, wherein entire quantity of elemental carbon is considered for computing methane generation potential. Nevertheless, these values cannot be expected in practice since much of the elemental carbon likely constitutes part of non-digestible components of substrate or even sometimes of substances inaccessible to microbial communities. These non-participating carbon quantities therefore restrict substrate's methane generation potential. Table 3 indicates that methane proportion in biogas increased with the addition of biochar. This increase suggests that biochar introduced more suitable conditions for microorganisms activity, provoking higher proportions of substrate be converted to methane.

To investigate any interactions between mixture components, it is of interest to consider the amount of gas that could be generated, if each mixture component was digested independently. For that reason, predicted biogas generation potential of a chicken droppings-biochar mixture on TS-basis was computed as the weighted sum of the individual generation (on TS-basis) attained by anaerobic digestion of substrate and biochar independently. Comparison of the predicted and experimental biogas and methane production potential for all mixtures of chicken droppings with biochar are shown in Table 4. Biogas released from mixtures with biochar prepared at 400 and 500 °C was lower by 71 and 93% than that expected if no interactions existed among mixture components. For anaerobic digestion systems, methane generation is of upmost interest and should be considered as primary indicator when analyzing an anaerobic digestion system performance. As for biogas, mixture of chicken droppings with high temperature biochar (biochar 1 (500 °C)) presented lower specific methane production, than that expected according to calculations, Table 4. Reduction of biochar generation temperature provoked increment of methane release. In particular, presence of biochar 2 (400 °C) in reactor resulted in 6% higher methane for chicken droppings than that calculated. In this line, even lower biochar generation temperature (300 °C) caused increment of up to almost 30% of methane production efficiency of substrate. These results suggest that interactions occurring when chicken droppings are digested in the presence of biochar promote methane generation, at least for temperatures between 300 and 400 °C. As mentioned above, biogas generation from the various biochars is almost the same either at raw volume, Table 2, or on TS-basis, Table 3, regardless of the pyrolysis temperature that biochar was prepared. This suggests that the amount of organics converted by microorganisms to methane during anaerobic digestion is the same for all biochars. The increased methane proportion in biogas, therefore, is presumably attributed to interactions between organic matter in biochar and digestible components contained in chicken droppings, provoking higher amounts of the latter to be digested. Those kind of interactions appear to be more intense as the temperature applied for biochar production was lowered.

Table 4: Predicted and experimental biogas and methane production for mixtures (TS-basis)

Mixture	**Biogas**		**Diff. Index**	**Methane**		**Diff. Index**
	measured	**predicted**		**measured**	**predicted**	
	$Nm^3kg_{TS}^{-1}$		**%**	**$Nm^3kg_{TS}^{-1}$**		**%**
Chicken droppings 50% - Biochar 1 (500°C) 50%	0.0556	0.0789	71	0.0467	0.0533	88
Chicken droppings 50% - Biochar 2 (400°C) 50%	0.0770	0.0832	93	0.0716	0.0674	106
Chicken droppings 50% - Biochar 3 (300°C) 50%	0.0959	0.0770	125	0.0705	0.0541	130

Conclusions

The solid digestate from a mesophilic agricultural biogas plant was used for production of biochar through pyrolysis, and the generated material was used as supporting material in anaerobic digestion of chicken droppings. Solid digestate was proven as a suitable material for biochar production. Both biochars prepared at temperatures of 300 and 400 °C had favorable effect on anaerobic digestion of the high-nitrogen chicken droppings. However, the most effective biochar was the one prepared at 300 °C. It is likely that the application of specific biochar in the digestion of other nitrogen-rich substrates will have a similar effect.

Theoretically, biochar application in an anaerobic digester can be performed in two main ways. Biochar can be added together with daily feeding mixture at biochar/substrate proportions much lower than those tested here. In this case, biochar cost should be considered as part of the operating cost along with substrate. According to another option, biochar is added to digester in large quantity only once at reactors start-up. An experimental approach of this option at laboratory scale is presented in the current study. In this case, material should be considered as catalyst or part of reactor construction and thus any related expenses should be included in investment costs. In this instance, a detailed verification of installation costs would be required before methods application. For any of the above options, however, there is always a potential risk for reactors operation due to biochars deposition after long operation period. More research should also be needed at laboratory scale to identify the potential of biochar to increase methane generation when it is added together with substrate on a daily basis.

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References

[1] Ward A.J., Hobbs P.J., Jones D.L. Bioresource Technology 2008, 99, 7928 – 7940.

[2] Sunyoto N.M.S., Minming Zhu M., Zhang Z., Zhang D. Effect of biochar addition on hydrogen and methane production in two-phase anaerobic digestion of aqueous carbohydrates food waste. Bioresource Technology, Volume 2019 (2016), 29 – 36. https://doi.org/10.1016/j.biortech.2016.07.089.

[3] Qiu L., Deng Y., Wang F., Davaritouchaee M., Yao Y. A review on biochar-mediated anaerobic digestion with enhanced methane recovery. Renewable Sustainable Energy Reviews, Volume 115 (2019), 109373.

[4] Mumme J., Strocke F., et al. Use of biochars in anaerobic digestion. Bioresource technology, Volume 164 (2014), 189 – 197. https://doi.org/10.1016/j.biortech.2014.05.008

[5] Watanabe R., Tada C., Baba Y., Fukuda Y., Nakai Y. Enhancing methane production during the anaerobic digestion of crude glycerol using Japanese cedar char-coal. Bioresource Technology, Volume 150 (2013), 387 – 392.

[6] Torri C., Fabbri, D. Biochar enables anaerobic digestion of aqueous phase from intermediate pyrolysis of biomass. Bioresource Technology, Volume 172 (2014), 335 – 341. https://doi.org/10.1016/j.biortech.2014.09.021

[7] EN 15933:2012 Sludge, treated biowaste and soil. Determination of pH.

[8] EN 15934: 2012 Sludge, treated biowaste, soil and waste. Calculation of dry matter fraction after determination of dry residue or water content.

[9] EN 15935:2012 Sludge, treated biowaste, soil and waste. Determination of loss on ignition.

[10] EN 12154:2014 Determination of density by volumetric displacement – Skeleton density by gas pycnometry.

[11] EN 18753:2017-TC. Tracked Changes. Fine ceramics (advanced ceramics, advanced technical ceramics). Determination of absolute density of ceramic powders by pycnometer.

[12] ASTM D5373-16 Standard Test Methods for Determination of Carbon, Hydrogen and Nitrogen in Analysis Samples of Coal and Carbon in Analysis Samples of Coal and Coke.

[13] EN 11734:1998 Evaluation of the "ultimate" anaerobic biodegradability of organic compounds in digested sludge – Method by measurement of the biogas production.

[14] VDI 4630: Vergärung organischer Stoffe – Substratcharakterisierung, Probenahme, Stoffdatenerhebung, Gäversuche.

[15] Panigrahi S., Dubey B.K. A critical review on operating parameters and strategies to improve the biogas yield from anaerobic digestion of organic fraction of municipal solid waste. Renewable Energy, Volume 143 (2019), 779 – 797. https://doi.org/10.1016/j.renene.2019.05.040.

[16] Richards B.K., Cummings R.J., White T.E., Jewell W.J. Methods for Kinetic Analysis of Methane Fermentation in High Solids Biomass Digesters. Biomass Bioenergy, Volume 1 (1991), 65 – 73. https://doi.org/10.1016/0961-9534(91)90028-B.

Příklad zvýšení produkce bioplynu a methanu aplikací biouhlu připraveného z digestátu do anaerobního fermentoru

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Souhrn

Předložený příspěvek uvádí výsledky testů produkce bioplynu a methanu vsádkovou jednostupňovou mezofilní anaerobní digescí. Slepičí trus byl vybrán jakožto substrát s vhodným dusíkatým obsahem. Biouhel byl připraven z tuhé fáze digestátu získaného ze zemědělské bioplynové stanice Pustějov II, Zemspol Studénka, a.s., Moravskoslezský kraj. Biouhel byl přidán jakožto podpůrný materiál, byl připraven při třech různých teplotách pyrolýzy, konkrétně se jedná o teploty 500 °C, 400 °C a 300 °C. Porovnáním naměřených hodnot měrné produkce CH_4 ze substrátů s měrnými produkcemi CH_4 ze směsí, vypočtenými váženým průměrem dle podílů substrátů, celkových sušin a substrátových produkcí methanu, bylo zjištěno, že směs s biouhlem připraveným při 500 °C velmi výhodná nebyla. Na druhou stranu směs s biouhlem připraveným při 400 °C poskytla o 6 % vyšší měrnou produkci CH_4, než bylo očekáváno dle teoretických výpočtů a směs s biouhlem připraveným při 300 °C poskytla o 30 % vyšší měrnou produkci methanu, než bylo teoreticky očekáváno.

***Klíčová slova**: anaerobní digesce, BMP, slepičí trus, dusík, biouhel*

Increase of Biodegradability of Acid Industrial Organic Waste by the Addition of Ash from Municipal Incineration Plant

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Abstract

The biodegradation of organic material is an attractive alternative in the field of waste utilization. Biodegradation is accompanied by the formation of a nutritious residue, whether under aerobic (compost) or anaerobic (digestate) conditions, in addition to the removal of the significant amount of waste. Anaerobic decomposition offers, in addition to the mentioned advantages, the possibility of energy recovery of organic materials by producing biogas with a high methane content.

This paper presents the suitability of the ash usage in the process of anaerobic decomposition of the selected organic materials with the aim of accelerating their biodegradability. The ash comes from a waste incineration plant. Distillery fruit stillage was used as organic material for biodegradability monitoring. Biodegradability was investigated at different batches of the ash (3.7, 1.8; and 0.9 % w/w - weight per weight dry matter of organic material used). The biogas production was monitored using the Oxi Top that uses the manometric principle.

The optimum ash content was determined 1.8 % of dry distillery grape stillage, with an increase in the biogas production of 37 %. The highest addition of the ash caused a reduction in biogas production, possibly due to the inhibition of methanogenesis despite accelerated hydrolysis of the fermented mixture.

The research results demonstrate that ash from municipal incineration plant can be used to increase biodegradation of the organic material under anaerobic conditions. However, it is necessary to determine the optimum amount of ash in laboratory investigations prior to the operational applications due to the variability of the input organic material (pH value, dry matter, loss on ignition).

Keywords: *organic waste, biodegradability, bottom ash.*

Introduction

In recent years, increased attention has been paid to the methods of organic waste treatment, especially in connection with the "landfill" directive of the EU (1999/331/ES), which banned deposit of waste on landfills. Popular methods of organic material treatment contain biological decomposition, whether under anaerobic (methanization) or aerobic (compost) conditions[1]. This paper focuses on the improvement of anaerobic biological decomposition of acid industrial organic waste – distillery fruit stillage, by alkali pretreatment of input raw material. Anaerobic decomposition of organic material comprises the complex of processes, connected by four phases: hydrolysis, acidogenesis, acetogenesis / dehydrogenation and methanogenesis[2]. The activity of microorganisms can be inhibited especially by disruption of optimal pH values, hydrogen concentration, or volatile fatty acids[3]. Considerable elimination of methanogenic bacteria at the pH values of 5.0 – 5.5 was proved[4].

Distillery stillage is a liquid by-product from the ethanol distillation after organic substances fermentation. Production of 1 litre of ethanol brings about approximately 20 litres of stillage. The potential of stillage pollution can exceed chemical oxygen demand (COD) values of 100,000 mg/l. Due to the high content of organic substances, anaerobic microbiological treatment of stillage dominates over the aerobic one.

Aerobic decomposition of material of high content of COD demands considerable aeration, while less than 20 % of COD will be converted into solid rests. Anaerobic digestion leads to conversion of significant amount of COD (>50 %) to biogas, which can be consequently used as biofuel. It follows that anaerobic treatment of stillage is more popular than the aerobic one[5]. As one of the possibilities for the improvement of conditions of anaerobic decomposition of acid food waste, alkali pretreatment of mixture using ash as a waste product is proposed. The increase of alkalinity prevents sharp decline of pH during the acidogenesis. Thus the stable environment for methanogenic bacteria is created[6]. Independent decomposition of waste from activated sludge was proved by the application of optimal dose of NaOH[7]. For the pH treatment, NaOH is the most often used, which is used e.g. for pretreatment of lignin of cellulose materials, because high NaOH concentrations (6 – 8 %) are able to decompose lignin, resistant to anaerobic decomposition[8].

Bottom ash is rough, granular, non-flammable by-product of the incineration process[9]. Due to the high content of calcium, ash, after its dissolution in water, creates alkaline environs by the production of $Ca(OH)_2$[10]. Calcium is an essential nutrient for the growth of certain strains of methanogenic bacteria. It is involved in the production of microbial aggregates. Excessive calcium concentration leads to the precipitation of carbonates and it affects the decrease of specific activity of methanogenic bacteria or the loss of buffer[11]. It follows that the pretreatment of acid industrial waste at optimal ash bottom doses of sufficient calcium content leads to the improvement of the fermentation process.

The main aim of the paper is the assessment of the use of ash bottom from the municipal waste incineration plant in order to the improvement of anaerobic decomposition of industrial organic waste. The used bottom ash did not have any dangerous properties. Efficiency of the addition of ash was studied in dependence on biogas production and with the monitoring of pH. Moreover, anaerobic decomposition of waste was evaluated using biological degradability indicators.

Material and methods

Industrial waste – distillery stillage was used. Its characteristics is summarised in Table 1. Distillery fruit stillage was taken from waste stream from a factory for alcohol distillation.

Table 1: Results of determination of dry matter yield and energy value of spontaneous fallows in the third year of research

Substrate	Dry matter	Loss on ignition	COD_{Cr}	BOD	pH
	%	%	mg/l	mg/l	-
Distillery fruit stillage	27	76	10,900	3,900	3.87

As inoculum, sludge from anaerobic waste treatment from a municipal waste water treatment plant was used. Characteristics of the inoculum is shown in Table 2. Bottom ash used for the pretreatment of the substrate was obtained from municipal incineration plant of separated waste. Its characteristics is presented in Table 2. Considering the mentioned literature[12,13], the following doses of ash were determined for optimal Ca concentration in the substrate: 3.7; 1.8; 0.9 % of dry matter of organic material.

Table 2: Characteristics of sludge and bottom ash

Substrate	Dry matter	Loss on ignition	COD_{Cr}	BOD	pH	Ca
	%	**%**	**mg/l**	**mg/l**	**-**	**mg/kg**
Sludge	1.4	99.49	13,833	1,100	7.46	-
Bottom ash	99.28	95.66	11.63	-	11.63	161,000

Experiment

Determination of biogas production with the monitoring of pH values during biological decomposition

The bottles of the system OxiTop of volume of 500 ml (600 ± 10 ml of total volume) were used in the experiment. Magnetic stirrer was put into the bottles. Consequently, the bottles were being blown through by inert N_2 for 2 minutes. After the addition of samples and inoculum, the bottles were incubated at the temperature of 30 ^{o}C for 24 hours. The test was performed during 10 days with continual stirring of the compound. Biogas production was measured on the basis of pressure difference at the constant volume, using recommended calculations according to the system OxiTop®. Measured pressure was recalculated to the volume of biogas. Besides measuring pressure in measuring heads, pH values were regularly measured (every two days) due to the monitoring of alkalinity of the process after the addition of ash of high content of Ca. Experiment was repeated six times.

Assessment of the biological degradability indicators

The compound was incubated for 10 days with the use of the same doses of bottom ash as in a case of the determination of biogas production. At the beginning and the end of the incubation, value of COD mixture was determined in order to calculate indicators of biological degradability. The indicators were biologically degradable ratio (BR) and specific speed of degradation (q). Experiment was repeated six times.

Analytic methods

Dry matter was determined according to the standard STN EN 14346 (83 8241)[14]. The sample is dried up under determined conditions (103 °C ± 2 °C) to constant weight. The content of dry matter in the sample is calculated from the difference of the sample weight before and after drying up.

Determination by the loss on ignition in waste is in compliance with the standard STN EN 15169 (83 8242)[15]. Experimental sample is heated in a furnace at 550 °C ± 25 °C. The loss by annealing is calculated from the difference of weight before and after heating.

pH value was determined electrochemically according to the standard STN ISO 10390[16].

Determination of COD was performed according to the standard STN ISO 6060[17] Determination by potassium dichromate / by titration. Biological oxygen demand (BOD_5) was determined as a difference of concentrations of dissolved oxygen in a sample before and after biochemical oxidation of organic substances under considerably standardised conditions of incubation of the sample. Determined loss of dissolved oxygen is proportional to the content of biochemically decomposable organic substances in the sample of water. Determination was performed in compliance with the standard STN EN 1899-2[18].

Measurement of biogas production

Biogas production was measured on the basis of pressure difference at the constant volume. Pressure difference was recalculated to the volume of biogas using the principle of ideal gas.

For the experiment, the device OxiTop® Control AN of the company WTW Xylem Analytics, Germany was used. The device works on respirometric measurement basis. If oxygen in closed sample bottle is being spent during the process, underpressure is created. On the contrary, if the gas is released during anaerobic decomposition, the overpressure emerges. This pressure change is detected and kept in measuring head all the time since the start of measurement. Controler OxiTop OC 110 saves pressure values from measuring heads and processes them on.

Preliminary calculations

Amount of substrate that was added for the process of anaerobic decomposition was calculated with regard to the limiting pressure in OxiTop. Declared maximum pressure difference was 300 hPa.

For this reason and regarding the ideal gas law, on condition of the composition of gas of 50:50 CH_4: CO_2 and volume of gaseous space of 370 ml due to the experiment setting, maximum permitted gas production at 35 ^oC was 0.0027 mol.

If CO_2 is not removed, it is expected that 0.00136 mol of CH_4 will be produced, or 0.0217 g of CH_4. Since stechiometrically 4 g of COD are reduced to 1 g of CH_4, maximum content of substrate, which is to be added, is 0.087 g of COD, i.e. loss of substrate concentration of 0.235 g of COD/l (Equation (1)):

$$S[gCOD] = 4\,[g\,COD * g\,CH_4^{-1}] * 50\,\% * \left(\frac{\Delta\mathrm{pmax}\,[Pa] * V_g\,[m^3]}{R[J/mol^{-1} * K^{-1}] * T\,[K]}\right) \qquad (1)\ ,$$

where *S* is addition of COD regarding maximum pressure difference in the device OxiTop [g COD], Δpmax stands for maximum pressure difference declared by the producer [Pa], Vg is volume of gas in a bottle OxiTop [m^3], R presents universal gas constant [8.314 J/mol*K] and T is incubation temperature [K].

Calculation of specific biogas production

Determination of biological degradability of organic compounds in fermented sludge is described in the standard DIN EN ISO 11734 or DEV L47[19] as a process consisting of biogas production during biological decomposition.

For practical reasons, gas pressure is measured in hectopascals, volume in millilitres and temperature in degrees Celsius. For the calculation, temperature is recalculated from the degrees Celsius to Kelvins, e. g. 35 °C = 308.15 K.

The calculation is based on the ideal gas law (Equation (2)):

$$n = \frac{p * V}{R * T} \qquad (2)\ ,$$

where n stands for amount of substance of produced gas [mol], p is gas pressure [Pa], V is gas volume [m^3], R is universal gas constant [8.314 J/mol*K] and T is incubation temperature [K].

Content of carbon in gaseous phase is represented by the sum of methane and carbon dioxide. Clean carbon, produced during anaerobic process (reduced by carbon created during blind sample fermentation) as a result of substrate degradation is calculated in the following way (Equation (3)):

$$n_{CO2+CH4} = \frac{\Delta p * V_g * 10^{-4}}{R * T} \qquad (3)\ ,$$

where nCO_2+CH_4 is amount of substance of the gas created by biological decomposition [mol], ∆p is pressure in a measuring head with the sample and inoculum reduced by pressure in the measuring head without the sample [hPa], Vg is volume of gas in a bottle OxiTop [ml], 10^{-4} is a converse factor from hPa to Pa and from millilitres to cubic metre.

