Hydrothermal hygienization of sewage sludge and analysis of the management of solid and liquid products of the process

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RESEARCH UNIVERSITY

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INTRODUCTION:

Incorrect sludge management can result in negative impacts on health and the environment. The sludge contains not only organic compounds, bacteria, and inorganic compounds, but also dangerous compounds, e.g. heavy metals, hormones, pharmaceuticals or pathogens, which can pose a serious threat to health and can be fatal. The epidemiological situation in 2020 has prompted scientists to test for the SARS-CoV-2 presence in municipal wastewater where the virus was indeed detected. Therefore, the proper disinfection of wastewater to remove a potential source of infection is an important issue. The most optimal alternative solutions for sludge hygienization are methods based on elevated temperatures, mainly above 60°C, which eliminate pathogens. An innovative method is the hydrothermal treatment of sewage sludge, which does not require high energy expenditure because the process is carried out in an aqueous environment leading to the following products: solid biofuel (hydrochar), liquid (process water), and gas. This method results in improved dewaterability and fuel properties of sewage sludge as well as in structural changes of hydrochar. Furthermore, it reduces the volume of waste, and besides, an appropriate treatment depending on optimal conditions of the process allows for the recovery of valuable components. However, the main problem is highly contaminated liquid phase which requires special treatment. Thus, the main aim of the project was to investigate the impact of temperature, the main parameter of the process, on the physical and chemical properties of hydrothermal products, treatment of process water and dewaterability of slurry derived from hydrothermal treatment of sewage sludge.

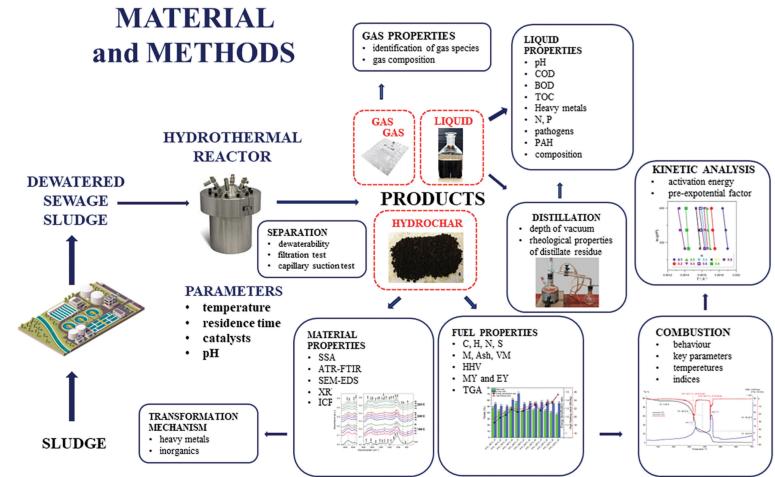
SEWAGE SLUGE as POTENTIAL RISK UNFAVOURABLE PROPERTIES of SEWAGE SLUDGE of SARS-COV-2 High content of moisture DROPLET ROUTE Insufficient dewaterability After mechanical dewatering ~20% d.m Organic content - biodegradable Bacteria. viruses. pathogens Pharmaceuticals Microplastics Heavy metals **FEACES** High volume of waste Frequently disposed in landfill

HYDROTHERMAL CARBONIZATION PROCESS HYDROCHAR HYDROTHERMAL ~10-20% **CARBONIZATION** POSTPROCESSING Sewage sludge 200 - 220 °C, 2h 80% moistur GAS IMPROVED PROPERTIES 20% thermal energy 100% thermal energy Biodegradability Microplastic removal Pharmaceutical removal

MATERIALS AND METHODS:

Dewatered sewage sludge was collected from Wastewater Treatment Plant in Lubin, Poland

