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The EFFECT of an ACID CATALYST on the HYDROTHERMAL CARBONIZATION of SEWAGE SLUDGE

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Keynote presentation - Session: Waste and wastewater treatment and reuse 2

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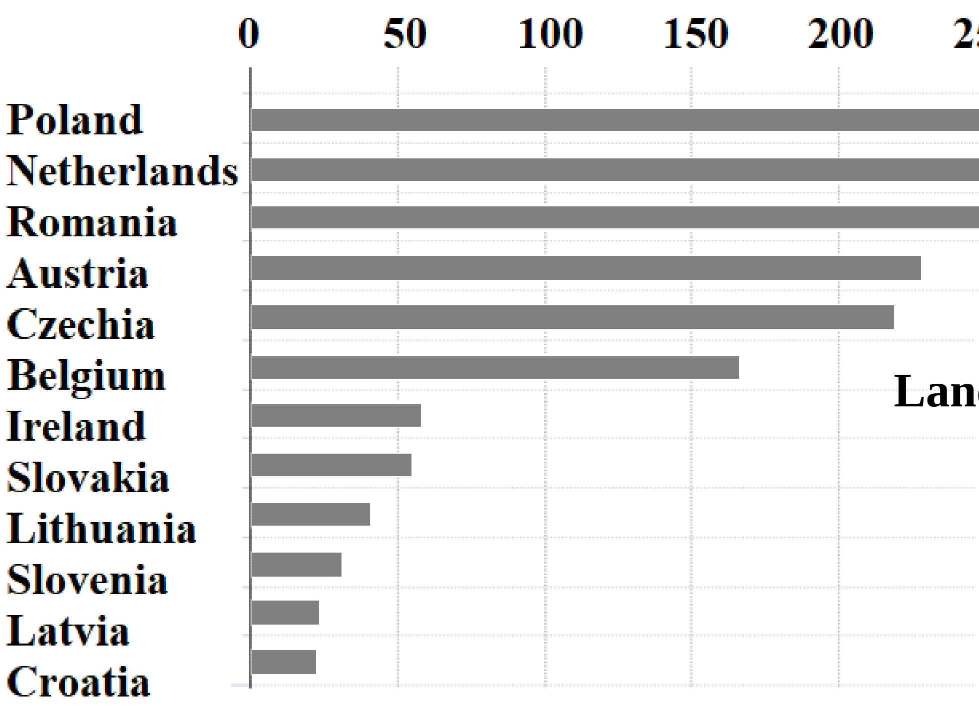
Outline