Specific biogas production [l/g of loss by annealing] is consequently calculated by the recalculation through the molar volume and related tog of loss by annealing substrate (Equation (4)):

$$\text{Specific biogas production} = \frac{n_{CO2+CH4}}{S_o} * 22{,}4 \qquad (4)\ ,$$

where 22.4 is molar volume of gas (l* mol^{-1} under standard conditions) and S_o is amount of added substrate from loss by annealing (g).

Calculation of biological degradability indicators

Biologically degradable ratio (BR)

To calculate BR, the value of COD is determined in a sample at the beginning and at the end of the organic material incubation. The following equation was used (Equation (5)):

$$BR = \frac{S_o - S_z}{S_o} * 100 \qquad (5),$$

where BR is biologically degradable ratio in mg/l; S_o is a value of COD at the beginning of the experiment; S_z is a value of COD sample in mg/l at the end of incubation of organic material.

Another criterion of biological degradability is a speed of biological degradation (S_{90}) used for the calculation of average specific speed of degradation (q) in mg of the removed COD. The basis for the calculation is time t_{90}, needed for the removal of 90 % of biologically degradable ratio. It is the time, which answers for residual value of COD.

Speed of biological degradation is calculated using the formula (Equation (6)):

$$S_{90} = S_o - (S_o - S_z) * 0.90 \qquad (6)$$

Average specific speed of degradation is calculated using the formula (Equation (7)):

$$q = \frac{S_o - S_{90}}{t_{90} * X_o} \qquad (7),$$

where q is specific speed of degradation in mg/(g.h); X_o is a value of dry matter of inoculum at the beginning of decomposition of organic waste in g/l.

Results and discussion

Effect of the addition of bottom ash on specific biogas production

Figure 1 displays the dependence of volume of biogas from the dose of bottom ash, including the extract of biogas without a preliminary treatment of a sample. Based on the achieved results, the optimal dose of bottom ash in distillery fruit stillage was 1.8 % of dry matter of stillage, when increased biogas production in 31 % was detected in comparison with untreated sample. The value of addition of bottom ash represents Ca concentration of 216 mg/l in a solution. This result corresponds approximately with the results of the study, in which optimal Ca concentration is 303 mg/l. At this concentration, biogas production increased in 50 % and time of the processing of input raw material decreased[20].

High calcium concentrations cause inhibition of anaerobic process. According to Yin[12] Ca concentration of 3,252 mg/l decreased considerably biogas production. Other results were achieved by the authors[13] who did research into anaerobic decomposition of waste water from the farm, where optimal dose of Ca^{2+} was even 3,000 mg/l. Inhibition of anaerobic process was observed at the concentrations of 5,000 and 7,000 Ca^{2+} mg/l. In this study the source of calcium was calcium chloride and not waste bottom ash from the incineration plant.

According to pH results, displayed in Figure 1, the increase of solution alkalinity is obvious. It prevents pH from decreasing during acidogenesis. Thus, stable environment for methanogenic bacteria is created. The effect of bottom ash addition of high calcium content is reinforced by acid nature of tested substrates. The highest biogas production was determined at the addition of 1.8 % of dry matter of organic waste, which was increased in comparison with untreated sample on the average of 37 %. During this treatment, pH ranged from 6.8 to 7.4. Lower biogas production in comparison with untreated sample was observed after the ash addition of 0.9 % of dry matter. There was an increase of 18 % in comparison with untreated sample, while pH values ranged from 7.5 – 6.9. Lower biogas production in comparison with untreated sample was found out after the ash addition of 3.7 % of dry matter. During this treatment, biogas production fell by 25 % in comparison with untreated waste sample, while pH values ranged between 6 and 8.1.

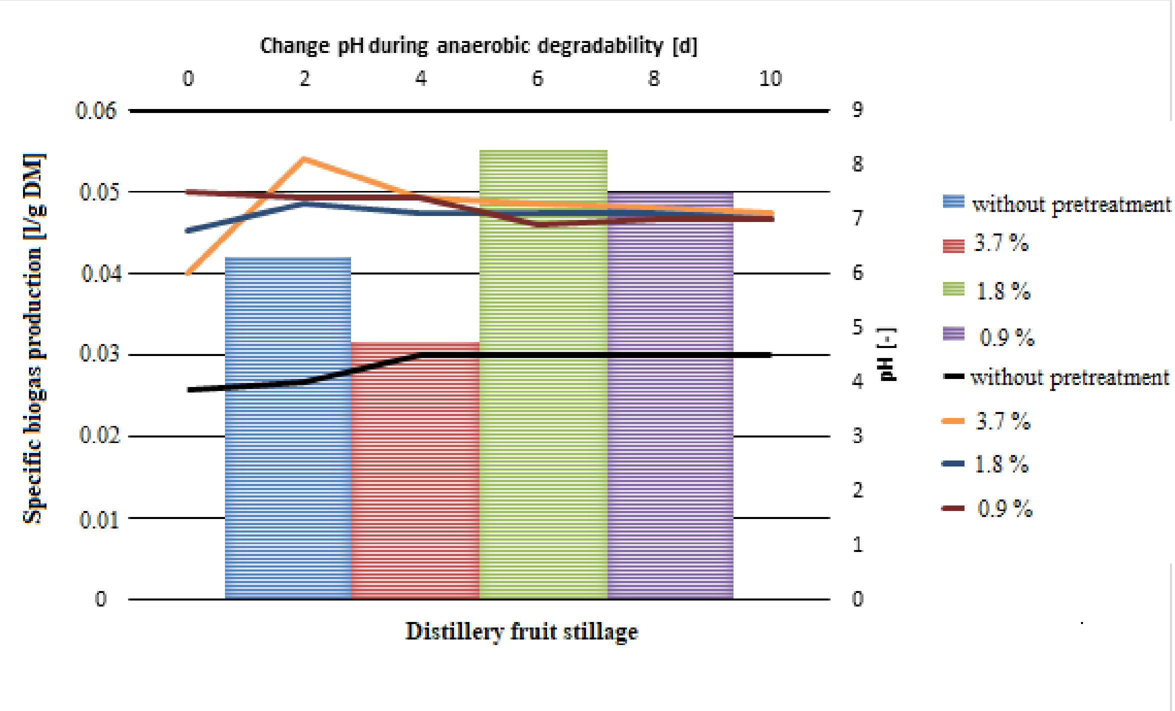

Figure 1: Effect of the substrate pretreatment on specific biogas production of distillery fruit stillage

Evaluation of biological degradability

The pretreatment effect was assessed on the basis of calculation of biologically degradable ratio and specific speed of degradation. Input and output COD values were determined during 10 days of incubation (Table 3). According to the study of other authors[21], optimal period was the one we chose, when retaining period was reduced from 20 to 11.7 day and the reduction of COD from 92.5 % to 78.9 % was observed.

Table 3: Biological degradability of distillery in dependence on bottom ash addition

Sample	**Biologically degradable ratio (BR)**	**Specific speed of degradation (q)**
	[%]	**[mg/(g*h)]**
A	48	6.3
B	56	6.7
C	67	8.0
D	46	8.7

A – without bottom ash addition; B – 0.9 % of dry matter; C – 1.8 % of dry matter; D – 3.7 % of dry matter

The highest value of BR was observed at the bottom ash dose of 1.8 % of dry matter of waste stillage. It was increased in 39.5 % in comparison with untreated sample. The lowest value of BR was determined after the addition of bottom ash of 3.7 % of dry matter. During this pretreatment, the lowest value of biologically degradable ratio was determined, which decreased in 4 % in comparison with untreated sample. Obtained results correspond with the biogas production from the previous experiment. After the addition of bottom ash of 1.8 % of dry matter of waste stillage, specific speed of degradation was increased in 27 % comparing with untreated sample. The highest specific speed of degradation was determined when adding bottom ash of 3.7 % of dry matter of stillage, but biogas production was lower at this dose.

Conclusion

It follows from the obtained results that addition of bottom ash has a positive effect on biogas production and speed of anaerobic degradation of distillery stillage, typical for its low pH values. The addition of bottom ash increases pH values and it is a source of calcium, which is one of the essential elements.

The highest biogas production was observed after the addition of bottom ash of 1.8 % of dry matter of waste stillage. During this treatment, pH values were kept in optimal range for anaerobic microorganisms. Bigger additions had inhibition effect. The lowest biogas production was detected after the addition of bottom ash of 2.7 % of stillage dry matter. During this treatment, the passage of pH into mildly alkali area was observed. It could cause inhibition of anaerobic decomposition and biogas production, too.

References

1. Walker L., Charles W., Cord-Ruwisch R.: Bioresour. Technol. *100*, 3799 (2018).
2. Gupta P., Singh R., Sachan A., Ambarish S. V., Gupta A.: Fuel. *95*, 495 (2012).
3. Feng Y., Zhang Y., Quan X., Chen S.: Water Res. *52*, 242 (2014).
4. Latif M. A., Mehta C. M., Batstone D. J. (2017). Water Res. *113*, 42 (2017).
5. Wilkie C., Riedesel K., Owens J.: Biomass Bioenergy. *19*, 63 (2000).
6. Lin J., Chang C., Chang S.: Bioresour. Technol. *62*, 85 (1997).
7. Salehian P., Karimi K., Zilouei H., Jeihanipour A.: Fuel. *106*, 484 (2013).
8. Gupta V. K., Mittal A., Malviya A., Mittal J.: J. Colloid Interface Sci. *335*, 24 (2009).
9. Del V. R., Formosa J., Chimenos J. M., Martínez M., Fernández A. I.: Waste Manage. *33*, 621 (2013).
10. Chen Y., Cheng J. J., Creamer K. S.: Bioresour. Technol. *99*, 4044 (2008).
11. Hm L., Chiang C. F., Tsao H. C., Pai T. Y., Liu M. H., Kurniawan T. A., Chao K. P., Liou C. T., Lin K. C., Chang C. Y., Wang S. C., Banks C. J., Lin C. Y., Liu W. F., Chen P. H., Chen C. K., Chiu H. Y., Wu H. Y., Chao T. W., Chen Y. R., Liou D. W., Lo F. C.: Waste Manage. Res. *30*, 32 (2017).
12. Yin, C., Shen Y., Zhu N., Huang Q., Lou Z., Yuan H.: Appl. Energy. *215*, 503 (2018).
13. Ahn, J., Do T. H., Kim S. D., Hwang S.: Biochem. Eng. J. *30*, 33 (2006).
12. European Standard Norm EN 14346: *Characterization of waste - Calculation of dry matter by determination of dry residue or water content* (2006).
13. European Standard Norm EN 15169:2007: *Characterization of waste - Determination of loss on ignition in waste, sludge and sediments*.
14. ISO 10390:2005: *Soil quality - Determination of pH*.
15. ISO 6060:1989: *Water quality. Determination of the chemical oxygen demand*.
16. ISO 5815:1989: *Water quality. Determination of biochemical oxygen demand after n days (BODn). Part 2: Method for undiluted samples*.
17. EN ISO 11734:1998: *Water quality. Evaluation of the "ultimate" anaerobic biodegradability of organic compounds in digested sludge. Method by measurement of the biogas production*.
18. Menon, A., Wang J., Giannis A.: Waste Manage. *59*, 465 (2017).
21. Sayedin F., Kermanshahi-Pour A., He Q.: Renew. Energy. *135*, 975 (2019).

Zvýšenie biodegradability kyslých priemyselných organických odpadov prídavkom popola z komunálnej spaľovne.

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Súhrn

Biologický rozklad organického materiálu je atraktívnou alternatívou v oblasti využívania odpadu. Okrem odstránenia významného množstva odpadu je biologický rozklad sprevádzaný tvorbou zvyšku s obsahom živín, či už za aeróbnych (kompost) alebo anaeróbnych (digestát) podmienok. Anaeróbny rozklad ponúka okrem spomenutých výhod aj možnosť energetického spätného získavania organických materiálov prostredníctvom výroby bioplynu s vysokým obsahom metánu.

Príspevok prezentuje vhodnosť použitia popola v procese anaeróbneho rozkladu vybraných organických materiálov s cieľom urýchliť ich biologickú odbúrateľnosť. Popol pochádza zo spaľovne odpadu. Ako organický materiál na sledovanie biologickej odbúrateľnosti boli použité výpalky z destilácie ovocného kvasu. Biologická odbúrateľnosť sa skúmala pri rôznych dávkach popola (3,7; 1,8; a 0,9 % hmotnostného percenta sušiny použitého organického materiálu). Produkcia bioplynu sa monitorovala pomocou prístroja Oxi Top, ktorý využíva manometrický princíp.

Optimálny obsah popola bol stanovený na 1,8 % suchých hroznových výpalkov so zvýšením produkcie bioplynu o 37 %. Najvyšší prídavok popola spôsobil zníženie výroby bioplynu, pravdepodobne v dôsledku inhibície metanogenézy napriek zrýchlenej hydrolýze fermentovanej zmesi.

Výsledky výskumu ukazujú, že popol z komunálnej spaľovne možno použiť na zvýšenie biodegradácie organického materiálu za anaeróbnych podmienok. Je však potrebné určiť optimálne množstvo popola pri laboratórnych skúškach pred praktickými aplikáciami z dôvodu variability vstupného organického materiálu (hodnota pH, sušina, strata žíhaním).

Kľúčové slová: *organický odpad, biodegradabilita, roštový popol*

The assessment of the firefighting agents residues impact on the soil through the phytotoxicity tests

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Abstract

The issue of contamination of soil caused by extinguishing wastewater and firefighting foam residues from wildland fires suppression is discussed in the paper. The samples of extinguishing water were collected after simulated wildland fire in the laboratory conditions. The cellulosic materials such as wood and straw were used. The samples were ignited and in the third stage of fire (full developed fire) extinguished with the hydrant water. The samples of contaminated soil after firefighting foam application were collected. Both types of samples were tested using phytotoxicity tests, test organism: seeds of higher cultivated plants: Pisum sativum and Sinapis alba. The obtained results show that the examined samples have an inhibitory effect on biomass production, which is proof of subchronical toxicity of used firefighting agents residues.

Key words: *wildland fire, fire suppression, extinguishing water, firefighting foam, subchronical toxicity, Pisum sativum, Sinapis alba*

Introduction

More than 200 days lasted the large-scale bushfire in Australia in the 2019-2020 fireseason. Although it was not the biggest fire (neither in the world nor in Australia), it certainly sparked a wide-ranging debate in the professional and lay worlds, and against the background of the Covid-19 situation it resonated in the public consciousness. In 2019, several large-scale forest fires (rainforest fire, Siberia fire, Australia fire) attracted attention, reminding the importance of this problem, as it is a major intervention in the ecosystems and impact on human health. The intensity of fire impact on ecosystem depends on ecosystem type and its "health" condition and on fire severity[1,2]. Damage of ecosystems occur during the fire itself such as damage due thermal damages to plant structures, death of macro- and microfauna but very important impact are the altered post-fire environmental conditions such as loss of nutrients, changes in soil structure, biochemical properties and water repellency[1,2,3,4].

The mostly used firefighting medium for wildland fire suppression is water due its availability, excellent chemical-physical properties, and also economic factors[5,6]. However, some properties reduce its extinguishing effect, in particular the high surface tension, which causes low adhesion of water to the extinguished surface, or the weight which complicates transport over long distances in natural fires or causes large dispersion of the affected area when extinguishing using the airplanes or helicopters[6,7]. For elimination of this negative properties are used new progressive substances as water additives (organic fluorine compounds, nanoparticles)[6,7], or are developed new firefighting media (extinguishing gel Firesorb)[5] or new way in using of conventional firefighting agents (firefighting foam)[5,8]. Residues of used extinguishing agents together with the entrapped smoke products remain in the fire place and leak into surface and subsurface water and soil[2,9,10].

An important ecotoxicological indicator of the ecosystem devastation degree is the phytotoxicity testing. The phytotoxicity tests monitor effects of tested compounds on the seed germination, the roots growth, the plant growth and biomass inhibition[2,3,11]. The agricultural crops seeds are mostly used as a testing organism. The acute and subchronical toxicity are assessed by these tests at the several exposition times, in the laboratory and also in the field. The container experiments capture the entire life cycle of the plant in the terms of the experimental design of tests with vascular plants[11,12].

The aim of the contribution is assessing of the impact of the water based extinguishing agents (water and foam) after simulated wildland fire suppression on the soil by the phytotoxicity tests.

Experimental part

Tested materials

Natural lignocellulosic materials were used to the simulation of wildland fire in the laboratory conditions – spruce wood and wheat straw. Samples of wood and straw were ignited in the metal container with diameter 30 cm. The simulated fire was extinguished with the common hydrant water in the third phase of fire (fully developed fire). Water after extinguishing was sampled and phytotoxicity tests were performed.

Samples of the soil after firefighting foam application were collected and phytotoxicity tests were performed. The firefighting foam was applicate on soil with grass during the firefighters training. The foam was prepared using foaming agent STHAMEX F-15, concentration 5%, which is concentration usually used. STHAMEX F-15 is synthetic foaming agent, the main components are tensides/surfactants, other are organic compounds as stabilisators and potash as a frost-resistant. The soil samples were collected from the depth 0 – 10 cm[13]. The area was not contaminated by anthropic activities.

Figure 1: Foam preparation from concentrate (right) and foam application (left)

Determination of the phytotoxicity

Test of the phytotoxicity: test for the effect on the growth of the aboveground part of pea (*Pisum sativum*) and white mustard (*Sinapis alba*)[11,14,15]. In the phytoxicity tests, test organisms were used – seeds of higher cultivated plants: *Pisum sativum* (legumes – *Leguminacea* – III, Plant category) and *Sinapis alba* (cabbage – *Brassiceacea*, belonging to category II of plants used standard in phytotoxicity tests).

All container experiments were performed in the laboratory by constant conditions (21°C temperature and 30 vol. % moisture of the sample)[16] within three months (March and May) in the year 2019. Moisture control in the samples was performed with a HH2 DT DELTA-DEVICES hygrometer (England) and drinking water was used to maintain it. The constant temperature was ensured by air conditioning in the laboratory and was 21 ± 2 °C. The standard duration of phytotoxicity tests is 14 days (tables 1-3). At the end of the test, the plants were removed from the soil, washed in distilled water to remove soil residues. The green part of the plants was used for gravimetric determination of biomass.

Terrestrial Plant Test with Sinapis alba

The principle of this subchronic phytotoxicity test is the effect of the waste extinguishing water on cultivation of *Sinapis alba* seeds uniformly lay out on the soil bottom. The monitored samples are compared with control sample. The test conditions are described in the Table 1.

Table 1: The conditions of subchronical phytotoxicity test using Sinapis alba[11,14]

Temperature	20 ± 1°C
Exposition duration	14 – 16 days
Sample volume	50 mL of waste extinguishing water and 50 mL of diluting water for the control uncontaminated soil
Amount of test organism	20 seeds of *Sinapis alba* (Mega C, germination 98%) uniformly lay out on the bottom of the testing container
Number of repetitions	6
Biomass determination	biomass (roots and green part of the plant) gravimetrically determined by the drying to the constant mass at the 105 ± 2°C in the laboratory dryer POL-EKO SL (Poland)
Monitored parameters	germination after 48 hours, I_{BIOMi}, calculating according to the formula (1)
Other conditions	samples posted in the incubator TS 606 CZ/2-Var (WTW, Germany), continuous irrigation with the drinking water

Terrestrial Plant Test with Pisum sativum

There are conditions of the test of the impact of the waste extinguishing water on the growth of *Pisum sativum* stated in the Tables 2 and 3. All tests were performed with collected wastewater and with control sample of drinking water.