The following conditions of the hydrothermal treatment were used: a temperature of 200 and 220°C and 2 hours of residence time in a 1000 ml steel Zipperclave Stirred Reactor. For solid products, dried sewage sludge and hydrochars (HTC), the following analyses were performed: the proximate according to the EU standards PN-EN ISO 18134-1:2015-11, EN 15403:2011, and EN 15402:2011; the ultimate on a Truespec CHNS628 Leco Elemental Analyzer according to the PKN-ISO/TS 12902:2007; X-ray fluorescence method on a WD-XRF ZSX Primus II Rigaku spectrometer (Rh lamp); Scanning electron microscopy supported by energy dispersive spectroscopy (SEM-EDS) by an FEI Inspect S50 microscope using a low vacuum with backscattered electrons; Specific Surface Area (SSA) by the Brunauer-Emmett-Teller multipoint adsorption method using an ASAP 2010 apparatus (Micromeritics Inst.); Fourier Transformation Infrared Spectroscopy (FTIR) in the range of 400–4000 cm-1 by Bruker spectroscope; thermal analysis (TGA) by a Mettler Toledo analyzer, STAR System TGA/DSC 3 HT 1600 with heating rate 10°C/min up to 900°C in an air environment with a flow rate of 50 ml/min. The following indicators were characterised in process water (PW) and distillates according to standard analytical methods: Chemical Oxygen Demand by PN-ISO 15705:2005; ammonium nitrogen by PN-ISO 7150-1:2002; Kjeldahl nitrogen by PN-EN 25663:2001; conductivity, total solids, viscosity, phosphorus by using a Spectrophotometer Merck Spectroquant Prove 100 and Thermoreactor Merck Spectroquant® Series TR 420; heavy metals (e.g. nickel, zinc, copper, mercury, cadmium, chromium, and lead) by the ICP-OES method according to PN-EN ISO 11885:2009; pH by PN-EN ISO 10523:2012; the ultimate analyses using the Truespec CHNS628 Leco Elemental Analyzer according to the standard PKN-ISO/TS 12902:2007; Total Organic Carbon, Total Carbon, and Inorganic Carbon on the TOC-L series analyzer (Shimadzu, Kioto, Prefektura Kioto, Japan). In order to eliminate odour and colour and for the purpose of purification, the post-processing liquid was distilled.



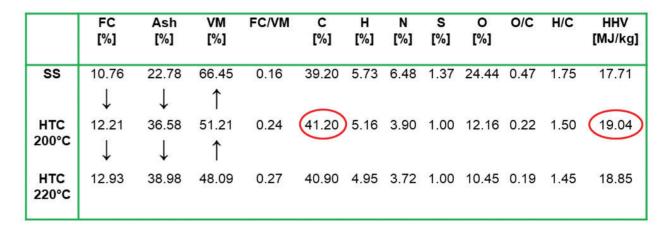
RESULTS AND DISCUSSION:

Hydrothermal treatment caused changes in the physical and chemical properties of sewage sludge. The hydrothermal slurry was more effectively filtered in comparison to sewage sludge. The proximate analysis of hydrochars (HTC) indicated that Ash (Ash) and Fixed Carbon (FC) increased in hydrochars and volatile matter (VM) decreased in comparison to the sewage sludge. As the temperature of the hydrothermal treatment increased, the ash and fixed carbon also increased due to the rapid loss of volatile matter as the temperature rose. The highest carbon value was found for 200°C of hydrothermal treatment and resulted in the highest HHV value. A noticeable reduction in sulphur and nitrogen contents in hydrochars had a positive effect on the potential risk of harmful NOx and SOx emissions during their combustion. A decrease in the H/C and O/C atomic ratios showed the positive effect of the process on hydrochar fuel properties which were moved into the lignite zone in comparison to sewage sludge. SEM-EDS confirmed degradation of material resulting in smaller, brittle, homogeneous particles (with 10 times higher specific surface area) caused by higher temperature of the process and identified carbon as the main element, whereas FTIR identified changes in functional groups due to dehydration, carbonization, demethanation reactions. Based on TGA data, the key combustion factors and indexes of the solid samples were determined indicating that higher temperature of hydrothermal carbonization caused an increase in the ignition temperature but also a decrease in the combustion temperature of the samples. The combustion indices: ignition index (Di) – illustrates the ease in which volatile matter was released from the fuel; combustion index (S) - mirrors the combustion, ignition, and burnout properties; and combustion stability index (Hf) - reflects the rate and intensity of combustion processes which indicated that hydrochars burn later and finish earlier in comparison to sewage sludge. XRF confirmed that higher temperature of the process resulted in higher amount of heavy metals accumulated

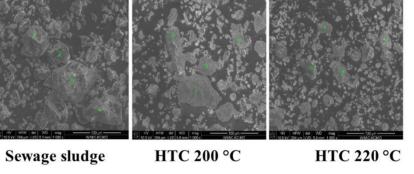
in HTC due to certain complex physical and chemical processes such as adsorption, precipitation complexation and recombination, occurring between heavy metals and hydrochar crystal lattices. Oxide forms of elements enable to assess the indices responsible for operational risk and they indicated a medium and high tendency to slagging. Analysis of the filtrate (PW) and distillate after 220°C of hydrothermal treatment results showed a decrease in pH, ammonium nitrogen, and total Kjeldahl nitrogen, might be due to decomposition of organic acids at higher temperature. A decrease in the content of the following elements: Mg, Ca, Cr, Cu, Cd, Ni, Pb, and Zn was found. Hg was an exception with an increase in both PW and distillates. None of the above elements exceeded the permissible content permissible content of heavy metals, therefore the liquids might be applied for soil reclamation applications or agricultural uses. The distillation process has an extremely significant impact on COD value, which decreased 32 times in the case of filtrate 200 and 22 times in the case of filtrate 220.