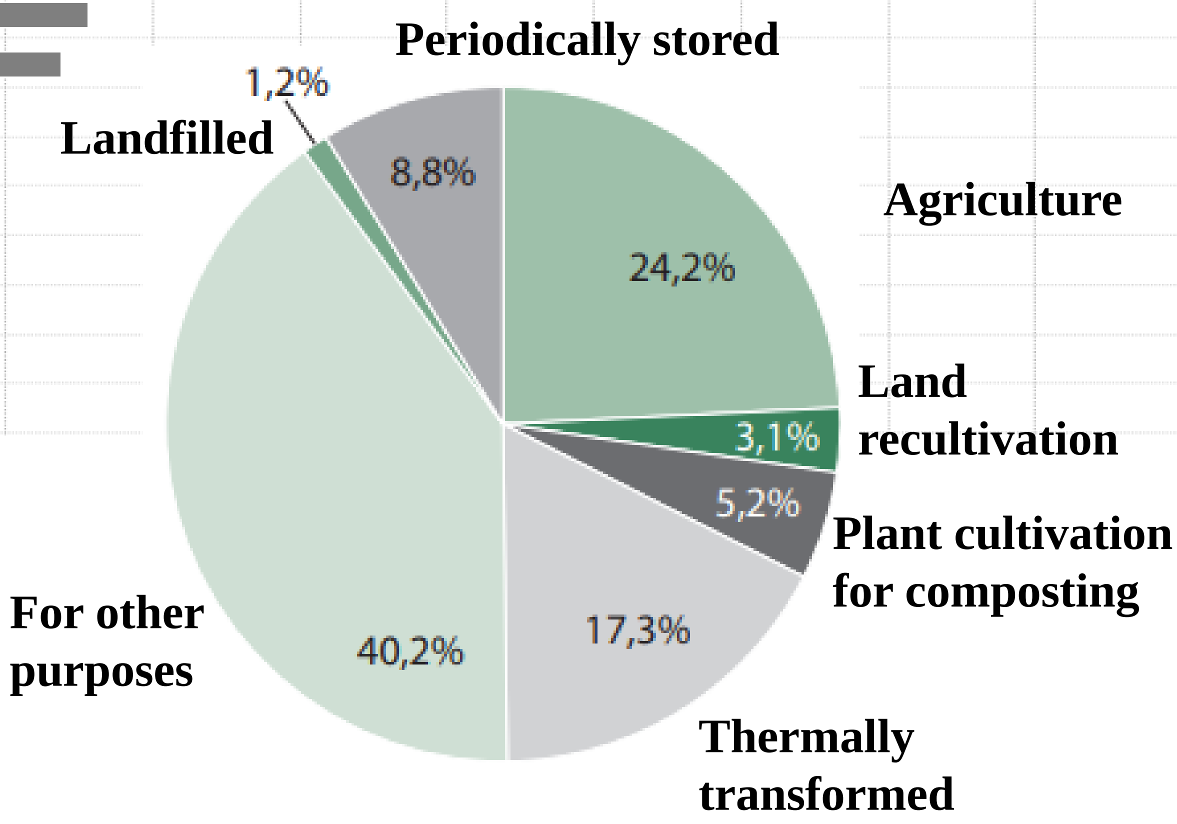
- Motivation
- Introduction
- Material:
  - sewage sludge
  - catalyst
- Methods:
  - hydrothermal carbonization
  - hydrochar and post-processing water analyses
- Results
- Conclusions

Motivation

Sewage sludge production and disposal from urban wastewater (in dry substance (d.s))