Table 2: The conditions of the test of the impact of the waste extinguishing water on the growth of Pisum sativum[14]

Temperature	20 ± 1°C
Exposition duration	14 days
Sample volume	100 ml extinguishing water applicate into 500 g soil in testing container
Amount of test organism	6 seeds of *Pisum sativum* Gambit C1 (germination 97%)
Number of repetitions	6
Monitored parameters	I_{BIOMi} (biomass inhibition), biomass inhibition is determined by calculating according formula (1) after drying of green part to the constant mass at 105 °C

Table 3: The conditions of the test of the impact of the firefigting foam contaminated soil on the Pisum sativum[14]

Temperature	20 ± 1°C
Exposition duration	14 days
Sample mass	500 g of soil contaminated by firefighting foam STHAMEX 5%[13]
Amount of test organism	6 seeds of *Pisum sativum* Gambit C1 (germination 97%)
Number of repetitions	6
Monitored parameters	I_{BIOMi} (biomass inhibition), calculating according to the formula (1)

Results processing

Biomass inhibition I_{BIOMi} will be calculated according to the formula:

$$I_{BIOMi} = \frac{m_k - m_v}{m_k} * 100 \tag{1}$$

I_{BIOMi}	biomass inhibition of i-sample,
m_v	the mass of i-sample biomass in g;
m_k	the mass of control sample in g[11].

Results are processed using STATISTICA 12, ANOVA programme, one factor analysis of variance (using 95% confidence intervals for the mean values of the individual samples).

Results and Discussion

The samples of waste extinguishing water were added to the soil in the container by single application for the subchronical toxicity (14 days' duration) determination on seeds of *Pisum sativum* and *Sinapis alba*. The soil contaminated by the firefighting foam STHAMEX F-15 (5%) was also tested by phytotoxicity tests using *Pisum sativum* and *Sinapis alba* seeds. Each of experiments was compared with the application of control sample of drinking water. All the experiments were performed by constant conditions (21 °C temperature and 30 vol. % moisture)[16].

The test with Sinapis alba

In a subchronic test with *Sinapis alba* seeds, the seeds germination was evaluated 48 hours after the application of the waste extinguishing water, which is shown in the Table 4. The lowest germination was in the samples from wood fire extinguishing. After 48 hours, the germinated seeds were inserted with tweezers under the soil bottom (1-1.2 cm). Due to the determined germination values (Table 4), it was possible to continue further testing for 14 days[14].

Table 4: Germination seeds of Sinapis alba

Germination seeds % after 48 hours	**Sample**		
	CONTROL	**WOOD**	**STRAW**
	96	86	90

There are values of *Sinapis alba* biomass inhibition (%) in the table 5 determined in individual samples compared to the control sample.

Table 5: Statistical characteristics of subchronic test of biomass inhibition with Sinapis alba

Sample	**Biomass inhibition, %**			
	Average	**Standard deviation**	**Confidence intervals**	
			-95%	**+95%**
WOOD	37.91	3.26	23.91	51.92
STRAW	43.79	5.46	20.29	67.28

The results indicate inhibition impact of waste extinguishing water from fire of both natural lignocellulosic materials. There was a higher inhibitory effect on the growth of *Sinapis alba* in the soil with applied straw-extinguishing water. By comparison with the values given in table 6[10], which are the values of the determined inhibition / stimulation of root growth only, evaluated as acute toxicity (the test lasted 72 hours), water from wood extinguishing had a stimulating effect on *Sinapis alba* root growth and from straw extinguishing inhibiting effect.

Table 6: Statistical characteristics of the of growth inhibition of higher cultivated plants (Sinapis alba) – acute test toxicity[10]

Sample	IC, %			
	Average	Standard deviation	Confidence intervals	
			-95%	+95%
WOOD	-13.98	5.09	-30.17	2.21
STRAW	3.87	3.56	-7.46	15.21

By evaluating the results from the point of view of extinguishing water as wastewater, according to STN 838303[12], negative values were determined (root growth inhibition <30% or stimulation <75% compared to control). However, quench water was found to have an inhibitory effect on the subsequent growth stages of Sinapis alba (effect on the growth of the green part of the plants) during the 14-day test.

The test with Pisum sativum

In the phytotoxicity test with seeds *Pisum sativum*, the most pronounced inhibitory effect was recorded in the sample with applied waste extinguishing water from the straw fire (Fig. 2). There was no significant difference in the determined biomass inhibition between soil samples contaminated with wood extinguishing water and soil contaminated with STHAMEX 5% firefighting foam (Table 7).

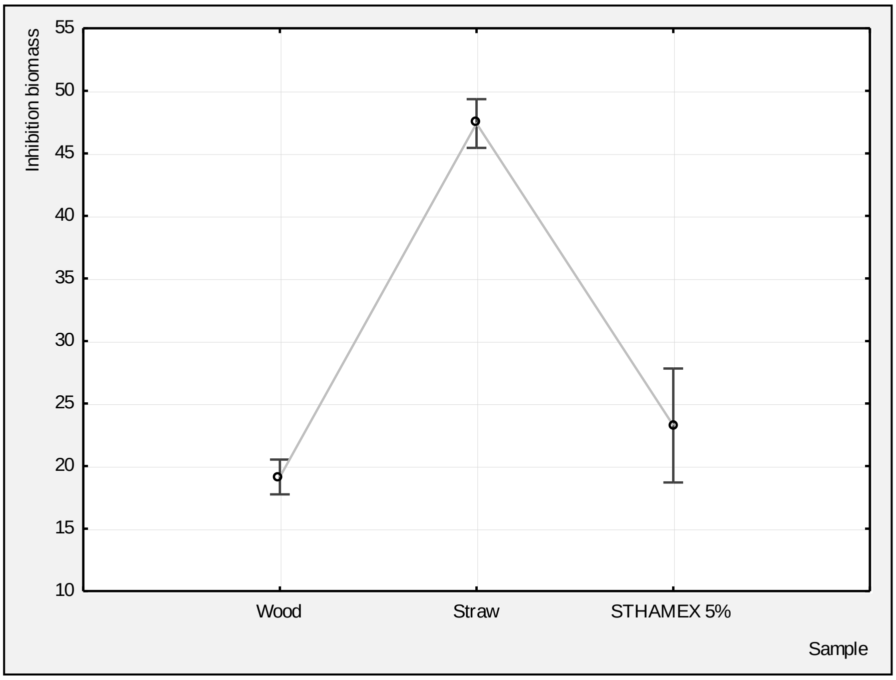

Figure 2: Biomass inhibition (%) in the phytotoxicity test with Pisum sativum

Table 7: Statistical characteristics of test phytotoxicity with Pisum sativum

Sample	Biomass inhibition, %			
	Average	Standard deviation	Confidence intervals	
			-95%	+95%
WOOD	19.13	0.44	17.74	20.52
STRAW	47.39	0.61	45.44	49.34
STHAMEX 5%	23.25	1.43	18.69	27.81

Based on the obtained results, we can state that the extinguishing water and the firefighting foam residues that enter the soil as a contaminant during the elimination of natural fires have inhibitory effects on agricultural crops used in our experiments.

The presence of pollutants in soil from anthropogenic activity is confirmed by the determination of ecotoxicity by means of acute and subchronic toxicity tests. The used test organisms belong to the first trophic level, the producent tests, which are standard used to the toxicants impact testing of the contaminants resistance, also for the environment samples[12,13,14]. The presence of toxicants negatively affects the biochemical processes in the soil, which are manifested mainly by a reduction in their soil structure and fertility, water repellency[2,17,18,19].

In their study Grynchyshyn and Poroshenko[20] investigated the impact of firefighting foams used for wildland fires extinction on the environment due the phytotoxicity tests. In the tests they used the *Sinapis alba* seeds as a representant of higher cultivated plants group. Their results show the negative effect of all tested firefighting foams on roots and shoots growth. The firefighting foam is dissolving during extinguishing process and the foaming agents solutions contaminate soil and migrate into water, the plants absorb the contaminated water which cause their growth inhibition[20].

Finger[21] reported about research in North Dakota prairie, where was the environmental impact of two firefighting foam agents investigated. Research results advert to high toxicity on aquatic ecosystems but in terrestrial ecosystems are the results not consistent. The growth of grass plants was not very effected, but vegetation species diversity decreased significantly[21].

When choosing an extinguishing agent, it is necessary to pay attention to the environment as well. During the intervention itself, contamination of soil and water (terrestrial and / or surface) occurs, which can disrupt the natural ecological stability in the soil as well as in the aquatic environment[9,17,18,19,21].

Lucas-Borja et al[22] acknowledge changes in the soil microbial ecosystem due to chemicals in the fire extinguishing media for wildland fire suppression like water and foam. Those changes in the microbioma effect the soil properties and many of soil functions, the soil microorganism activity, and plants reclonization included[22].

Extinguishing media are used in environments where endangered or economically important plants and animal species are often found. At present, information on the toxicity of some extinguishing agents (substances) is limited to reports from manufacturers[21], e. g. on packaging and safety data sheets, which are sometimes not even complete. However, the impact of the most used extinguishing agent, which is water, its direct impact and impact on organisms in the soil and aquatic ecosystem, is less well known.

It is generally known that water from a hydrant source that is drinkable or water from a natural source is used for extinguishing. Therefore, it is generally considered to be an environmentally friendly extinguishing agent, the impact of which has not been sufficiently investigated after the extinguishing of natural fires. The established results of the toxic effect of extinguishing water and firefighting foam, which are presented in this article, point to the need to pay attention to this issue.

Conclusions

The samples of two kinds of residues of firefighting agents were examined and its phytotoxicity was determinated. Extinguishing water was obtained from natural lignocellulosic materials suppression in laboratory conditions with water from a hydrant network. Wood and straw were used to simulate the fire. Firefighting foam was applicate on grassland and contaminated soil collected. Subchronic phytotoxicity tests were performed by applying samples of extinguishing water to clear soil in laboratory conditions with test organisms – seeds of higher cultivated plants *Sinapis alba* and *Pisum sativum*.

Based on the obtained results, we can state that the extinguishing wastewater that enters the soil as a contaminant during the elimination of wildland fires has inhibitory effects on the growth of agricultural crops used in container experiments. Evidence of this is determined by the inhibition of biomass from aboveground parts of plants.

The results of the experiments are proof that the wastewater generated by fire suppression with water and water based extinguishing agents poses an environmental risk to the terrestrial environment and ecotoxicological tests are a suitable means of assessing their effects on the environment. The lack of information about environmental impact of wildland fire fighting agents using gives assumption for further research on this field.

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Literature

1. Coogan S.C.P., Robinne F.-N., Jain P., Flannigan M.D.: Can. J. For. Res. *49*, 1015 (2019).
2. Pereira P., Mataix-Solera J., Úbeda X., Rein G., Cerdà A.: *Fire effects on soil properties*, p. 391. CRC Press, Leiden, Netherland, 2019.
3. Fernández-Garcia V., Marcos E., Reyes O., Calvo L.: Forests *11*, 274 (2020).
4. Whitman E., Parisien M.-A., Thompson D.K., Flannigan M.D.: Forests *9*, 151 (2018).
5. Majlingová A.: *Risk management of wildland fires (Manažment rizík požiarov v prírodnom prostredí)* (Majlingová A., Toman B. ed.), p. 18. Požiarnotechnický a expertízny ústav MV SR, Bratislava 2015.
6. Marková I.: *Water and water based extinguishing agents. (Voda a hasiace látky na báze vody)*, p. 104. Technical University in Zvolen, Zvolen, Slovakia, 2006.
7. Toropov D., Ivanov A., Dali F., Perlin A., Lebedev A., Shidlovsky G.: Delta *13*, 22 (2019).
8. Smirnov A., Smirnov A., Majlingova A.: Delta *12*, 27 (2018).
9. Särdqvist S., in book: *Water and other extinguishing agents* (Göransson A. L. ed.), chapter 2.13, p. 180. Swedish Rescue Services Agency, Karlstad, Sweden, 2002.
10. Veľková V., Hybská H., Lobotková M., Palugová M.: Waste Forum 2019, 235.
11. Hybská H., Samešová D.: *Ecotoxicology,* p. 78. Technical University in Zvolen, Zvolen, Slovakia, 2015.
12. STN 838303. 1999. *Testing of dangerous properties of wastes. Ecotoxicity. Acute toxicity tests on aquatic organisms and growth inhibition tests of algae and higher cultivated plants*.
13. STN ISO 10381-6: *Soil quality. Sampling. Part 6: Guidance on the collection, handling and storage of soil for the assessment of aerobic microbial processes in the laboratory*
14. OECD 208: 2006: *Terrestrial Plant Test: Seedling Emergence and Seedling Growth Test*.
15. Wang S.: IOP Conf. Ser.: Earth Environ. Sci. *113*, 012124 (2018)
16. Szombathová N., Sobocká J.: *Soil anthropization (Antropizácia pôdy)*, p. 114. Slovenská poľnohospodárska univerzita, Nitra, Slovakia, 2006.
17. Xu W., Jiang Z., Zhao Q., Zhang Z., Su H., Gao X., Ye Z.: Environ. Sci. Pollut. Res. *23*, 22803 (2016).
18. Lors C., Ponge J.-F., Aldaya M. M., Damidot D.: Environ. Pol. *158*, 2640 (2010)
19. Archibald S., Lehmann C.E.R., Belcher C.M., Bond W.J., Bradstock R.A. et al.: Environ. Res. Lett. *13*, 033003 (2018).
20. Grynchyshyn N. N., Poroshenko S. S. Scientific Bulletin of UNFU, *27*, 77 (2017).
21. Finger S.E.: *Proceedings: International Wildland Fire Foam Symposium and Workshop,* p. 119. Canadian Forest Service, Chalk River, ON 1994
22. Lucas-Borja M.E., Mirales I., Ortega R., Plaza-Álvarez P.A., Gonzales-Romero J. et al.: Sci. Total. Environ. *696*, 134033 (2019).

Hodnotenie vplyvu odpadu z hasiacich médií na pôdu prostredníctvom testov fytotoxicity

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Souhrn

Príspevok sa zaoberá problematikou hodnotenia kontaminácie pôdy odpadmi z hasenia prírodných požiarov vodou a penou. Skúmané boli vzorky vody po hasení simulovaných požiarov prírodných materiálov. Na simuláciu požiaru v laboratóriu boli použité lignocelulózové materiály – drevo a slama, ktoré boli zapálené a v tretej faze požiaru (plne rozvinutý požiar) uhasené vodou z hydrantovej siete. Vzorky kontaminovanej pôdy boli odobraté z pôdy po aplikácii hasiacej peny po výcviku hasičov na zásah pri prírodných požiaroch z hĺbky 0 – 10 cm. Vzorky hasiacej vody a kontaminovanej pôdy boli podrobené testom fytotoxicity s využitím semien vyšších kultúrnych rastlín – Hrach siaty a Horčica biela – ako testovacích organizmov. Získané výsledky potvrdili inhibičný efekt na produkciu biomasy u všetkých skúmaných vzoriek, čo poukazuje na subchronické toxické účinky odpadov z hasiacich médií po hasení.

Klíčová slova: *prírodné požiare, hasenie, hasiaca voda, hasiaca pena, subchronická toxicita, Hrach siaty, Horčica biela*

Effect of use of non-traditional raw materials on properties and microstructure of cement-bonded particleboards

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Abstract

This paper presents the topic of modification of composition of cement-bonded particleboards (CBPB). Specifically, cement matrix was modified by partial replacement of cement with finely ground slag (domestic source Oslavany), limestone (product from limestone quarry Kotouc Stramberk) and separated powder <0.063 mm from CBPB ground offcuts as a by-product from board processing. The offcuts are produced as a by-product during the board to the required dimensions. The aim of the research is the evaluation of influence of modification of composition of CBPB with the focus on mechanical properties and microstructure, respectively. The modification of composition was in terms of partial replacement of cement by 5 – 15%. Mechanical properties (bending strength, modulus of elasticity, transverse tensile strength) and microstructure (Scanning electron microscopy) were studied with respect to the changes in time (14, 28 and 90 days).

Keywords: *Cement-bonded particleboards, binder modification, composition of non-traditional raw material, properties, performance, microstructure, development in time.*

Introduction

Thanks to the mechanical properties and high durability, cement-bonded particleboards are a highly desirable material all over the world. These boards are based on cement, water, wood chips and mineralizing additives. Approximate proportioning is $50_{\mathrm{CEM}} : 30_{\mathrm{Water}} : 18_{\mathrm{Wood}} : 2_{\mathrm{Additives}}$ by weight ($25_{\mathrm{CEM}} : 10_{\mathrm{Water}} : 63_{\mathrm{Wood}} : 2_{\mathrm{Additives}}$ by volume). The wood in the matrix serves as a lightweight aggregate and at the same time reinforcing element transmitting tensile stresses and the cement matrix ensures the cohesion and durability of the composite both indoors and outdoors, whether as a wall slab, facade element or a protective road wall[1].

Demands for the sustainable use of natural resources and the economics of production create the opportunities for the development of technologies that limit the use of primary raw materials, such as Portland cement, while encouraging the use of secondary raw materials and energy by-products from industrial production and combustion. Costly landfilling and disposal of these raw materials are avoided thanks to their re-use. These re-used materials can have the potential for utilization due to their latent hydraulic or pozzolanic properties.

Research in the field of production and modification of wood-cement composites presents results mainly in the field of modification of fillers, but also binders, additives and treatment methods[2-7].

V. Caprai et al.[4] used bottom ash from a municipal waste incinerator as a partial replacement for cement in the amount of 5, 10, 15, 20, 30, 40 and 50% by weight in fibre cement boards, where there was a need for a higher dose of water with increasing replacement, a negative impact on compressive strength but a positive impact on flexural strength at a dose of 30% where there was an increase in flexural strength of 27%. A. J. Miranda de Lima et al.[5] modified the cement matrix with metakaolin (30%) and calcined ceramic waste from ceramic production (30%) and studied the impact on strength characteristics over time during natural and accelerated treatment. The results showed a slight decrease in the mechanical properties with a higher cement replacement and their decrease over time of accelerated and non-accelerated curing conditions as well. Viet-Anh Vu et al.[6] used wood-burning ash at a rate of 10 – 50% as a cement substitute, with 30% of the substitution appearing to be the optimal dose.

The aim of this work is to monitor the impact of cement replacement with ground limestone, slag from the waste incinerator and fine fraction from the crushed offcuts from CBPB production on the mechanical properties and microstructure of modified CBPB.

Materials and Methods

Materials

CEM I 42.5 R cement according to EN 197-1[8], spruce chips, aluminium sulphate ($Al_2 [SO_4]_3$), water glass (Na_2SiO_3), water and modifying raw materials (slag from the waste incinerator, finely ground limestone, dust from CBPB offcuts) as a partial replacement for cement. The mixture (only reference composition) proportioning is taken from a domestic board manufacturer.

Finely ground limestone is a domestic product from the Stramberk locality with a high $CaCO_3$ content.

The offcuts can be characterized as a composite material containing spruce chips that have been mineralized with water glass and bonded with Portland cement with a rapid increase in strength. These CBPB offcuts were crushed in jaw crusher (following research by Melichar et al.[9,10]) and the fine fraction passed through a 0.063 mm sieve was used as a raw material to replace the Portland cement. This powder contains about 3.9% of wood mass comparing to the cement-bonded particleboards which contain wood in amount 23.2% (determined by TOC analysis).