PHYSICAL and CHEMICAL PROPERTIES of SOLID SAMPLES

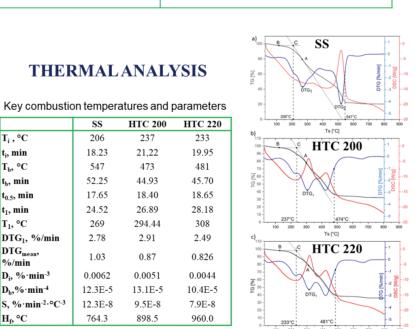




SEM ANALYSIS



Sorptive analysis HTC 200 HTC 220 Specific Surface Area, m²/g 0.3689 3.5568



—HTC 220

Wavenumber (cm⁻¹)

FTIR ANALYSIS

XRFANALYSIS

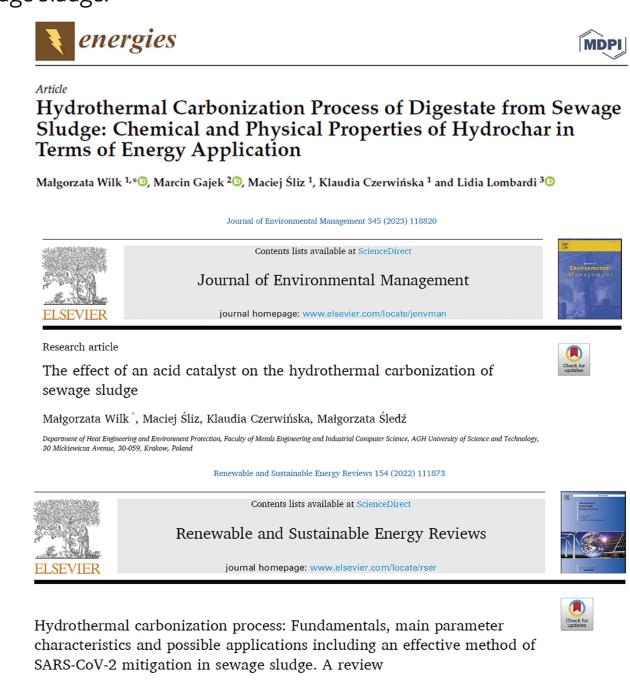
	SS	HTC 200	HTC 220
R_B	low melting point	low melting point	low melting point
$R_{B/A}$	Medium slagging	Medium slagging	Medium slagging
	tendency	tendency	tendency
S_R	High slagging	High slagging	High slagging
	tendency	tendency	tendency
R_S	High slagging	Medium slagging	Medium slagging
	tendency	tendency	tendency
$F_{\rm u}$	High contamination	High contamination	High contamination
	tendency	tendency	tendency
Fe ₂ O ₃ / CaO	Formation of	Formation of	Formation of
	outactics	autactics	autactics

LOW VACCUM DISTILLATION

	PW	Distillate	PW	Distillate
	HTC 200	200	HTC 220	220
pH	5.7	8.4	6.7	9.3
COD, mgO_2/L	45 900	1 430	43 500	1 970
Loss on ignition, mg/L	38 350	70	31 550	100
Dry residue, mg/L	40 722	124	34 150	92
Ammonium nitrogen (NH4-N), mg/L	1.64	< 0.040	3.46	0.43
Total Kjeldahl nitrogen (N), mg/L	4558	278	4650	684
Hg, mg/L	< 0.0005	0.0462	< 0.0005	0.0293
Ca, mg/L	28.3	1.90	11.0	1.82
Cd, mg/L	< 0.0025	< 0.0025	< 0.0025	< 0.0025
Cr, mg/L	0.812	< 0.025	0.561	< 0.025
Cu, mg/L	0.321	0.119	< 0.025	0.0521
Mg, mg/L	17.6	< 0.500	8.88	< 0.500
Ni, mg/L	0.42	< 0.237	0.20	< 0.025
P, mg/L	606	0.237	534	< 0.050
Pb, mg/L	0.107	0.037	< 0.0250	< 0.025
Zn, mg/L	1.43	< 0.100	0.162	< 0.100
Density, g/mL	1.012	1.002	1.012	1.001
Conductivity, mS/cm	9.15	1.25	13.09	1.66

CONCLUSION:

The hydrothermal treatment indicated that hydrochar (c.a. 10%) may be converted to a fuel or fertilizer. Hydrochars with slightly improved carbonaceous properties demonstrated better energy properties and dewaterability than in the case of raw sewage sludge, including improved chemical composition, a higher fixed carbon content, and it also gained more effective filtration. TGA and XRF data highlighted that both hydrochars might combust more stably and faster than sewage but had a similar high slagging tendency. The highly toxic process water (c.a. 80%) might be successfully treated by distillation as proved by a 32 times decrease of COD. Also, the fate of trace pollutants, especially heavy metals in solid product (derived from sewage sludge) was evaluated and verified before its final disposal to omit the environmental risk of the HTC processed sewage sludge.



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