EUROSTATE 2020



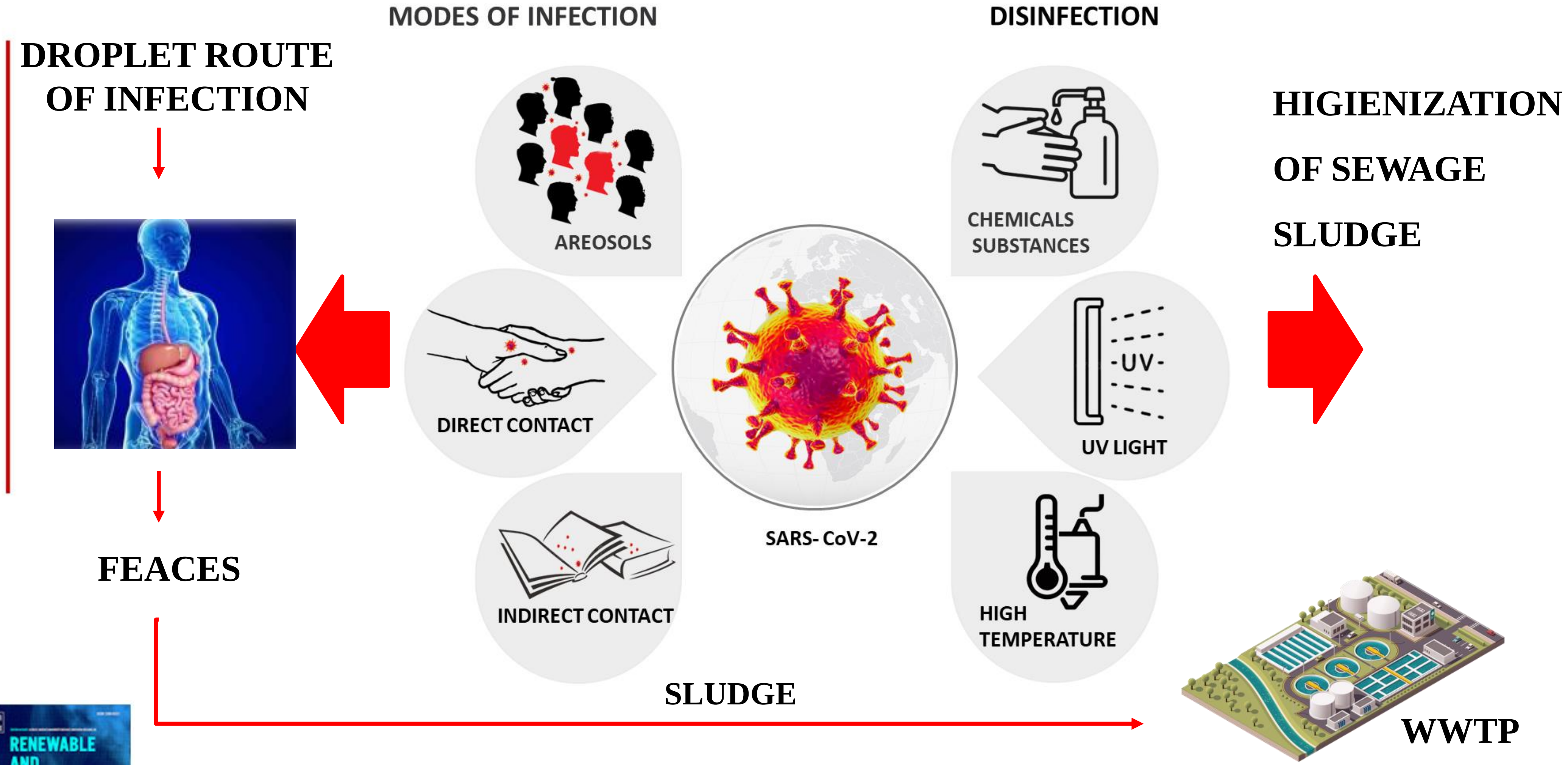
STATISTICS POLAND 2020

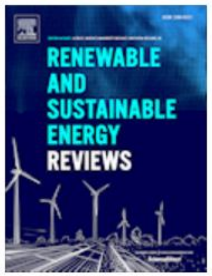
UNFAVOURABLE PROPERTIES of SEWAGE SLUDGE

- High content of moisture
- Insufficient dewaterability
- After mechanical dewatering dry mass c.a. 20%
- Organic content - biodegradable
- Bacteria, viruses, pathogens
- Pharmaceuticals
- Microplastics
- Heavy metals
- Odour
- High volume of waste
- Frequently disposed in landfill