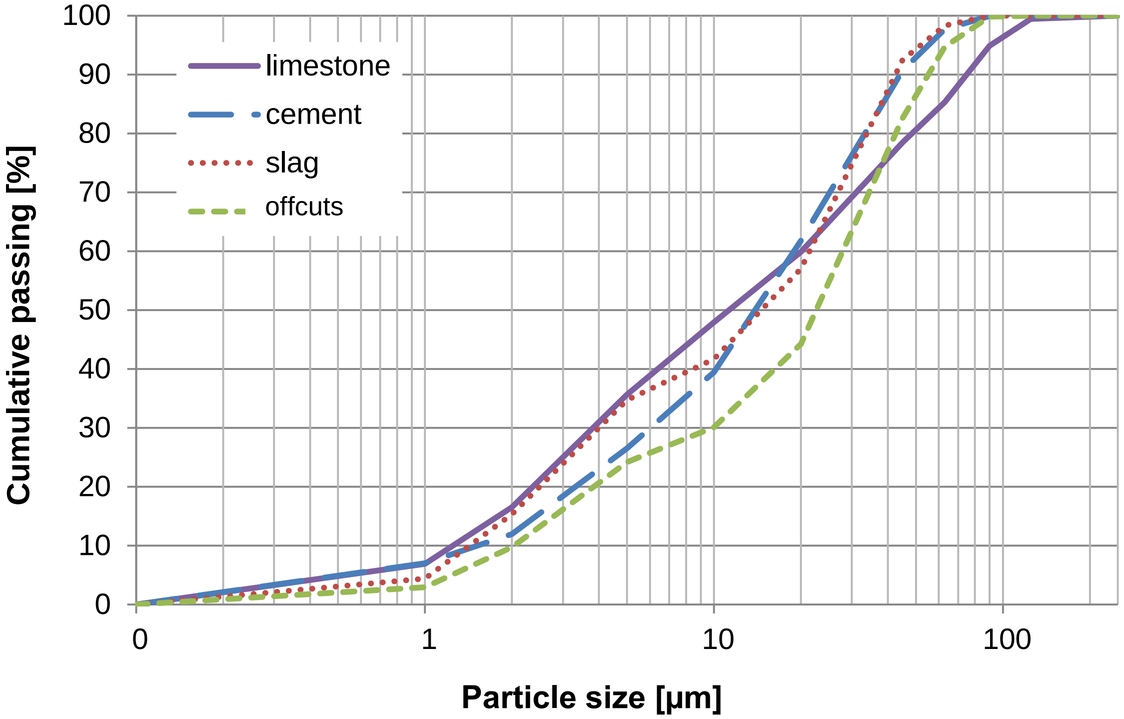

Figure 1: Cumulative particle size distribution of limestone (Kotouc Stramberk), cement (CEM I 42.5 R), slag (from Oslavany) and offcuts (from cement-bonded particleboards production – separated grains 0 - 63 µm after crushing in jaw crusher).

Particle size distribution of primary and alternative raw materials for matrix could be characterized as very similar. The slag from the Oslavany waste incinerator is predominantly a glassy sintered material with a high SiO_2 amorphous content, which was ground in a ball mill to a high fineness.

Table 1: Composition and properties of raw materials

	CEM	**Ground limestone (LI)**	**Ground Slag (SL)**	**Ground CBPB (CU)**
Component	**Content [%]**			
SiO_2	18.3	1.3	51.0	12.1
Al_2O_3	5.0	0.3	22.4	13.4
Fe_2O_3	3.7	0.1	0.9	4.7
TiO_2	-	-	0.8	-
P_2O_5	-	0.1	0.4	-
CaO	64.9	-	4.4	42.7
MgO	2.0	-	1.7	0.08
MnO	-	< 0.1	0.1	0.04
K_2O	1.0	< 0.1	3.3	0.1
Na_2O	0.2	< 0.1	1.8	0.3
SO_3	3.7	0.1	1.1	0.5
$MgCO_3$	-	1.1	8.6	-
$CaCO_3$	-	96.5	-	-
Loss on ignition [%]	1.3	41.8	3.6	19.6
Density [kg/m^3]	3170	2600	2700	2580
Specific surface area [m^2/kg]	378	567	473	359

Methods

Density of raw materials was measured with AccuPyc II 1340 Pycnometer of which accuracy is 0.03%. The specific surface area of raw materials was determined using the Blain permeable method on three samples of each and mean was calculated (ZEB MAXAM PC-Blaine Star) and the chemical composition was determined with X-ray fluorescence spectrometer Empyrean Panalytical AXIOS.

CBPB were prepared by adding cement and any substitutes to the wet sawdust mixed with aluminium sulphate and water glass and the mixture was mixed thoroughly for 3 minutes using a construction mixer. Subsequently, a layer of the mixture was sieved through a sieve with a mesh opening size up to 2 mm in a thickness of approximately 1-2 mm was applied to the plates of steel mould 450 × 450 mm.

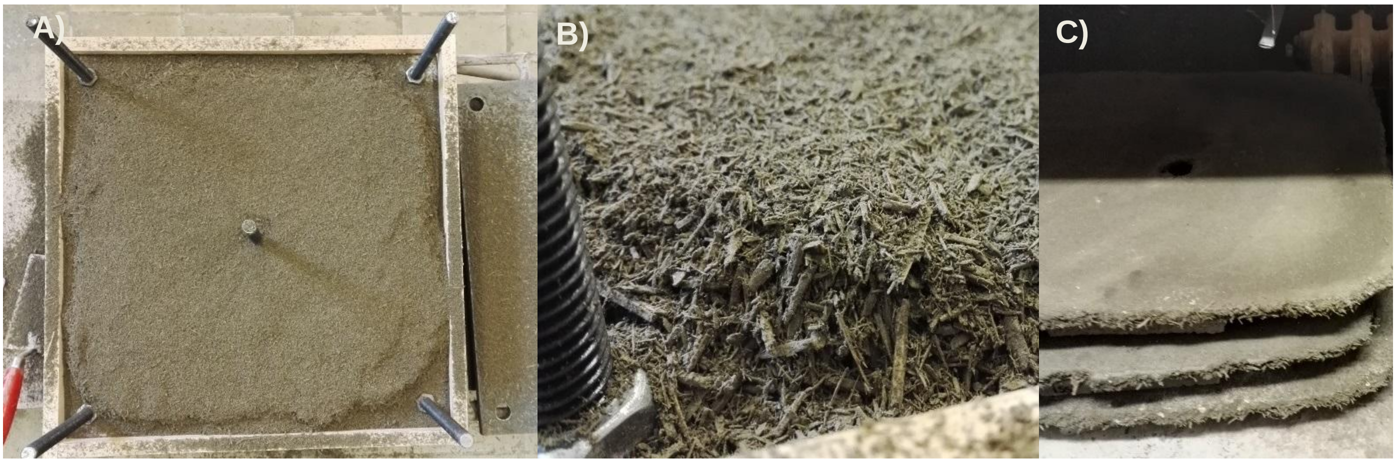

Figure 1: Manufacturing of CBPB – A) mould and wooden frame with layered fresh mixture; B) detailed view of layers; C) thermally treated boards (before specimen preparation - cutting)

Another layer of the mixture approximately 30 mm thick was applied through a sieve with a mesh opening size of 8 mm and again as a final layer a fraction <2 mm was applied in approximately 1 – 2 mm thickness. The second steel plate was placed on the prepared layers and the mixture was pressed to a thickness of 13 – 15 mm by tightening the nuts.

After pressing the fresh cementitious chipboard mixture into the moulds, they were placed in a heat chamber, where they were cured at elevated temperature. The hardened particleboards were then removed from the moulds and placed in laboratory conditions (20 °C, 50% relative humidity) for a week. After this ageing, the boards were placed in the heat chamber where drying was carried out at temperature up to 85 °C. Subsequently, the boards were cut to size on a wet circular saw in two test specimen sets: 13 - 15 × 50 × 310 – 350 mm and 13 – 15 × 50 × 50 mm, which were transferred to a drying chamber where they were dried out to constant weight at 60 °C.

The dried test specimens were weighed using KERN PCB 1000-2 scales with readability of 0.01 g and the dimensions were measured with a digital caliper KINEX 600/100 mm with a resolution of 0.01 mm. From the measured values, the bulk density of CBPB was calculated and rounded to the nearest 10 kg/m^3.

Mechanical properties were tested on a Testometric M350-20CT instrument with a 20kN load cell and accuracy of ± 0.5% of reading down to 1/1000 of the load cell capacity. Determination of modulus of elasticity in bending and bending strength were carried out according to EN 310[11], transverse tensile strength perpendicular to the plane of the board according to EN 319[12].

The microstructure was observed on images taken with TESCAN MIRA3 XMU scanning electron microscope with resolution 1.2 nm at 30 kV for test specimens aged 28 days in a standardized laboratory environment (20 °C and 50% relative humidity).

Results and discussion

Physical and mechanical parameters

The results of the determination of the **density** of the cement-bonded particleboards, given in Figure 2 and Table 2, show that all the boards meet the minimum requirements given by the standard EN 634-2[13], which requires a value of at least 1000 kg/m^3. The bulk densities of all produced boards range from 1120 - 1240 kg/m^3 and at all times of age the values show a decreasing tendency with increasing dose of cement substitution.

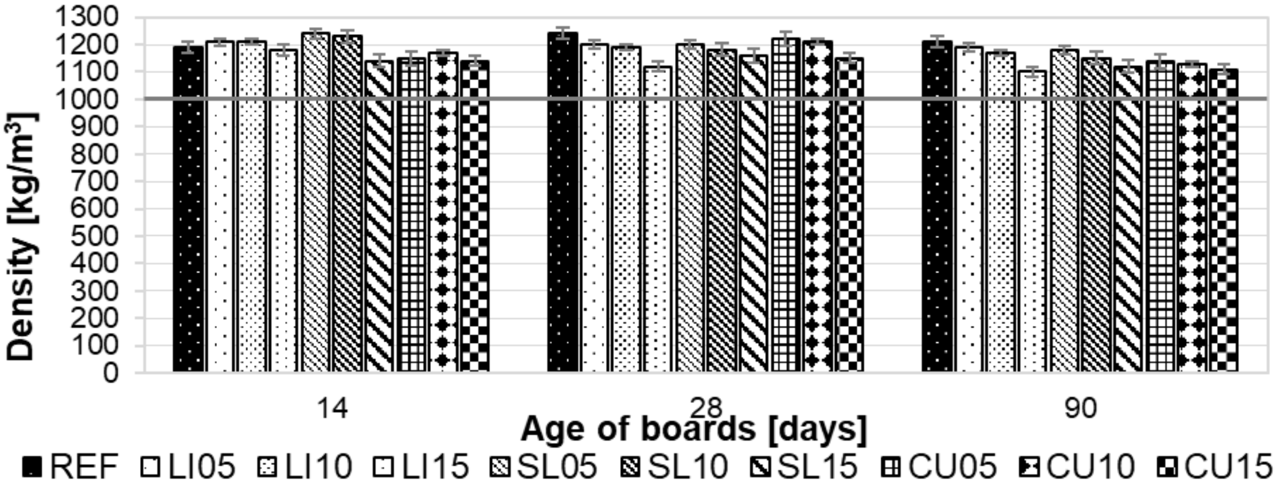

Figure 2: Comparison of cement-bonded particleboards density, horizontal line represents the standard[13] requirements

Table 2: Percentual deviations of density and bending strength

Mixture	**Density deviation [%]**			**Bending strength deviation [%]**		
	Age [days]			**Age [days]**		
	14	**28**	**90**	**14**	**28**	**90**
REF	0.0	0.0	0.0	0.0	0.0	0.0
LI 05	1.7	-3.2	-1.7	-12.8	-2.2	-4.8
LI 10	1.7	-4.0	-3.3	-17.9	-3.7	-3.7
LI 15	-0.8	-9.7	-9.1	-22.6	-7.5	-9.8
SL 05	4.2	-3.2	-2.5	-13.7	-5.2	-0.5
SL 10	3.4	-4.8	-5.0	-19.7	-13.3	-4.7
SL 15	-4.2	-6.5	-7.4	-23.1	-21.5	-11.7
CU 05	-3.4	-1.6	-5.8	-17.9	-12.6	-4.5
CU 10	-1.7	-2.4	-6.6	-19.7	-23.0	-17.5
CU 15	-4.2	-7.3	-8.3	-43.9	-42.2	-40.2

The **bending strength** results shown in Figure 5 indicate that by replacing the cement up to 10% by weight, the strengths do not fall below the level required by the standard (9 MPa), but at the age of 14 days it is very close to the limit value. Replacement of cement with dust from the offcuts leads to a more significant decrease in bending strengths in the dose higher than 10% and in the case of replacement of 15% the board no longer meets the standard. In bending strengths, the increasing dose of cement replacement was reflected in a decrease in strength of up to 43.9%. The age of the specimens appears to be a key parameter influencing flexural strength, especially at early age up to 28 days at given curing conditions. According to Miranda de Lima et al.[5] can be negatively affected when wet/drying cycles are applied as a curing conditions as the excessive humidity and presence of water leads to dimensional instability rather than contribution to strength due to pozzolanic activity. Water is also considered as a major factor decreasing mechanical performance by Drdlova et al.[1].

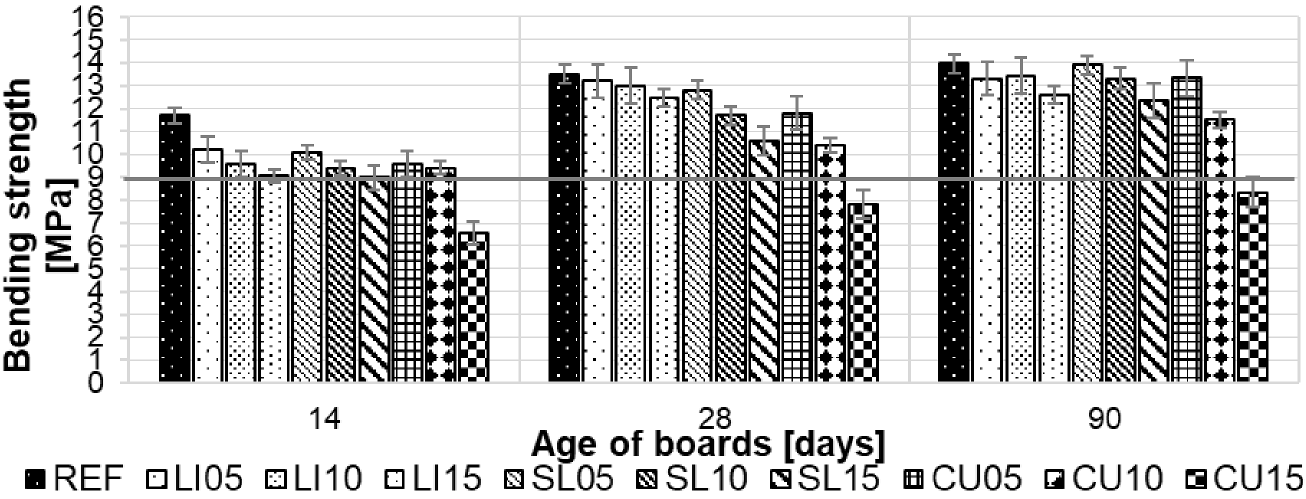

Figure 3: Comparison of cement-bonded particleboards bending strength, horizontal line represents standard[13] requirements

The **modulus of elasticity in bending** of the boards show mostly a slight decrease of values depending on the type of raw material but mostly the percentage replacement of cement plays the key role. At the age of 14 days, boards with a 15% cement replacement for CBPB dust don't meet the requirements of class 1, however, they meet ones of class 2 of the standard (Class 1 - 4500 GPa, Class 2 - 4000 GPa) even though they reduce the modulus of elasticity by approximately 30%. The increase of stiffness and bending strength over time is in line with Vu et al.[6]. The modulus of elasticity of samples with ground limestone show marginal decrease (below 10%) possibly due to the size of limestone particles capable of partially penetrate into the wooden strands according to Caprai et al.[4].

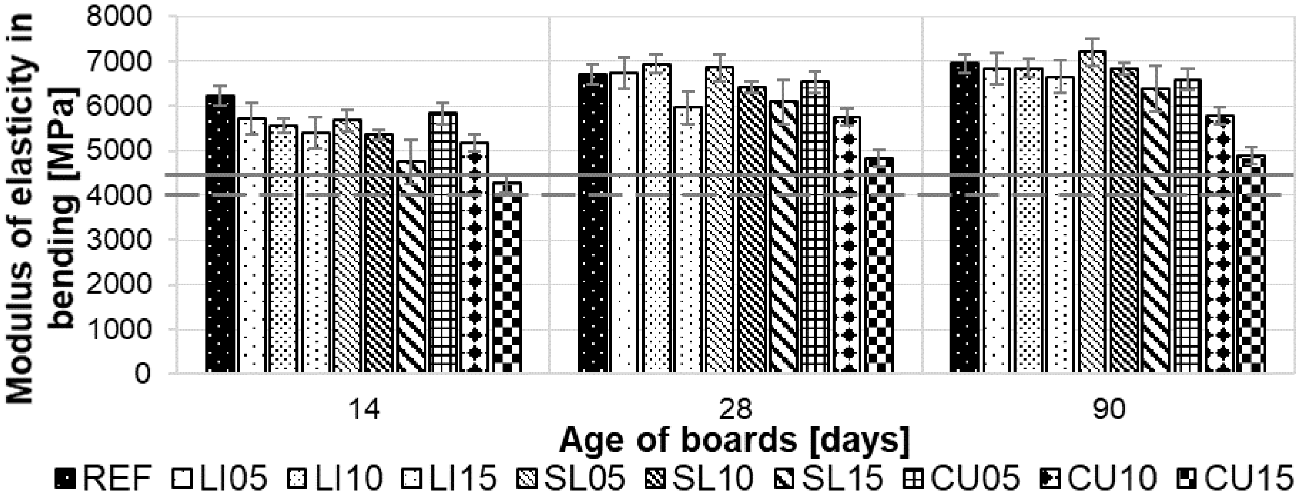

Figure 4: Comparison of cement-bonded particleboards modulus of elasticity in bending, horizontal lines represent standard[13] requirements of class 1 (top line) and class 3 (bottom line)

Table 3: Percentual deviations of modulus of elasticity and transverse tensile strength perpendicular to the plane of the board

Mixture	**Modulus of elasticity deviation [%]**			**Transverse Tensile strength deviation [%]**		
	Age [days]			**Age [days]**		
	14	**28**	**90**	**14**	**28**	**90**
REF	0.0	0.0	0.0	0.0	0.0	0.0
LI 05	-8.0	0.4	-1.9	-10.8	-9.3	4.1
LI 10	-10.8	3.4	-1.6	-15.2	-14.7	-4.9
LI 15	-13.3	-11.2	-4.3	-29.1	-15.4	-11.4
SL 05	-8.8	2.1	3.7	-6.0	2.8	2.4
SL 10	-14.0	-4.3	-1.7	-18.8	-4.2	-9.8
SL 15	-23.8	-9.2	-8.2	-20.4	-8.3	-17.1
CU 05	-6.3	-2.5	-5.2	-4.1	0.0	-8.9
CU 10	-16.9	-14.5	-16.8	-13.7	-13.0	-16.3
CU 15	-31.5	-28.0	-29.6	-17.5	-17.6	-25.2

The declining tendency of **transverse tensile strength perpendicular to the plane of the board** with increasing replacement for cement is also evident in the results shown in Table 3 and Figure 5, where the most noticeable decrease (by 29.1% compared to the reference mixture) is evident in the dose of 15% of limestone. However, a dose of 5% of slag and CBPB dust slightly increases the 28-day tensile strength perpendicular to the plane of the board, and at 90 days of age, the addition of 5% of limestone and slag shows a slight improvement in strength. All recipes met the requirements of the standard, which indicates a minimum value of 0.5 MPa.

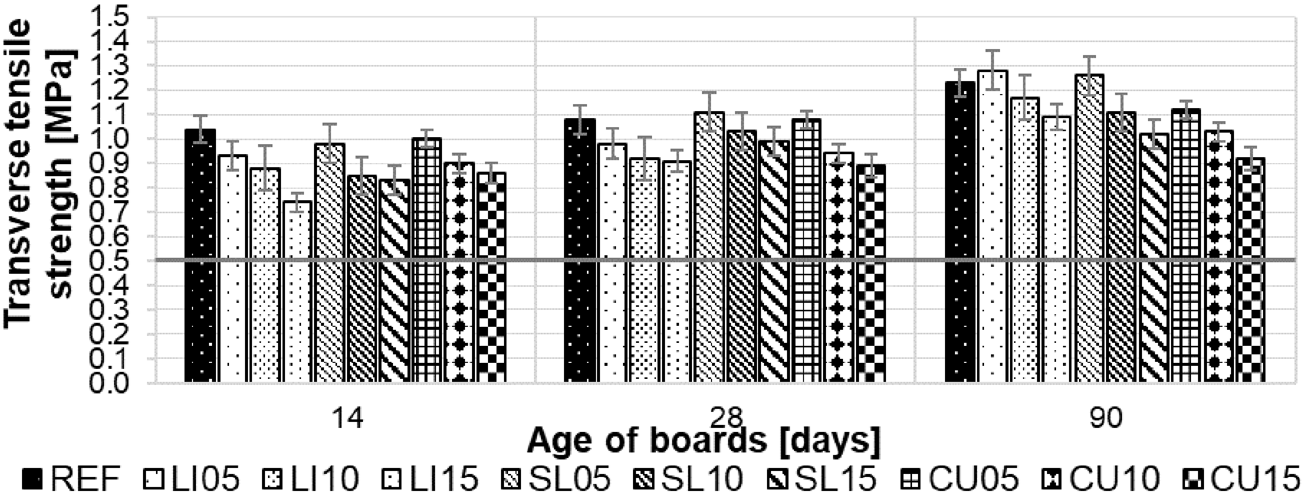

Figure 5: Comparison of cement-bonded particleboards transverse tensile strength perpendicular to the plane of the board, horizontal line represents standard[13] requirements

Microstructure Analysis

In the SEM micrograph 6A, the dense structure of the matrix surrounding the wood chips in the reference body can be observed.

SEM micrograph 6B shows the interfacial transition zone (ITZ) between mineralized wood and cement matrix formed by a predominantly amorphous C-S-H phase randomly covered by needle-like ettringite formations.

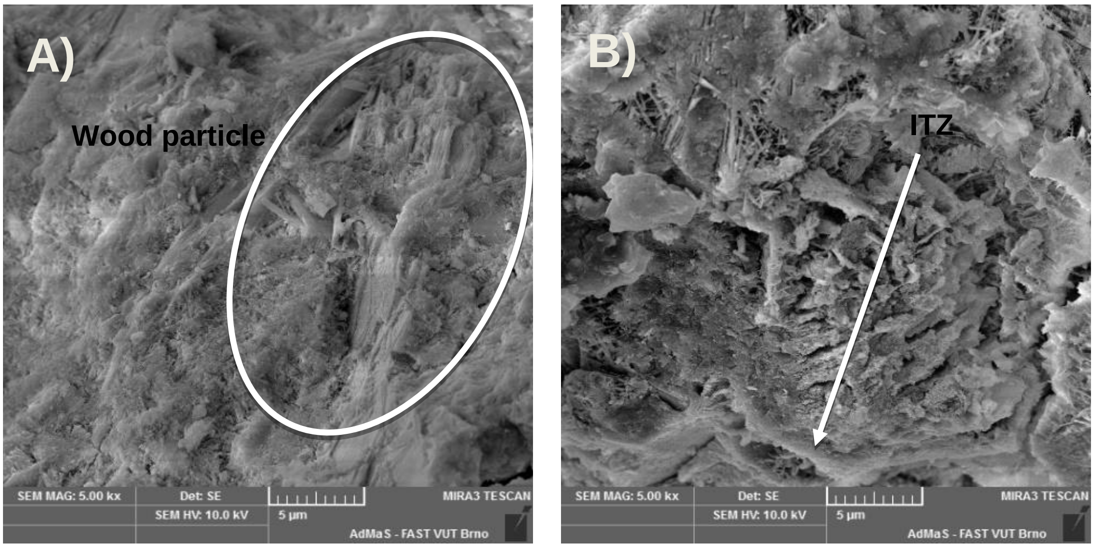

Figure 6: SEM micrographs of A) REF specimen, B) LI15 at 28 days

In Figure 7A it can be observed that the slag grain did not have enough time and suitable conditions to engage in chemical reactions and thus acts mainly as a filler. SEM picture 7B shows a slightly porous cementitious matrix with clusters of grains coated with ettringite.

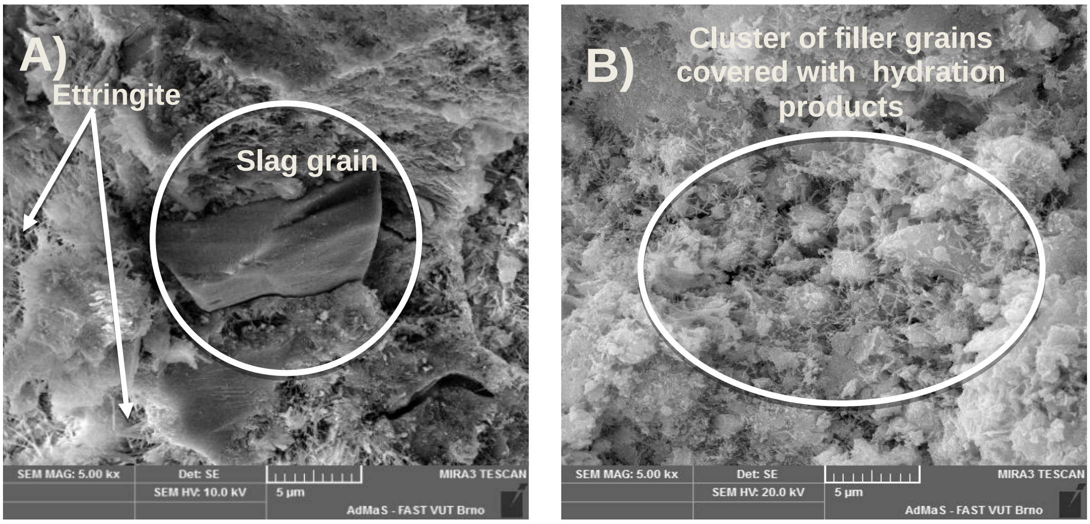

Figure 7: SEM micrographs of A) SL15 and B) CU15 at 28 days

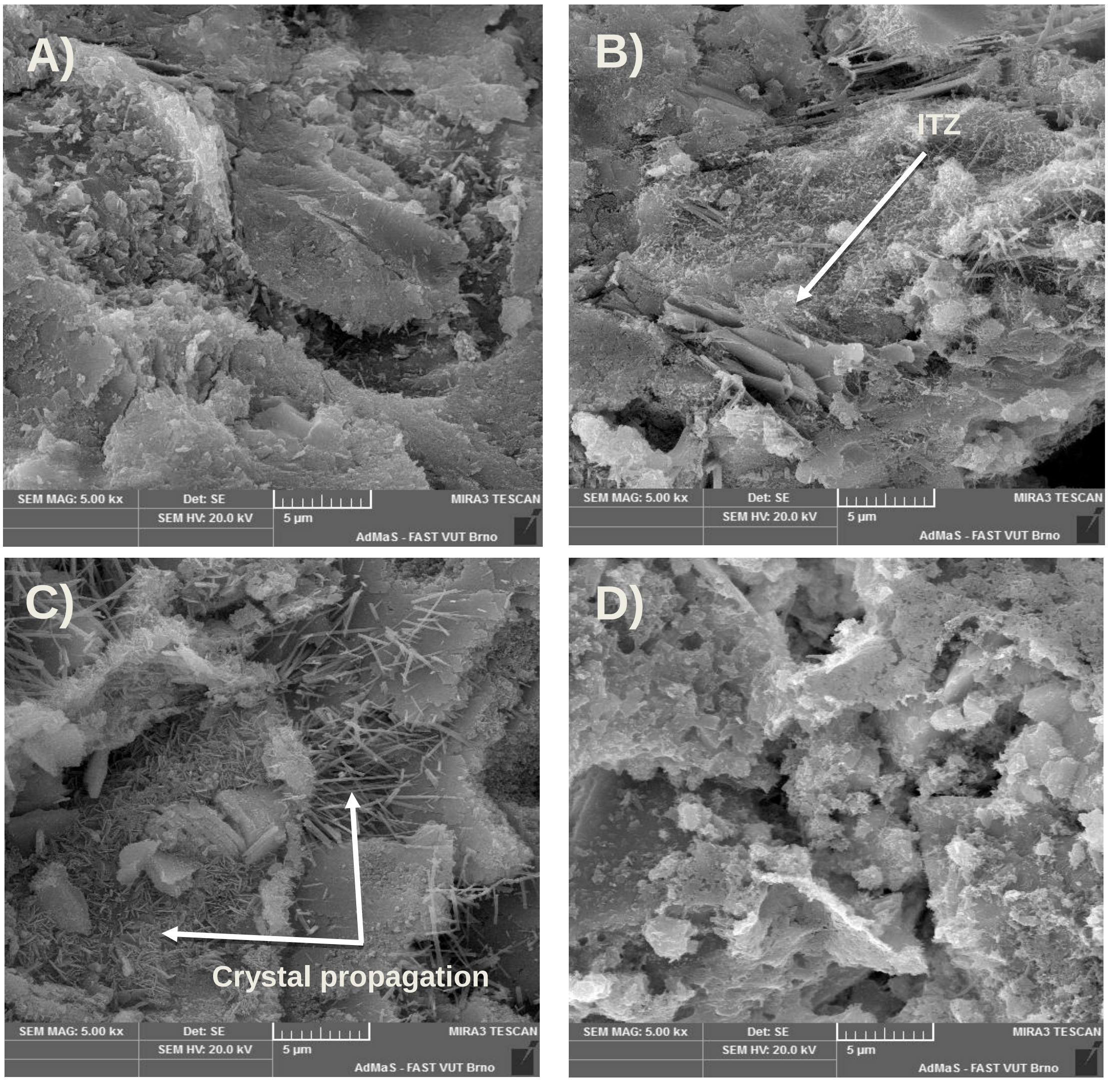

Figure 8: SEM micrographs of A) REF specimen, B) LI15, C) SL15 and D) CU15 at 90 days

In the SEM micrograph 8A, the dense structure remained almost unchanged, thus the mechanical performance of the reference matrix shows the best results. 8B shows the surroundings of interfacial transition zone covered with small amorphous phases and needle like crystals of ettringite. In Figure 8C there are larger needle-like flat crystals that cross each other, which look like tobermorite phase and small plate-like crystals of calcium aluminate hydrate. Apparently, the silica and alumina rich slag promotes additional crystalline formation over time. 8D shows that porous matrix remains nearly unchanged and no further crystal growth or a gel formation can be observed.

Conclusions

The results of experiments with partial replacement of cement for non-traditional alternative raw materials to produce cement-bonded particleboards can be summarized in the following findings:

- Increasing replacement of cement, as the primary binder component, had a negative effect on the mechanical properties, besides, 15% replacement of dust from CBPB offcuts did not reduce the requirements of EN 634-2.

- Micronized limestone can be safely dosed up to 15% by weight of cement and reveals a slight contribution to microstructure improvement over time.

- Ground slag from a waste incinerator appears to be a suitable cement substitute for up to 5% unless a rapid increase in strength is required. In the long run, slag can be used in a dose of up to 15% and at suitable conditions additionally engages in chemical reactions producing additional crystalline phases.

- Dust from crushed CBPB offcuts can be dosed up to a maximum of 10% by weight of cement, in higher doses there is a rapid decrease in mechanical properties and doesn’t contribute to further improvement of matrix at conditions applied in this research.

- Placing the boards in an environment of 20 °C and 50% relative humidity allows the bodies to mature which leads to further increase in strength.

- Micronized limestone and slag act as a micro-filler rather than engaging in the formation of hydration products at early ages, resulting in a similar sealing of the structure due to the similar shape of the cement grains, while the dust from crushed offcuts tends to form a porous cementitious structure due to the more rough surface.

- Contribution of slag and limestone to formation of matrix products could be noticed after 90 days ageing, which is partially confirmed by results of physical and mechanical parameters such as development of microstructure, while dust from crushed offcuts acts only as an inert fine-grained filler.

- Partial replacement of cement with secondary raw materials can achieve sufficient mechanical properties of cement-bonded particleboard.

- Subsequent research shows the potential in combining secondary raw materials with suitable additives and optimizing treatment conditions. Very important would be durability assessment – frost and de-icing chemicals such as CO_2 and SO_2 resistance.

Acknowledgment

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References

1. DRDLOVÁ., M.,POPOVIČ, M., ŠEBÍK, M. The behavior of cement-bonded wood-chip material under static and impact load. *IOP Conference Series: Materials Science and Engineering* [online]. 2018. **379** [cit. 2020-10-07]. ISSN 1757-8981. doi:10.1088/1757-899X/379/1/012025.
2. WANG, Lei, Season S. CHEN. Daniel C.W. TSANG, Chi-Sun POON, Jian-Guo DAI. CO_2 curing and fibre reinforcement for green recycling of contaminated wood into high-performance cement-bonded particleboards. *Journal of CO_2 Utilization* [online]. 2017. **18**. 107 – 116 [cit. 2020-10-07]. ISSN 22129820. doi:10.1016/j.jcou.2017.01.018.
3. SOROUSHIAN. Parviz. Jong-Pil WON, Maan HASSAN. Durability and microstructure analysis of CO_2-cured cement-bonded wood particleboard. *Cement and Concrete Composites* [online]. 2013. **41**. 34 – 44 [cit. 2020-10-07]. ISSN 09589465. doi:10.1016/j.cemconcomp.2013.04.014.
4. CAPRAI. V., F. GAUVIN. K. SCHOLLBACH, H.J.H. BROUWERS. MSWI bottom ash as binder replacement in wood cement composites. *Construction and Building Materials* [online]. 2019. **196**. 672 – 680 [cit. 2020-10-07]. ISSN 09500618. doi:10.1016/j.conbuildmat.2018.11.153.
5. MIRANDA DE LIMA. Adauto José. Setsuo IWAKIRI. Kestur G. SATYANARAYANA, María Guadalupe LOMELÍ-RAMÍREZ. Preparation and characterization of wood-cement particleboards produced using metakaolin. calcined ceramics and residues of Pinus spp. *Journal of Building Engineering* [online]. 2020. **32** [cit. 2020-10-07]. ISSN 23527102. doi:10.1016/j.jobe.2020.101722.
6. VU. Viet-Anh. Alain CLOUTIER, Benoit BISSONNETTE, Pierre BLANCHET, Josée DUCHESNE. The Effect of Wood Ash as a Partial Cement Replacement Material for Making Wood-Cement Panels. *Materials* [online]. 2019. **12**(17) [cit. 2020-10-07]. ISSN 1996-1944. doi:10.3390/ma12172766.
7. HU. Lingling, Zhen HE, Shipeng ZHANG. Sustainable use of rice husk ash in cement-based materials: Environmental evaluation and performance improvement. Journal of Cleaner Production [online]. 2020. **264** [cit. 2020-07-02]. DOI: 10.1016/j.jclepro.2020.121744. ISSN 09596526.
8. EN 197-1: Cement. Composition, specifications and conformity criteria for common cements.
9. MELICHAR, T., BYDŽOVSKÝ, J., DUFKA, A. Detailed analysis of modified by-product from cement-bonded particle board fabrication. *WSEAS Transactions on Environment and Development*. 2018. **14**. 408 – 417. ISSN: 1790-5079. http://www.wseas.org/multimedia/journals/environment/2018/b025915-abs.pdf.
10. MELICHAR, T., BYDZOVSKY, J., DUFKA, A., Seldom Used By-product from Trimming Cement-bonded Particleboards Shows Potential for Modifying Building Materials Composition. WasteForum. 2019. No. **4**. pp. 368 – 377.ISSN 1804-0195.
11. EN 310: Wood based panels. Determination of modulus of elasticity in bending and of bending strength.
12. EN 319: Particleboards and fibreboards. Determination of tensile strength perpendicular to the plane of the board.
13. EN 634-2: Cement-bonded particleboards - Specifications - Part 2: Requirements for OPC bonded particleboards for use in dry, humid and external conditions.
14. EN 323 Wood-based panels. Determination of density.

Vliv netradičních surovin na vlastnosti a mikrostrukturu cementotřískových desek

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Souhrn

Článek prezentuje problematiku modifikace složení cementotřískových desek. Konkrétně bylo upraveno složení matrice desek jemně mletou škvárou (z haldy v Oslavanech), jemně mletým vápencem (Kotouč Štramberk) a dále drcenými odřezky (vedlejší produkt z výroby cementotřískových desek). Odřezky vznikají jako vedlejší produkt při řezání cementotřískových desek (úprava na požadovaný formát).

Záměrem prezentovaného výzkumu bylo posouzení vlivu úpravy složení cementotřískových desek s ohledem na jejich vlastnosti a změny struktury. Modifikace složení byla realizována jako substituce cementu v množství 5 až 15 %. Vlastnosti (pevnostní charakteristiky, modul pružnosti atd.) a struktura (elektronovým mikroskopem) byly analyzovány i z hlediska jejich vývoje v čase, tj. desky byly testovány ve stáří 14, 28 a 90 dní.

Klíčová slova: *Cementotřísková deska, modifikace, složení netradiční suroviny, vlastnosti, chování, mikrostruktura, vývoj v čase.*

Wastes perception in construction projects life cycle

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Abstract

Research on lean technologies in construction and waste minimization has attracted widespread attention of researchers several decades ago. However, this area still has not been fully explored. Construction waste generates during whole construction projects life cycle, but the most waste occurs during construction phase. However, the authors believe that the planning and design phases play a critical role in minimizing waste. Waste reduction in a broader sense can help to improve the effectiveness and efficiency of the construction projects and to minimize costs. The aim of this review is to contribute to the better understanding of waste perception in construction as well as to identify causes of wasteful activities in every phase of construction project life cycle.

***Keywords:** construction, construction waste, lean construction, wasteful activities, construction project life cycle, modern methods of construction*

Introduction

It is obvious that the world is changing faster than ever before. Over the past decades, the amount of waste has increased significantly due to rising living standards, changing consumption habits, natural population growth[1] and extensive urbanization. The world's urban areas population increasing by 200,000 people per day and all of whom need affordable housing as well as transportation, social and utility infrastructure[2]. It is estimated that by year 2050 almost 85% of Europeans will be living in urban areas. Cities cover about 3% of the earth's land, however, they produce more than 70% of its greenhouse gas emissions[3]. Building and construction are responsible for 39% of all carbon emissions in the world[4]. For example, the construction sector in Sweden accounts for 20% of total CO_2 emissions, a significant part of which is caused by wrong logistic[5]. Construction industry faces challenges never seen before, so it is almost under a moral obligation to transform[2].

The value of the construction industry is expected to grow steadily with the development of modern technologies and the adoption of integrated approaches to improving construction performance indicators[6]. However, the tremendous growth of the construction industry generates huge amounts of construction waste. Construction waste generates throughout the entire construction project life cycle, consisting of a planning phase, a design phase, a construction phase and a phase of operation and maintenance. Yet, there is a need to distinguish between construction and demolition waste and construction waste in a broader context. Even when these two notions are inseparable and one follows from the other. As a result, waste has serious environmental impacts such as air pollution, noise pollution, depletion of natural resources, public health risks, pollution of surface and ground waters and the loss of significant land resources for waste landfilling[7].

In order to reduce environmental problems were established different concepts like Zero waste and Circular economy concept. The Zero Waste International Alliance defined zero waste as "the conservation of all resources by means of responsible production, consumption, recovery and reuse of products, packaging and materials without burning and with no discharges to land, water, or air that threaten the environment or human health"[8]. Whereas, the circular economy concept promises restorative and regenerative system that is an alternative to the current linear economy guided by take-make-use-dispose principles. Circular economy minimize resource use, emissions and waste by narrowing or efficient resource use, slowing or temporally prolonged use and closing or cycling material loops[9].

Except environmental concerns to improve construction waste minimization practices there are also economic and industry concerns[10]. The schedule and cost of a construction project are problematic to predict accurately due to the presence of various uncertain variables throughout a project, complexity of procedures therefore even experienced construction professionals, and experts struggle with it. Many researchers have tried to find and recommend methods that can positively influence the cost and schedule of a project and achieve the most desired value[6]. Thus, one of such methods is using lean construction technics for the identification and minimization waste of construction projects.

As described in[11], the Lean concept based on the deployment of reproducible activities (Taylor's theory) that led to the invention of the conveyor belt by Henry Ford and the emergence of mass production in the 19th century. The next shift in the manufacturing philosophy was the introduction of the Toyota Manufacturing System in Japan in 1949, which led to the establishment of Lean production in the 1990s. Lean production principles kept Toyota profitable every year from 1950 to 2008 until the global crisis[12]. Later, the Toyota Production System and its derivatives like Lean Manufacturing were carried over and adapted to other industries such as construction[13]. The idea of Lean manufacturing concept lies in identifying, eliminating or reducing waste in any production process[14]. Despite the fact that the term "waste" has been known for a long time, there is still lack of the research in this area. A literature review showed that most of the recent publications focus on solid or demolition waste rather than other types of waste - in terms of losses, like waiting, motion, etc. Therefore, it is crucial to identify the root causes of construction waste in order to reduce waste incidence and reduce environmental impact[15]. Lean construction techniques can reduce waste in construction process and improve the economic impact of projects. Thus, there is a need to develop proper technics for identification construction waste in order to eliminate its impact on the project.