TREATMENT/ CONDITIONING/ PRETREATMENT

SEWAGE SLUGE as POTENTIAL RISK of SARS-COV-2





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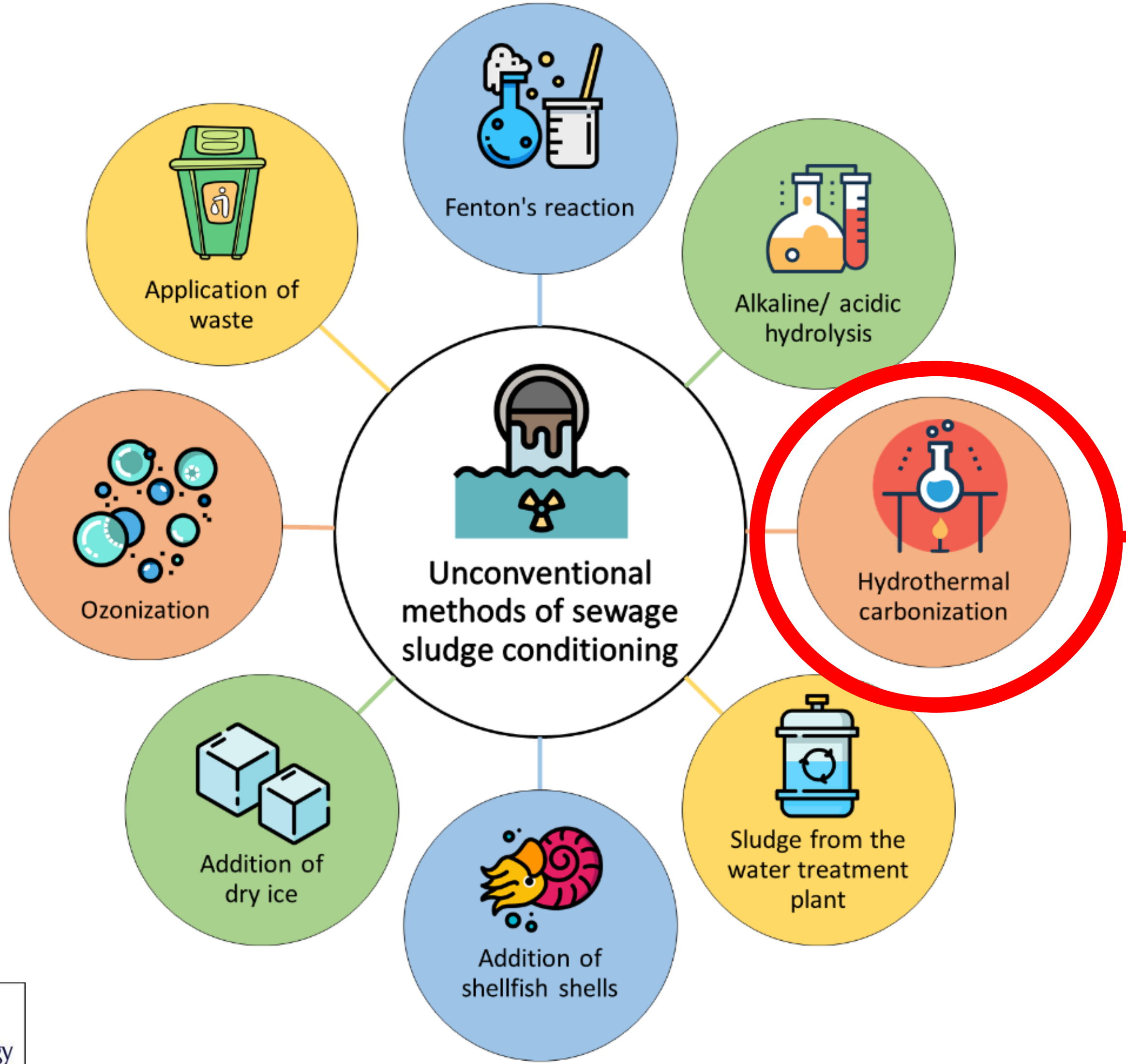
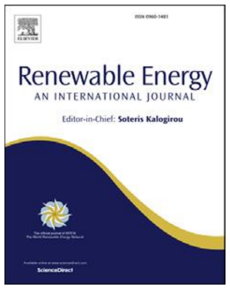
SEWAGE SLUDGE TREATMENTS



IMPROVED PROPERTIES OF SEWAGE SLUDGE

- Dewaterability
- Disinfection
- Reduction of waste volume
- Biodegradability
- Microplastic removal
- Pharmaceutical removal



Wilk M., Śliz M., Lubieniecki B., Hydrothermal co-carbonization of sewage sludge and fuel additives: Combustion performance of hydrochar. Renewable Energy 178 (2021) 1046–1056