This review mainly focuses on a socio-economic retrospective of wasteful activities than on demolition waste, because authors argue that physical waste prevention is possible through a better waste management at the planning stage. The purpose of this review is to promote a better understanding of waste in construction and identify the causes of wasteful activity at every stage of the life cycle of a construction project.

The method of literature review was used to achieve the aim of the article. The review started with a wide-ranging search of the literature based on the 'keyword', 'title', 'abstract' search in academic databases Web of Science, Scopus and Google Scholar. The primary analysis was used specifically in the selection of theoretical sources. The method of synthesis and the method of generalization were used to formulate theoretical conclusions. Conclusions and suggestions for further research are drawn at the end of the article. The paper is intended to create a space for discussion of important findings and suggestions for further research.

Waste from a construction viewpoint

Traditionally, construction stakeholders have viewed waste as an inevitable by-product, so on-site waste management was addressed within a legislative, health and safety context. However, the introduction of environmental regulations and rising client awareness helped to redefine the concept of waste from "by-products" to missed opportunities to improve project performance, cut costs, and enhance company's business prospects[16].

Construction waste is generally assumed as physical waste generated during construction. But it is not completely true, because construction waste not only depends on the amount of waste generated at the site, but is also closely related to other inefficient activities produced at all stages of construction project life cycle[15]. Construction waste is often classified into physical and non-physical waste[1,17]. Physical construction waste is defined as waste that is generated from construction or that may be found at a construction site, for example, demolition and renovation activities, land excavation or formation, civil engineering and construction, site clearance, road works, etc. While, non-physical waste associated with time and cost overrun in a construction projects[1]. Figure 1 shows the classification of physical and non-physical construction waste.

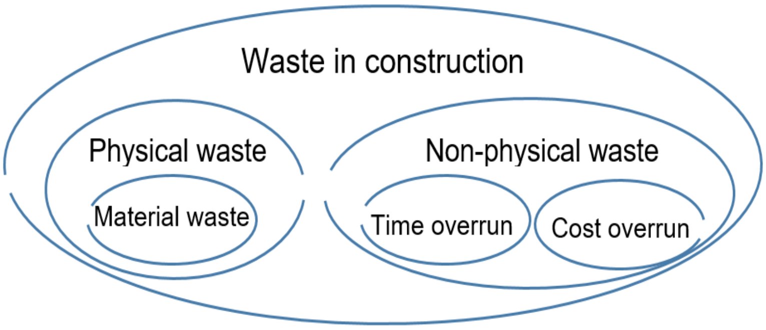

Figure 1: Classification of construction waste[1]

Lean philosophy brought in seven types of waste, namely the overproduction, waiting, transportation, over-processing, movement, defects and inventory[11,12,13,18,19]. Several researchers suggested for another types of waste, which can broadly categorized as: waste of unutilized people or failure to use people's talents, skills and capabilities, behavioral waste, information waste, wasting good ideas[13]. In addition, unnecessary talking and smoking on a construction site can be classified as waste called "break"[18]. Koskela et al. identified another type of waste – "Making-do" or insufficient preparation, when task begins without all the necessary standard input data (e.g. equipment, stuff, tools, environmental conditions, instructions, and so on)[13,19]. Hence, term "waste" should be understood as any non-value added activities that lead to the reuse of equipment, materials, labor or capital in larger quantities than is necessary for production[19]. Figure 2 shows the classification of construction waste according to[11,13,19]. Moreover, according to the reviewed literature, the range of value-adding activities among all activities presented on a construction site cover 10%-33%, essential non-value added activities cover 33%-41% and absolutely non-value added activities or pure waste cover 26% – 57% in the construction industry[12,18]. These non-value added activities only increase costs and entire production time, but do not increase the value of the product[14].

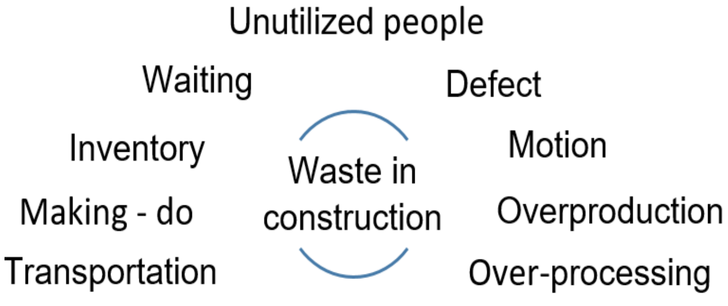

Figure 2: Classification of construction waste according to[11,13,19]

Nevertheless, what is value for one side don't need to be value for another. In this regard, what is waste for one side, don't need to be waste for another. It is very common for the construction get different sides involved in the design, production and maintain phase[13]. For a more precise definition of waste, it is necessary to indicate what is waste for the producer and what for the customer? (see Fig.3)

Many authors doubted the sufficiency of the classical list of wastes from a construction retrospective and tried to explore alternative wastes in cases where the classical list is not found enough appropriate. For example, Koskela et al.[13] admits that the described seven wastes originated from a mass production context do not cover the design phase commonly found in construction. Bolviken et al.[20]. designed the taxonomy of the construction wastes in the context of the Transformation – Flow – Value theory of production. They established three main categories of waste, namely: material waste, time loss and value loss. Figure 3 shows taxonomy of the wastes of production in construction based on[13, 20].

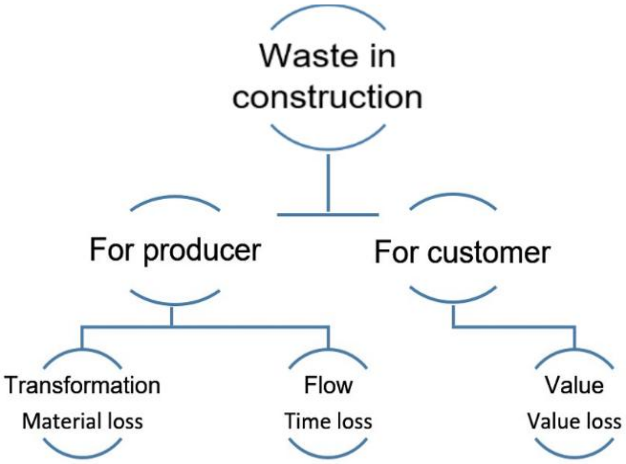

Figure 3: Taxonomy of construction waste according to[13, 20]

In the transformation perspective material loss means material waste, non-optimal use of material (unnecessary amount used in the product), non-optimal use of machinery, labour or energy in the production process. In the flow perspective, time is introduced as a production resource. Time loss in the work flow include unnecessary movement, unnecessary or inefficient work and waiting. Time loss in the product flow include space not being worked, materials not being processed and unnecessary transportation of material. In the value perspective value loss have been identified related to the main product (lack of quality, lack of intended use) and related to by-products (harmful emissions, injuries and work related sickness)[20].

Results and discussion

There are many different approaches to the classification of the causes of construction waste. Causes of waste can be characterized as controllable or uncontrollable. Issa and Salama (2018), as cited from[21] proposed method for determining responsibilities for many causes of wastes before applying lean construction techniques in Kingdom of Saudi Arabia. They found that about 88% of controllable causes of waste could be fully or partially affected by lean technics.

Kaliannan et al.[15] discovered 5 main root causes of construction waste generation. The most important root cause that contributes to the formation of construction waste is “Constant design changes” during construction work due to misunderstandings between designers, contractors and clients during the design phase. The second most important root cause is “Improper Material Storage”, which can delay the project implementation and lead to physical waste. The third leading cause is “Poor Material Handling” followed by “The Weather Influence”. The fifth main root cause is Order Errors due to over-ordering or ordering material without particular specification details or poor quality of materials. Whereas, four of the root causes can be controllable by construction practitioners, weather or climate change is one of the factors that are beyond our control.

Issa and Alqurashi[21] proposed a Lean Building Assessment Model (LCEM) for evaluating the causes of waste generation in construction projects and for identifying the impact of lean technologies on them. The model has been applied on construction projects in Egypt and Kingdom of Saudi Arabia. Study identified 42 causes of waste generation, which were classified according to their controllability. According to the[21], “Deficiencies and changes in project scope” is considered the most controllable one in Egypt, while the lowest controllable is “Delay due to administrative approvals”. On the contrary, in Kingdom of Saudi Arabia the highest controllable cause of waste is “Poor site safety” while the lowest one is “Delay in running bill payments to the contractor or consultant”. Moreover, was discovered that only three cause of wastes are appeared together in top 10 ranked in the two countries, there are: Client slow response and slow decision-making mechanism, Contractor selection before consultant, Lack of consultant's experience in design, supervision and quality control.

In the study conducted in Malaysia[22] the authors identified 46 factors of construction waste generation under 7 categories (Information and Communication, Equipment, Project and Contract Management, Material, Delivery/Procurement, External/Unpredictable and Human Resources/Manpower) and clustered them according to the phases of the construction life cycle. This study showed that construction phase is most critical where majority of the identified factors occurred. It is followed by design phase, finishing phase and planning phase in the respective order. These findings are in accordance with the literature review from[23], which found that many researchers have focused on on-site waste management[24,25] by viewing it as the phase where waste is generated. However, Osmani[16] believes that the designing phase is even more important than construction phase and architects need to focus designing out waste rather than reducing waste already been produced.

Moreover, construction industry has been identified as one of the most hazardous industries. Injuries on the construction sites lead to wasted time, unnecessary compensation costs, reduced productivity and efficiency, increased employee turnover, material waste and, what is more important, to human suffering. According to the International Labor Organization annual report in the year 2015, the cost of inappropriate safety practices accounts for 4% of the world's annual gross domestic product. Therefore, poor safety practices are could be considered as a form of waste. The research, conducted by Mahfuth et al.[17], showed relationship between commitment to safety system during the implementation phase and the minimization of waste. Among identified 24 safety factors the seven most important factors were proved to have positive effects on waste minimization. There are handling, management, external factors, workers, procurement, site condition and appropriate scaffolding.

The process of construction directly depends from the activities of the supply chain management. Forbes and Ahmed (2004), as cited from[21], have indicated that up to 30% of construction project costs are attributed to inefficiencies, errors, delays and poor connectivity between stakeholders. In addition, the implementation of more efficient logistics and transport solutions could reduce the total cost of the project by 20%[5]. Survey, conducted in United Kingdom[16] showed, that the majority of contractors and architects assume that design waste could be minimised by implementing off-site manufacturing and prefabrication methods during construction. Emerging information technologies, GPS, GIS, wide area networks (WANs), bar coding systems and BIM techniques can be adopted to assist architects minimize waste in their design projects[16]. Pereira et al. lists some technologies that can be effectively used to enhance lean practices. There are CPS, IoT, Big Data, Cloud, VR and AR, 3D Printing, Robotics, Video-based and 3D Models, Simulation, Optimization Algorithms[26]. Moreover, construction project owners are showing an increased interest in using technology trends such as sensor-based resource tracking, building information modeling (BIM), machine learning, automation and robotics[6].

Conclusions

This review contributed to a comprehensive understanding of construction waste to identify and eliminate wasteful activities by summarizing the results of existing research.

As we can see, different authors define waste in different ways, but they all agree that waste is unnecessary and unwanted actions, reducing or limiting which can improve the efficiency of construction projects. Construction waste generation factors occur at every stage of the construction project life cycle, but the most critical is the construction phase. The authors assume that this is due not only to the fact that waste is mainly produced during site operation, as indicated in[22], but also due to the lack of research at other stages. In addition, the dominant part of research focuses on the management of waste that has already been produced, rather than waste prevention through better project management at the planning stage. There is a need to concentrate on causes of waste generation in the early stages of project life cycle, namely at planning and design phases, and to designing out waste. Also, special attention should be paid to the better logistics management and labor safety system. Moreover, review showed that the main controllable cause of waste could be affected by using modern technologies and modern construction methods like Building information modeling, offside construction methods, sensor-based resource tracking, automation, machine learning, robotics, etc.

We hope this review will help researchers to identify areas where further research is most needed and to set future research directions.

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References

1. Nagapan S., Rahman Is. Abd., Asmi Ade : Factors Contributing to Physical and Non-Physical Waste Generation in Construction Industry, Inter. Jour. of Advan. in Appl. Sci. (IJAAS) *1(1)*, 1 (2012).
2. World Economic Forum: Shaping the Future of Construction A Breakthrough in Mindset and Technology, Industry Agenda, REF 22041, 2016.
3. Climate-neutral and smart cities [online]. *European Commission*, 2020. https://missions-get-involved.ec.europa.eu/conferences/cities, accessed September 5, 2020.
4. Global Status Report 2017 [online]. *UN Environment and the International Energy Agency*, 2017. https://www.worldgbc.org/news-media/global-status-report-2017, accessed September 1, 2020.
5. Hulthén K., Sundquist V., in the book: *The Connectivity of Innovation in the Construction Industry* (Havenvid M. Ing., Linné Å.,. Bygballe L. E, Harty Chr., ed.) chap. 5. Routledge, London 2019.
6. Nguyen P., Akhavian R.: Synergistic effect of integrated project delivery, lean construction, and building information modeling on project performance measures: a quantitative and qualitative analysis, Advan. in Civ. Engin. *2019*, 1.
7. Enshassi Ad., Kochendoerfer B., Rizq Eh.: An evaluation of environmental impacts of construction projects, Rev. ing. constr. *29 (3),* 1 (2014).
8. Zero Waste Definition [online]. *ZWIA, Zero Waste International Alliance*, 2018. http://zwia.org/standards/zw-definition/, accessed October 16, 2020.
9. Reike, D., Vermeulen, W. J. V., & Witjes, S.: The circular economy: New or refurbished as CE 3.0? — Exploring controversies in the conceptualization of the circular economy through a focus on history and resource value retention options, Res., Conserv. and Recycl.*135*, 246 (2018).
10. Osmani, M., Glass, J., Price, A.: Architect and Contractor Attitudes to Waste Minimisation, Waste and Res. Manag.*159 (WR2)*, 65 (2006).
11. Sarhan J., Xia B., Fawzia S., Karim A.: Lean Construction Implementation in the Saudi Arabian Construction Industry, Constr. Econ. and Build. *17(1),* 46 (2017).
12. Bayhan H. G.: Enablers and Barriers of Lean Implementation in Construction Projects, IOP Conf. Ser.: Mater. Sci. Eng. *2019*,471.
13. Koskela L., Bølviken T., Rooke J.: Which Are the Wastes of Construction?, *21st Annual Conference of the Internatiional Group for Lean Construction, Fortazela,n31st July - 2nd Aug. 2013,* Proceedings IGLC-21(no editor), p. 3.
14. Maradzano I., Dondofema R. A., Matope S.: Application of lean principles in the South African construction industry, South Afr. Jour. of Ind. Engin. *30(3)*, 210 (2019).
15. Kaliannan S., Nagapan S., Abdullah A. H., Sohu S., Jhatial A. A.: Determining Root Cause of Construction Waste Generation: A Global Context, Civ. Engin. Jour. *4 (11)*, 2539 (2018).
16. Osmani M.: Design waste mapping: a project life cycle approach, Proc. of the ICE-Waste and Res. Man. *166 (3),* 114 (2013).

17. Mahfuth K., Loulizi A., Hallaq Al Kh., Tayeh B. A.: Implementation Phase Safety System for Minimising Construction Project Waste, Buildings *9*, 25 (2019).
18. Hossain A., Bissenova A., Kim J. R.: Investigation of Wasteful Activities Using Lean Methodology: In Perspective of Kazakhstan’s Construction Industry, Buildings *9*, 113, (2019).
19. Boateng A.: Supply chain management and lean concept in construction: a case of Ghanaian building construction industry, Org. Tech. and Manag. in Constr. *11*, 2034 (2019).
20. Bølviken T., Rooke J., Koskela L.: The Wastes of Production in Construction – A TFV Based Taxonomy, Waste in Constr. *2014*,811.
21. Issa Us. H., Alqurashi M.: A Model For Evaluating Causes Of Wastes And Lean Implementation In Construction Projects, Jour. of Civ. Eng. and Man. *26 (4),* 331 (2020).
22. Akhir Nor S. Md., Rahman Is. Abd., Memon Aft. H., and Nagapan S.: Factors of Waste Generation throughout Construction Life Cycle, *Conference on Engineering & Technology (MUCET), 3-4 Dec., 2013,* Proceedings, (no editor), Malaysian Technical Universities in Kuantan, Pahang, 2013.
23. Lu W., Webster Ch., Xiaoling K. Ch., Chen Zh. X.: Computational Building Information Modelling for construction waste management: Moving from rhetoric to reality, Renew. and Sustain. Energ. Rev. *68*, 587 (2017).
24. Baldwin A., Poon Ch.-S., Shen Li-Y., Austin S., Wong I.: Designing out waste in high-rise residential buildings: Analysis of precasting methods and traditional construction, Renew. Energ. *34*, 2067 (2009).
25. Bakshan, A., Srour, I., Chehab, G., El-Fadel, M.: A field based methodology for estimating waste generation rates at various stages of construction projects, Res., Conserv. and Recycl. *100*, 70 (2015).
26. Pereira C., Dinis-Carvalho J., Alves A. C., Arezes P.: How Industry 4.0 Can Enhance Lean Practices, FME Transact. *47*, 810 (2019).

Vnímanie odpadov v životnom cykle stavebných projektov

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Abstrakt

Výskum štíhlych technológií v stavebníctve a minimalizácia odpadov, respektíve strát, priťahovali rozsiahlu pozornosť výskumných pracovníkov už pred niekoľkými desaťročiami. Napriek tomu, táto oblasť stále nie je dostatočne preskúmaná. Plytvanie je súčasťou celého životného cyklu stavebných projektov, pričom najviac strát v stavebných projektoch sa vyskytuje počas fázy výstavby. Je to spôsobené nielen skutočnosťou, že odpady vznikajú hlavne počas uskutočňovania stavby, ale aj nedostatkom preskúmania iných etáp stavebných projektov. Domnievame sa, že práve fázy plánovania a projektovania zohrávajú rozhodujúcu úlohu pri minimalizácii odpadov a strát. Redukcia strát môže pomôcť zvýšiť efektívnosť a účinnosť stavebných projektov a minimalizovať náklady. Preto je potrebné prispieť k lepšiemu vnímaniu odpadov, resp. strát v stavebníctve a identifikovať príčiny nehospodárnych činností v každej fáze životného cyklu stavebného projektu.

Rýchly vývoj v stavebnom priemysle vedie aj k tvorbe obrovského množstva stavebného odpadu. Za posledné desaťročia sa významne zvýšilo množstvo odpadu v dôsledku zvyšovania životnej úrovne, zmeny spotrebiteľských návykov, prirodzeného prírastku populácie a rozsiahlej urbanizácie. Stavebný odpad vzniká počas celého životného cyklu stavebného projektu, ktorý pozostáva z fázy plánovania, fázy projektovania, fázy výstavby a fázy prevádzky a údržby stavby.

Tradične bol odpad v stavebníctve považovaný za nevyhnutný vedľajší produkt výroby, preto otázky nakladania s odpadom boli posudzované v legislatívnom, zdravotnom aj v bezpečnostnom kontexte. Zavedenie environmentálnych predpisov a rastúce povedomie spotrebiteľov však pomohlo predefinovať koncept odpadu z „vedľajších produktov“ na straty a premeškané príležitosti na zlepšenie výkonnosti projektu, zníženie nákladov a zlepšenie obchodných vyhliadok spoločností.

Stavebný odpad (strata) môže byť klasifikovaný ako fyzický (plytvanie materiálom) a nefyzický (strata času a nákladov). Štíhla filozofia (Lean Production) prináša pohľad na niekoľko druhov strát, a to z pohľadu nadprodukcie, čakania, presunov, nadmerného spracovania, pohybu, defektov a pod.. Rôzne výskumy poukazujú aj na iné druhy strát, ako napríklad plytvanie pracovnými kapacitami alebo nevyužitie talentov a schopností ľudí, plytvanie dobrými nápadmi alebo strata informácií. Napríklad aj prerušenie práce na pracovisku kvôli zbytočnému rozprávaniu a fajčeniu možno klasifikovať ako stratu. Štúdie identifikovali aj špecifický druh plytvania „Making-do“, ktorým vyjadruje nedostatočnú prípravu, kedy sa úloha začína realizovať bez potrebných vstupných údajov. Pojem „plytvanie“ (wastes) by sa preto mal chápať ako akákoľvek činnosť bez pridanej hodnoty, ktorá vedie k použitiu zariadenia, materiálu, pracovnej sily alebo kapitálu vo väčšom množstve, ako je potrebné na výrobu. Spomínané štúdie však pripúšťajú, že odpady pochádzajúce z hromadnej výroby nepokrývajú fázu navrhovania, ktorá sa bežne nachádza v stavebníctve. Preto iné štúdie navrhli taxonómiu plytvania v rámci stavebných projektov, v kontexte teórie výroby „transformácia – tok – hodnota“ a stanovili tri hlavné kategórie plytvaní: plytvanie materiálom, strata času a strata hodnoty, ktoré revidovali aj z pohľadu výrobcu aj zákazníka.

Štúdie ukazujú, že až 30 % nákladov na stavebné projekty vzniká kvôli neefektívnosti, chybám, oneskoreniam a zlej komunikácii medzi zainteresovanými stranami. Zavedenie účinnejších logistických a dopravných riešení by navyše mohlo znížiť celkové náklady na projekt o 20 %. Nové informačné technológie, GPS, GIS, rozsiahle siete (WAN), systémy čiarových kódov a techniky BIM môžu pomoc architektom a návrhárom minimalizovať plytvanie už vo fáze projektovania. Podľa inej štúdie, väčšina dodávateľov a architektov sa domnieva, že plytvanie je možné minimalizovať zavedením metód mimo staveniskovej výroby (off-site construction) a použitím prefabrikovaných konštrukcií počas výstavby.

Možno konštatovať, že hoci rôzni autori definujú odpady, straty a plytvanie rôznymi spôsobmi, všetci sa zhodujú v tom, že ide o zbytočné a nežiaduce konanie, ktorého zníženie alebo obmedzenie môže zvýšiť celkovú efektívnosť stavebných projektov. Z preskúmaných štúdií vyplynulo, že dominantná časť výskumu sa zameriava na nakladanie s odpadom, ktorý už bol vyprodukovaný, a nie na predchádzanie vzniku odpadu, prostredníctvom lepšieho projektového riadenia už od fázy plánovania. Je potrebné sústrediť sa na príčiny vzniku strát v počiatočných fázach životného cyklu projektu, najmä vo fázach plánovania a projektovania. Osobitná pozornosť by sa mala venovať aj lepšiemu systému riadenia logistiky a bezpečnosti práce. Rešerš preskúmaných štúdií navyše ukázal, že kontrolovateľné príčiny výskytu odpadov, resp. strát, je možné ovplyvniť použitím moderných technológií a metód výstavby, ako je napríklad informačné modelovanie budov (BIM), mimo stavenisková výroba, sledovanie zdrojov založené na senzoroch, automatizácia, strojové učenie, robotika a pod. Informácie z preskúmaných štúdií majú za cieľ pomôcť pri identifikovaní oblastí, do ktorých je najviac potrebné zamerať ďalší výskum.

***Kľúčové slová:** stavebníctvo, plytvanie v stavebníctve, štíhla výstavba, nehospodárne činnosti, životný cyklus projektu, moderné metódy výstavby*

Využití odpadních termoplastů pro účely stínění ionizujícího záření

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Souhrn

Recyklace plastového odpadu je jednou z cest snížení celkového znečištění životního prostředí. Jednou ze speciálních metod zpracování polymerního odpadu je výroba polymerbetonu, který při vhodném složení může sloužit jako stínící materiál různých druhů ionizujícího záření, jako například neutronového záření nebo záření gama. Vhodnost použití dané polymerbetonové směsi pro stínění ionizujícího záření byla testována pomocí stochastické metody Monte Carlo.

Z uvažovaných plastů se jako vhodné zdá použití polypropylenu (PP) nebo polyethylenu (PE), s podílem plniva (testovány byly sklo a písek) v rozmezí 0,3 – 0,4. Rozdíl mezi sklem a pískem je v těchto kombinacích malý. Nižší dávky jsou pozorovány při použití skla, nicméně obě kombinace dávají (za stínící vrstvou polymerbetonu) nižší dávkový příkon než v případě referenčního betonu. Horší výsledky jsou při použití pojiva na bázi polyethylentereftalátu (PET). Kombinace PET se sklem je vhodnější než s pískem, nicméně obě kombinace vykazují horší stínící vlastnosti než referenční beton. Velký vliv na efektivitu stínění neutronů má i přidání boraxu do kompozitní směsi – podíl 1 % boraxu snižuje hodnotu prostorového dávkového ekvivalentu (H(10)) o cca 40 %, vyšší podíl boraxu vede samozřejmě k ještě většímu snížení hodnot.*

Klíčová slova: *recyklace, polymerbeton, ionizující záření, simulace Monte Carlo*

Úvod

Produkce plastového odpadu během posledních let po celém světě dramaticky vzrostla. Běžný plastový odpad patří k biologicky nerozložitelným materiálům, které přispívají k dlouhodobému znečištění životního prostředí. Recyklace plastového odpadu přispívá ke snížení celkového znečištění životního prostředí a opakované využití odpadních surovin má i ekonomické výhody.

Zajímavou metodu recyklace plastového odpadu nabízí zpracování plastů do polymerbetonu[1,2]. Jedná se o unikátní druh kompozitního materiálu na bázi odpadních termoplastů (jako pojiva) a různých inertních plniv. Tento materiál skýtá několik výhod jako ekonomická dostupnost, dobrá manipulovatelnost a tvárnost. Při vhodném složení je možné využití polymerbetonu rozšířit i do oblasti radiační ochrany. Z polymerbetonu je možné vyrábět stínící materiál ionizujícího záření.

Z hlediska ochrany před ionizujícím zářením je důležité stínit fotonové a neutronové záření. Jedná se o pronikavé, nepřímo ionizující záření, jehož stínění je založeno na interakci záření s látkovým prostředím. Nejintenzivnějším zdrojem neutronového záření jsou jaderné reaktory. Více rozšířené je pak využití radionuklidových zdrojů nebo generátorů neutronů, např. i pro výzkumné účely. Fotonové zdroje jsou široce využívány ve zdravotnictví, v průmyslu, ale také ve výzkumných organizacích.

Stínění fotonů i neutronů probíhá v důsledku interakcí s prostředím, částice postupně ztrácí svou energii a nakonec se v materiálu absorbuje. Především v případě vysoce energetických neutronů je nezbytné neutron nejprve zpomalit, tj. snížit jeho energii, a pak se snadno absorbuje. Obecně platí, že pro stínění fotonového záření jsou vhodné těžké materiály s vysokou hustotou, např. olovo. Naopak efektivní stínění neutronů je založeno na jejich interakci s lehkými materiály – materiály obsahujícími vodík, např. voda nebo většina organických sloučenin. Efektivitu stínění neutronů lze pak dále zvýšit přidáním materiálu, který silně absorbuje neutrony – nejběžnější je ^{10}B (např. borax) a ^{113}Cd. U stínění neutronů je potřeba odstínit i fotony, které vnikají v důsledku interakcí neutronů ve stínění. Při výrobě stínění je také potřeba hlídat, aby nedocházelo k aktivaci stínění, tj. aby stínění samo nevyzařovalo ionizující záření a nedocházelo ke zhoršení radiační situace v okolí stínění. Obecně platí, že čím vyšší je energie záření (fotony i neutrony), tím větší tloušťka stínění je potřeba.

Bylo vyvinuto mnoho stínících materiálů ionizujícího záření, počínaje od borovaných polymerů bohatých na vodík, ke kovovým pěnám nebo kovovým keramickým kompozitům. Například voda, polyethylen (PE) a beton jsou některé z nejčastěji používaných materiálů pro stínění neutronů v jaderných aplikacích. Beton je víceúčelový při stínění neutronového záření, stínění gama záření a poskytování strukturální podpory nebo ochrany před nárazem. Beton je stabilní při vysokých teplotách, ale má relativně vysokou hustotu mezi 2,3 a 6,4 $g \cdot cm^{-3}$. Voda má naopak hustotu ~1,0 $g \cdot cm^{-3}$, ale relativně nízký bod varu, proto může být požadavek na chladicí systém. Podobně polyethylen zpomaluje a absorbuje neutrony velmi dobře. Stínící schopnosti jak vody, betonu, tak polyethylenu mohou být podpořeny aditivy absorbujícími neutrony, jako je kyselina boritá, karbid boru a nanotrubice boru[3].

Při návrhu stínících bariér je třeba také respektovat, pro jaký účel má být stínění využito. Pokud se se stíněním má pravidelně manipulovat, je rozhodující hmotnost a velikost jednotlivých dílů stínících konstrukcí. Při návrhu (zejména mobilních) stínících konstrukcí je také třeba dávat pozor na místa se sníženou (efektivní) tloušťkou stínící vrstvy, tj. místa s napojením jednotlivých částí/stínících bloků, kudy by mohlo záření projít bez interakce se stínícím materiálem.

Jak již bylo také zmíněno, naším cílem je vytvoření kompozitního materiálu z odpadních termoplastů a inertních plniv pro účely stínění neutronového záření. K předpovědi účinku stínění a optimalizaci složení směsi byla použita stochastická metoda Monte Carlo, která je v takovýchto případech teoretických předpovědí mocným nástrojem.

Experimentální část

Materiály

Na základě předchozího výzkumu polymerbetonu[1,2] byla pro účely testování vybrána tato pojiva: polyethylen (PE), polypropylen (PP) a polyethylentereftalát (PET). Jako plniva se zkoumaly odpadní písek a odpadní sklo. Stupeň plnění byl volen s ohledem nejen na stínící vlastnosti, ale také na mechanické a ekonomické vlastnosti.

Veličiny radiační ochrany a jejich vztah k výsledkům modelových výpočtů

Základními výsledky simulací transportu záření jsou počty částic (přesněji fluence částic) v daném místě simulovaného prostoru, běžně vztažené na jednu simulovanou částici generovanou ve zdroji.

Jedna ze základních veličin radiační ochrany je prostorový dávkový ekvivalent (PDE) – značí se H*(10) a uvádí se v jednotkách sievert, značka Sv, (veličina má úzký vztah k limitované veličině efektivní dávka – pokud je splněn limit pro (prostorový) dávkový ekvivalent, předpokládá se splnění limitu i pro efektivní dávku). V reportu mezinárodní komise ICRP-74 jsou uvedeny doporučené konverzní faktory pro přepočet fluence radiačního pole daných typů částic na prostorový dávkový ekvivalent[4], pro neutrony jsou konverzní faktory přepočtu fluence na prostorový dávkový ekvivalent uvedeny v tabulce A.42 v reportu ICRP-74[4] .

Existuje jistá pravděpodobnost, že při interakci neutronů je produkován foton a naopak, přitom druhá možnost je méně pravděpodobná (produkce neutronů probíhá jen při reakcích fotonů s energií několik MeV). Z tohoto důvodu je třeba při simulačních výpočtech s neutronovými zdroji uvažovat i transport fotonů (a v případě simulace fotonových zdrojů vyšších energií potom uvažovat i transport neutronů). Při odhadu H*(10) v daném místě je tedy v simulačních výpočtech nutné nastavit nejenom skórování příspěvku od neutronů, ale i od sekundárních fotonů. Celková hodnota H*(10) v daném místě je tak tvořena dvěma komponenty (neutronovou a fotonovou). Konverzní faktory pro přepočet fluence fotonů na H*(10) jsou uvedeny v reportu ICRP-74, tabulka A.21[4].

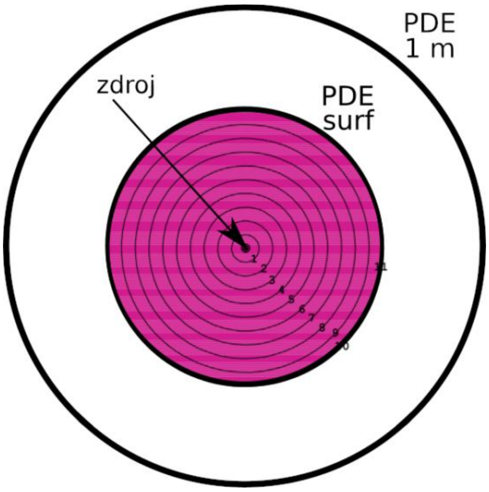
Geometrie simulačních výpočtů, skórování

Geometrie parametrické studie pro neutronový zdroj je zobrazena na obrázku 1. Jedná se o kulovou stínící vrstvu (poloměr koule = stínící vrstva tloušťky 50 cm) se zdrojovým členem ve středu koule. Fluence, resp. prostorový dávkový ekvivalent H*(10) byl počítán na povrchu stínění a na kulové ploše o poloměru 100 cm (použita tally 4 a konverzní faktory ICRP-74[4]). Výhodou kulové geometrie je odstranění závislosti na směru emise zdrojového členu. Zároveň tento postup zcela zohledňuje vliv tloušťky stínící vrstvy a intenzitu zdrojového členu, které je plně škálovatelná (viz normování intenzity zdroje). Prezentace i interpretace výsledků je v souladu s použitou geometrií simulačních výpočtů.

Simulace byla provedena pro různé typy zdrojů neutronů – Wattovo spektrum (štěpné spektrum ^{235}U v reaktoru), AmBe (radionuklidový zdroj). ^{252}Cf (zdroj neutronů ze samovolného štěpení) a generátory neutronů (D-D, resp. D-T). Pro jednotlivé zdroje neutronů byla analyzována efektivita stínění pro různé typy a podíly pojiva a plniva. V této fázi analýzy nebyly zohledňovány mechanické vlastnosti použitých směsí, jedná se čistě o studii zaměřenou na efektivitu stínění ionizujícího záření.

Standardně používaný stínící materiál je barytový beton, proto byly získané výsledky porovnávány právě s tímto materiálem použitým ve stejné geometrii a se stejným zdrojovým členem.

Výpočty byly provedeny pomocí výpočetního kódu MCNP6.2[5,6] s knihovnou ENDF/B-VII.1, data pro O-18 byla použita z knihovny JEFF3.2 (tento izotop není v knihovně ENDF/B-VII.1)



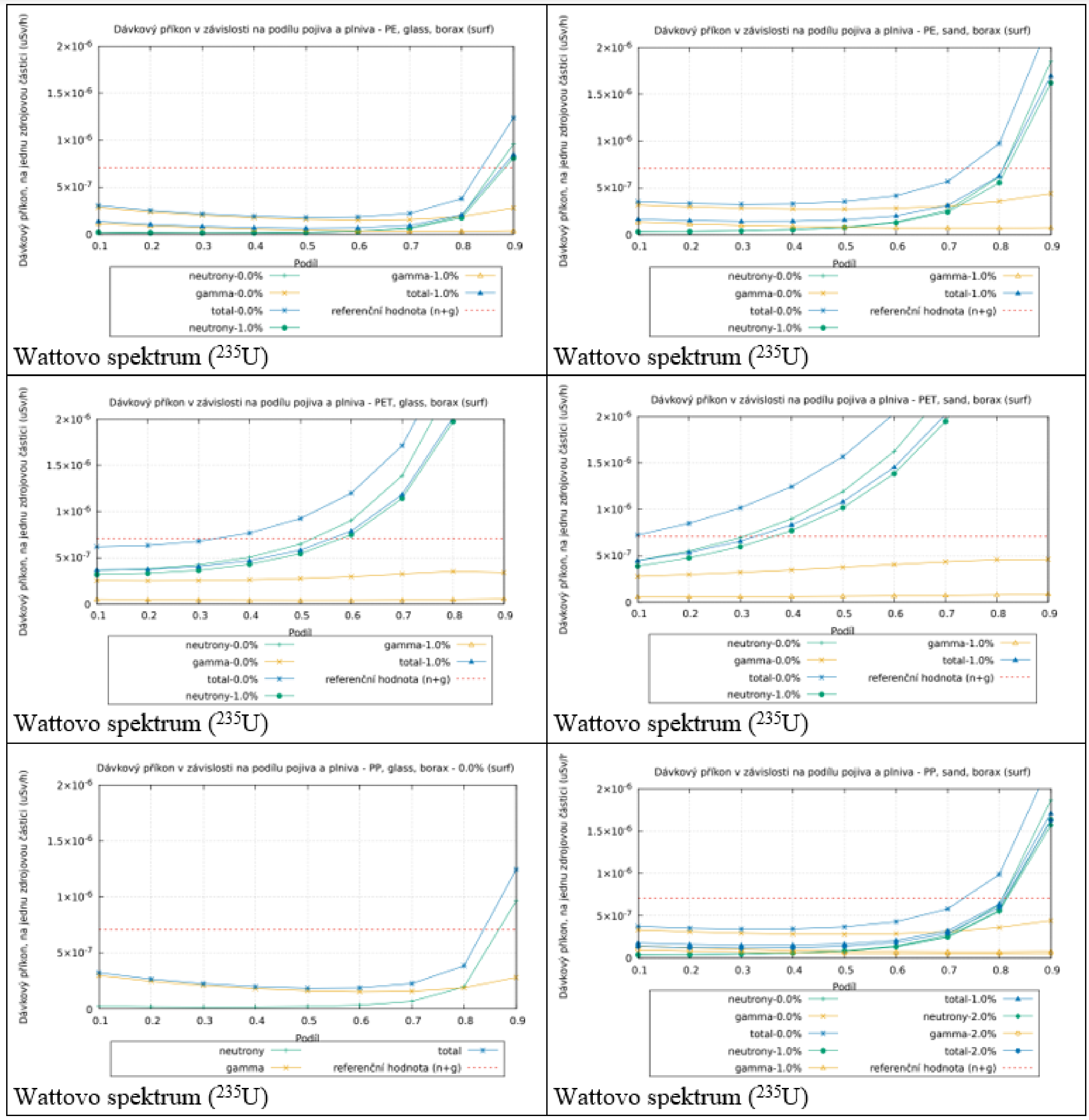
Obrázek 1: Geometrie simulačních výpočtů pro simulace s neutronovým zdrojem

Výsledky a diskuse

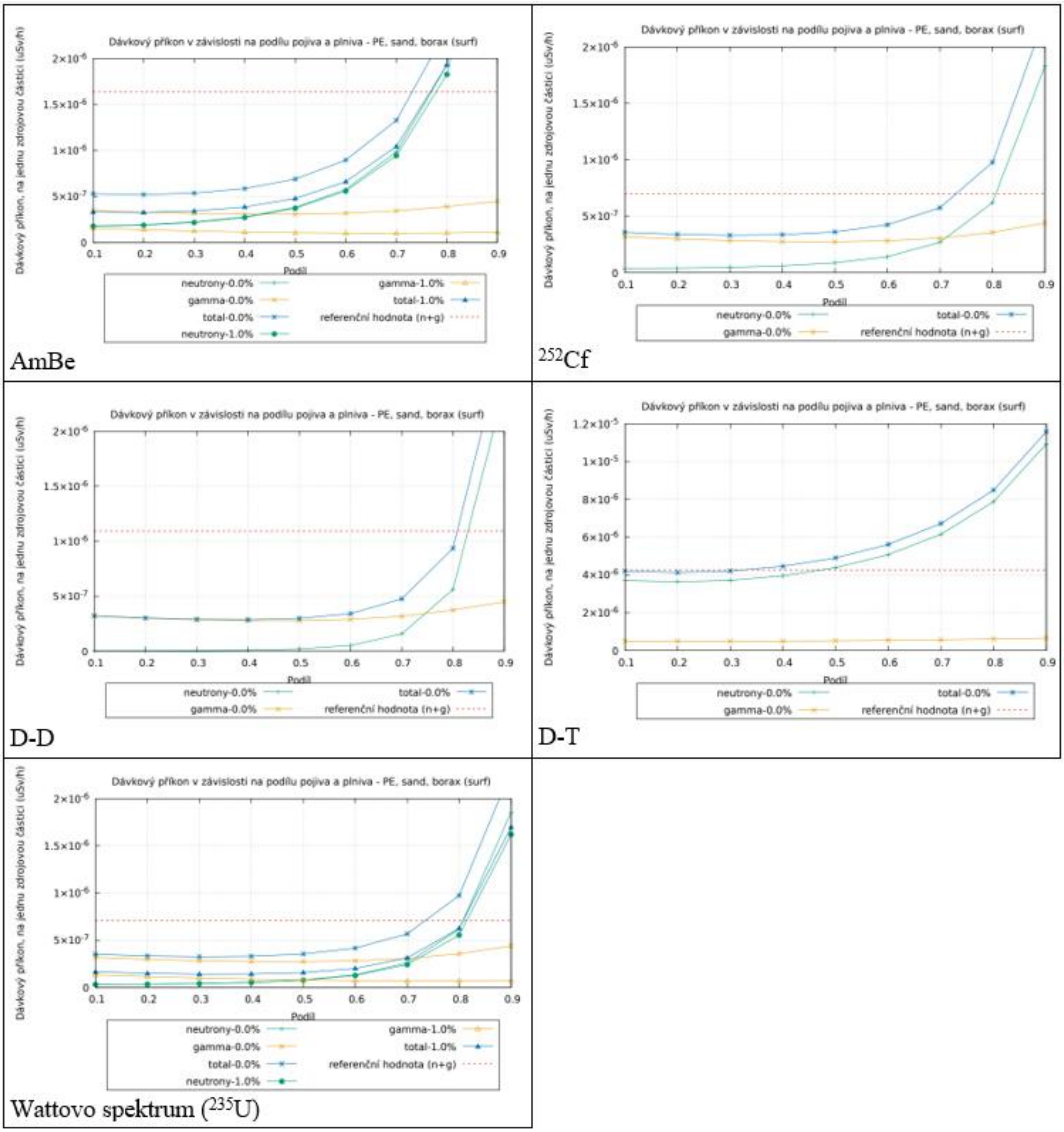
Pro uvažované kombinace pojiv a plniv a různé typy zdrojů byly stanoveny hodnoty prostoru dávkového ekvivalentu H*(10) na povrchu stínění (PDE, surf) a ve vzdálenosti 1 m od zdroje (PDE, 1 m). Obsah plniva se postupně zvyšoval od 10 % do 90 % (s krokem 10 %). Provedená sada výpočtů dává představu o vlivu poměru pojiva a plniva na stínění neutronů (a sekundárních fotonů), tj. dává představu o radiační situaci na povrchu stínící koule.

Jak již bylo zmíněno výše, standardně využívaným materiálem je barytový beton, proto byl tento materiál použit jako referenční a získané hodnoty jsou porovnávány s hodnotou H*(10) na povrchu koule z barytového betonu.

Na obrázku 2 jsou příklady spočtených závislostí H*(10) na povrchu stínění kolem zdroje emitujícího neutrony s Wattovým spektrem, tj. štěpení ^{235}U v reaktoru pro všechny uvažované kombinace materiálů. Na obrázku 3 jsou pak závislosti H*(10) pro kombinaci PE a sklo a všechny uvažované zdroje neutronů. V grafech jsou uvedeny také závislosti H*(10) pro případ zahrnutí dodatečného absorbátoru ve formě boraxu (podíl boraxu udávají procenta v legendě grafu). V grafech jsou uvedeny absolutní hodnoty vztažené na jednu částici emitovanou ze zdroje.



Obrázek 2: Hodnota dávkového příkonu H*(10) na povrchu stínící koule o poloměru 50 cm v závislosti na podílu pojiva a plniva ve směsi, jsou rozděleny příspěvky od neutronů a sekundárních fotonů, procenta udávají podíl boraxu ve směsi. Referenční hodnota odpovídá dávkovému příkonu na povrchu koule o poloměru 50 cm z barytového betonu. Zdrojový člen je definován Wattovým spektrem, které simuluje neutrony vznikající ze štěpení ^{235}U v reaktoru.



Obrázek 3: Hodnota dávkového příkonu H*(10) na povrchu stínící koule o poloměru 50 cm v závislosti na podílu PE a skla ve směsi, jsou rozděleny příspěvky od neutronů a sekundárních fotonů, procenta udávají podíl boraxu ve směsi. Referenční hodnota odpovídá dávkovému příkonu na povrchu koule o poloměru 50 cm z barytového betonu. Jednotlivé grafy zobrazují závislosti pro všechny uvažované typy zdrojů neutronů

V další části analýzy byly srovnány dávkové příkony pro konkrétní kombinaci materiálů. Geometrie výpočtu a parametry Wattova spektra pro štěpení ^{235}U jsou stejné, jako v parametrické studii (koule o poloměru 50 cm, zdroj ve středu koule). Složení vybraných kompozitních materiálů s vyznačeným zastoupením jednotlivých složek a spočtené hodnoty H*(10) jsou uvedeny v tabulce 1. Pro lepší názornost nejsou tyto hodnoty vztaženy na 1 neutron ze zdroje, ale je uvažován zdroj, který emituje

10^8 neutronů za sekundu. Pro srovnání, dávkový příkon od přírodního pozadí se v ČR pohybuje na úrovni 0,1 – 0,2 µSv/h.

Tabulka 1: Složení vybraných kompozitních materiálů s vyznačeným zastoupením jednotlivých složek a dávkové příkony od neutronů a sekundárních fotonů na povrchu koule o poloměru 50 cm, Wattovo spektrum (^{235}U), hodnoty odpovídají zdroji s emisí 10^8 neutronů za sekundu

Pojivo	**Plnivo**	**Pojivo (hm. %)**	**Plnivo (hm. %)**	**Hustota ($g \cdot cm^{-3}$)**	**H*(10) (µSv/h)**	**H*(10) (µSv/h)**
					neutrony	**fotony**
PET	písek	30	70	2,225	32,7	18,5
PET	písek	50	50	1,975	2,2	17,7
PET	sklo	30	70	2,155	81,5	24,4
PET	sklo	50	50	1,925	39,3	20,9
PE	písek	50	50	1,760	0,7	10,8
PE	písek	40	60	1,940	0,9	9,5
PP	sklo	50	50	1,705	1,1	12,0

Výpočetní kód MCNP byl využit v mnoha studiích zabývajících se stíněním neutronů[7,8]. V jedné z těchto studiích se kombinují dva různé materiály dohromady (polyethylen a železo) a rozhodujícím kritériem je poměr mezi jednotlivými tloušťkami celkové stínící vrstvy[7]. Ve druhé studii se uvažuje betonová vrstva mezi borovaným polyethylenem a olovem, přičemž s 10 cm betonu mezi borovaným polyethylenem a olovem byla celková dávka snížena na 2 µSv/h. S 15 cm betonového tlustého štítu získali efektivní dávkový příkon 1,08 µSv/h. Nakonec 20 cm betonu snížilo dávkový příkon na 0,58 µSv/h[8]. Naše studie porovnává výsledky pro jednu geometrii (různých kompozitních materiálů) a z nich potom vyvozuje závěry. Dalším předmětem výzkumu bude výzkum stínění neutronů u kombinace několika různých druhů materiálů ve vrstvách na sobě.

Závěry

Z analýzy simulačních výpočtů s neutronovým zdrojem je zřejmé, že materiály ze směsi termoplastu se sklem nebo pískem jsou použitelné pro stínění neutronů a pro některé typy zdrojů neutronů může být toto stínění efektivnější než referenční beton. Z uvažovaných plastů je vhodný PP a PE s podílem plniva v rozmezí 0,3 – 0,4. Rozdíl mezi sklem a pískem (jako plniva) je v těchto kombinacích malý. Nižší dávky jsou pozorovány při použití skla, nicméně obě kombinace dávají nižší dávkový příkon než v případě referenčního betonu. Horší výsledky jsou při použití PET. Kombinace PET a skla je vhodnější než PET a písek, přitom ale obě kombinace vykazují horší stínící vlastnosti než referenční beton. Velký vliv na stínící účinky má i přidání boraxu do kompozitní směsi – podíl 1 % boraxu snižuje hodnotu H*(10) o cca 40 %, vyšší podíl boraxu vede samozřejmě ještě k většímu snížení hodnot. Výzkum tedy prokázal použitelnost polymerního betonu z odpadních materiálů, jakožto stínícího materiálu, jehož parametry mohou přesahovat stínící vlastnosti konvenčního betonu. S ohledem na nižší mechanické pevnosti polymerního betonu, které odpovídají pevnostní třídě C12/15, může být tento materiál využit při stavbě mobilních stínících prvků, panelů, obkladů, bloků či stěn, které nemají statickou úlohu ve stavební konstrukci.

Poděkování

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Literatura

1. KULOVANÁ, E., ČERNÝ, M., KOIŠ, J., KRESA, J., JOHN, J., JANČÁŘ, J.: Vliv znečištění PET na teplotní okrajové podmínky při výrobě polymerbetonu. *WASTE FORUM*, 2018, roč. 2018, č. 4, str. 525 – 532. ISSN: 1804-0195.
2. KULOVANÁ, E., ČERNÝ, M., ONDRAČKA, T., KOIŠ, J., KRESA, J., JOHN, J., JANČÁŘ, J.: Využití výmětu pro přípravu polymerbetonu. *WASTE FORUM*, 2019, roč. 2019, č. 2, str. 116 – 122. ISSN: 1804-0195.
3. CASTLEY, D., GOODWIN, C., LIU, J.: Computational and experimental comparison of boron karbide, gadolinium oxide, samarium oxide, and graphene paltes as additives for a neutron shield. *RADIATION PHYSICS AMD CHEMISTRY*. 2019, roč. 165, str. 108435.
4. ICRP, 1996. Conversion Coefficients for use in Radiological Protection against External Radiation. ICRP Publication 74. Ann. ICRP 26 (3-4).
5. WERNER, C. J. (editor). MCNP Users Manual - Code Version 6.2, LA-UR-17-29981. 2017.
6. WERNER, C. J., BULL, J. S., SOLOMON, C. J., et al. MCNP6.2 Release Notes, LA-UR-18-20808. 2018.
7. ZUO, Y., ZHU, J., NIU, S., XIE H., SHANG P.: Monte Carlo optimization simulation of neutron shielding performance of iron/polyethylene combined structure. *MATEC Web of Conferences*. 2018, roč. 189, str. 02001.
8. PETROVIC, S., CARSON, M.: MCNP modelling of a neutron generator and its shielding for PGNAA in mineral exploration. *ASEG Extended Abstracts*. 2019, roč. 1, str. 1 – 4.

Utilization of waste thermoplastics for ionizing radiation shielding purposes

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Summary

Recycling of plastic waste allows to reduce the overall environmental pollution. One of the special methods of processing polymer waste is the production of polymer concrete. In addition to the options used so far, polymer concrete can also be used in radiation protection as a shielding for ionizing radiation, especially neutron radiation.

Monte Carlo simulations were used for evalutation of shielding properties for different mixtures based on thermoplastic and glass or sand. Based on the results, the use of polypropylene (PP) and polyethylene (PE) gives a dose rate comparable to or lower than the reference concrete. Optimal filler ratio is 0,3-0,4, there is very small difference between sand and glass.

Worse results were obtained with polyethylene terephthalate (PET). The combination PET with glass is more suitable than with sand, but both combinations show worse shielding properties than the reference concrete. The addition of borax to the composite mixture also has a great influence on the shielding effects - the proportion of 1% borax reduces the value of ambient dose equivalent (H(10)) by about 40%, the higher proportion of borax leads, of course, to an even greater decrease in values.*

Keywords: *recycling, polymer concrete, ionizing radiation, Monte Carlo simulation*

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- k seznámení představitelů výzkumné obce s potřebami reálného „podnikového života“ a případnému navázání spolupráce.

Původně vyhlášený program poté, co ani v náhradním listopadovém termínu se nemohl konat, **zůstává v naprosté většině v platnosti a až do 15. 1. 2021 je možné jej doplnit o nově přihlášené příspěvky**. **Původní přihlášky k účasti automaticky zůstávají v platnosti** (pokud ji účastník sám svou účast nezruší), **nově se k účasti lze přihlásit do 15. 2. 2021**.

K tradičním problémovým okruhům:

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- Snižování a měření emisí
- Doprava a lokální zdroje
- Kvalita ovzduší a zdravotní rizika

Věda a výzkum pro oběhové hospodářství:

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- Nové zdroje surovin a energie
- Inovativní technologické postupy a inovativní technologie
- Nové materiály a jejich aplikace (bio- a nanomateriály)

je tentokrát ve spolupráci s Centrem výzkumu Řež opět zařazeno téma **Radioaktivní odpady**.

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Přihlášky příspěvků lze zasílat do naplnění kapacity – přihlašovací formulář naleznete ZDE**.** Úspěšné odeslání přihlášky je automaticky potvrzeno. Zhruba měsíc před konáním konference bude na www.tvip.cz zveřejněn aktualizovaný program. Autoři příspěvků budou požádáni, aby zkontrolovali správnost informací uvedených v programu.

Abstrakta (souhrn) přednášek – stručný souhrn obsahu přednášky i vývěsky je nedílnou součástí přihlášky příspěvků, rozsah textu max. 500 znaků (včetně mezer). Abstrakt bude zahrnut do tištěného programu konference.

Plné texty přednášek – autory všech příspěvků, **tj. přednášek i vývěsek**, žádáme o včasné předání graficky upraveného plného textu příspěvku v **elektronické podobě** (MS Word) **nejpozději do 15. 2. 2021**. Po tomto termínu nemůžeme garantovat jejich zařazení do sborníku na CD-ROM, který obdrží účastníci konference při registraci.

Grafická úprava textu - příspěvky před zařazením do sborníku konference neprocházejí redakční a ani grafickou úpravou, při jejich psaní můžete s výhodou využít šablonu, kterou spolu s detailním popisem formátování najdete na www.tvip.cz v sekci Informace pro autory.

Prezentace – je nutné předat přítomné obsluze nejpozději 5 minut před začátkem sekce, do které je zařazena přednáška. Pokud prezentaci obdržíme do 15. 2. 2021, bude rovněž zařazena do sborníku na CD-ROM.

Pro vlastní prezentaci přednášky mají přednášející (pokud není uvedeno jinak) k dispozici **15 minut a 5 minut je vyhrazeno pro diskusi**. Ve spolupráci s předsedajícími sekcí se budeme snažit o maximální dodržování vyhlášeného časového rozvrhu.

Přednáškové místnosti budou vybaveny **dataprojektory**, včetně **notebooků**. Použití vlastního notebooku je možné, funkčnost propojení je třeba na místě předem ověřit ve spolupráci s technikem a současně je nezbytné poskytnout prezentaci obsluze pro další zpracování na DVD.

Vývěsky – formátu **A0** (na výšku) budou přichyceny lepicí páskou na tvrdý podklad (sklo, dřevěné obklady). Vystaveny budou po celou dobu konference v chodbě před hlavním sálem nebo přímo v sále. V programu bude vymezen časový prostor („Autorská prezentace vývěsek“), kdy by autoři měli být přítomni u své vývěsky.

Účast autorů: Autoři se rovněž přihlašují k účasti, na konferenci musí být přihlášen a **osobně přítomen alespoň jeden z autorů** příspěvku, anebo jím pověřená osoba. Jednacím jazykem je **čeština** a **slovenština**. **Zahraniční hosté** jsou srdečně zváni, tlumočení však organizátor nezajišťuje, prezentace příspěvků v angličtině je možná. **Za neodpřednášenou přednášku nebo nevystavený poster bude dodatečně autorovi fakturován poplatek 1000 Kč** (bez DPH) za zařazení příspěvku do programu a jeho uveřejnění ve sborníku.

Recenze: Organizátor konference nemá námitek, aby autoři nabídli svůj příspěvek z konference k uveřejnění v některém recenzovaném časopise, včetně časopisu WASTE FORUM, který je indexován v databázi **SCOPUS**.

Komerční přednášky či krátká sdělení jsou za úplatu možné. Rozsah možností firemní prezentace je široký, stejně jako cenové rozpětí *(více* ***ZDE****)*. Rozhodně není možné komerční sdělení prezentovat jako odbornou přednášku či vývěsku. V případě porušení této zásady bude dodatečně fakturována příslušná částka podle výše zmíněného ceníku.

INFORMACE PRO ÚČASTNÍKY

Hotel Amande, kde se TVIP 2021 koná, se nalézá na adrese Husova 8, Hustopeče.

Vložné na **TVIP** zahrnuje vstup na obě akce (APROCHEM i ODPADOVÉ FÓRUM), brožuru s programem a souhrny všech příspěvků a CD-ROM či flashdisk s plnými texty příspěvků a předem včas dodanými prezentacemi. Vybírat je možné ze tří typů vložného:

Plné vložné (4 450 Kč bez DPH)
Dvoudenní vložné (3 950 Kč bez DPH)
Jednodenní vložné (3 450 Kč bez DPH)

Přihlášky účasti je možné zasílat **do 15. 2. 2021** (dále možné po dohodě s pořadatelem) prostřednictvím připraveného internetového formuláře. V přihlášce specifikujte také veškeré požadavky na stravu a ubytování.

Ubytování a stravování zajišťuje pořadatel. Vzhledem k omezené ubytovací kapacitě **hotelu Amande Hustopeče** nabízíme ubytování také v těsně sousedícím **hotelu Rustikal a v Penzionu pod Radnicí**. Ubytování je možné v jednolůžkových anebo dvojlůžkových pokojích. V případě dvojlůžkového pokoje je nutné v přihlášce účasti specifikovat jméno spolubydlícího.

Stravování během konference pro ty, kteří je mají objednáno, je zajištěno v hotelu Amande, výjimkou jsou snídaně, ty má každý účastník v tom hotelu, kde je ubytován.

Podrobnější informace, včetně cen ubytování a stravování najdete na www.tvip.cz v sekci Informace pro účastníky.

Open Innovation Matchmaking in Ecology (Waste Management)

Cílem symposia je mj. napomoci setkávání a propojování účastníků za účelem navazování nových příležitostí ke spolupráci. Abychom tento aspekt podpořili, připravili jsme **ve spolupráci s WASTen, z.s.,** tzv. **„Open Innovation Matchmaking in Ecology (Waste Management)“**. Každý, kdo bude mít zájem o asistované propojení s jiným účastníkem, může tak učinit předem prostřednictvím připraveného formuláře nebo na místě na registraci TVIP.

Exkurze

Exkurze je plánována do Vetropack Moravia Glass, jednoho z největších výrobců obalového skla a současně jednoho ze dvou zpracovatelů odpadového skla v ČR, nebo bude možné zavítat do areálu společnosti **HANTÁLY, a.s.** navštívit provoz skládky, dotřiďovací linky, kompostárny a **pyrolýzní jednotky**,

Exkurze, včetně dopravy na místo, jsou zdarma. **Zájem o účast je nutné uvést v přihlášce účasti nebo dodatečně emailem na** cemc@cemc.cz**.**

DŮLEŽITÉ TERMÍNY na závěr:

Termín konání: 3. – 5. 3. 2021, z toho
Odpadové fórum: 3. – 5. 3. 2021
Aprochem: 4. – 5. 3. 2021

Přihlášky příspěvků**: 15. 1. 2021** (dále po dohodě s pořadateli)

Zaslání plných textů: 15. 2. 2021

Přihlášky účasti**: 15. 2. 2021**

wasten

centrum
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KONZULTAČNÍ SYSTÉM KLASTRU WASTEN, z. s. V OBLASTI ODPADOVÉHO HOSPODÁŘSTVÍ

Špičkový experti vám poskytnou své znalosti a cenné rady v oblasti oběhového hospodářství, materiálového i energetického využití odpadů. Zaručujeme špičkové know-how, zahraniční zkušenosti i výsledky moderního výzkumu.

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