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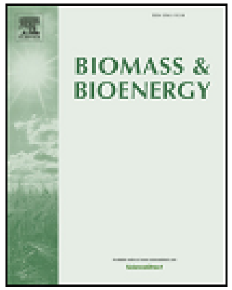


MATERIAL:

Wastewater Treatment Plant in Lubin, Poland

OPEN DIGESTION CHAMBERS

SEWAGE SLUDGE

HYDROTHERMAL CARBONIZATION

Sewage sludge

~ 80% moisture

100% mass
100% thermal energy

HYDROTHERMAL CARBONIZATION

200 °C, 2 h, 150 rpm

Water vapour pressure

Aqueous environment

HYDROCHAR

~2-15%

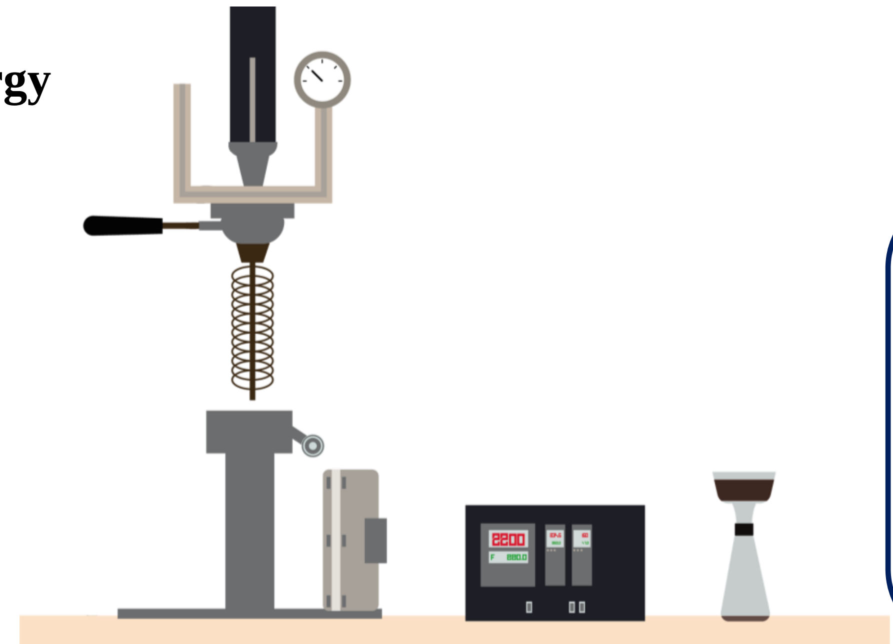
POST-PROCESSING LIQUID

~90-85%

GAS

~1%

75% mass
20% thermal energy



Catalyst:

Sulphuric acid (IV) 30%

3 ml → pH = 5

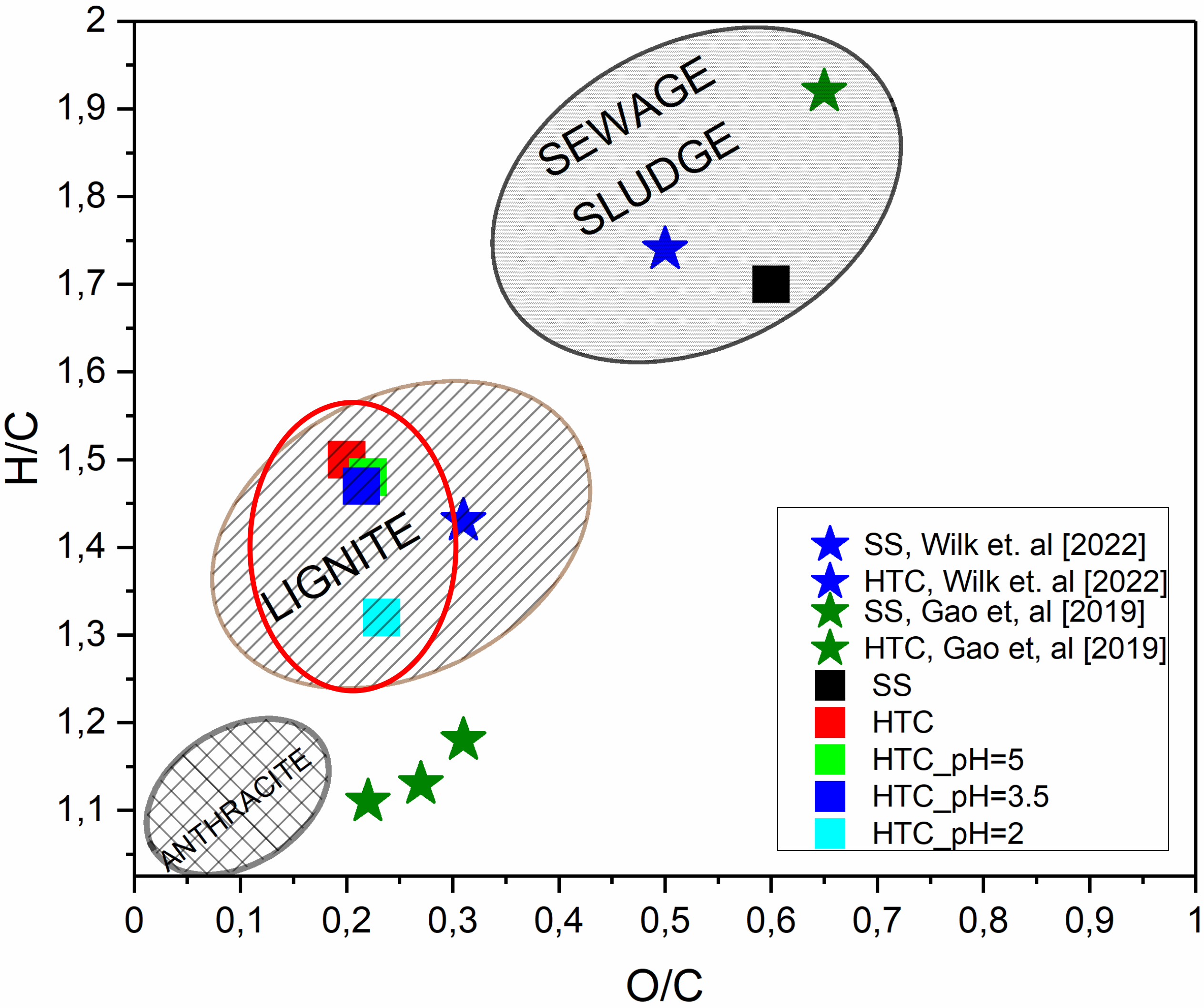
7 ml → pH = 3.5

10 ml → pH = 2

ANALYTICAL METHODS for SOLID SAMPLES

Type of analysis	Norm/method	Instrument
Ultimate analysis (Carbon, Hydrogen, Nitrogen, Sulphur content)	PKN-ISO/TS 12902:2007	Elemental Analyser Truespec CHNS 628 Leco, USA
Moisture content	EN ISO 18134-2:2017	Universal oven UN75plus, Memmert, Germany
Ash content	EN ISO 18122:2015	Muffle furnace FCF 22SHM CZYLOK Ltd., Poland
Volatile matter content	EN ISO 18123:2016	Muffle furnace FCF 22SHM CZYLOK Ltd., Poland
Higher heating value	PN-ISO 1928:2002	Leco AC500 isoperibolic calorimeter, USA
Thermal analysis (TGA)	-	Mettler Toledo Analyzer STAR W 16.10, Switzerland
Fourier Transformation Infrared Spectroscopy	range 400 – 4000 cm^{-1}	Bruker spectroscope, USA
X-ray fluorescence method	Rh lamp	ZSX Primus II Rigaku spectrometer, Japan

Van Krevelen diagram for sewage sludge and hydrochars



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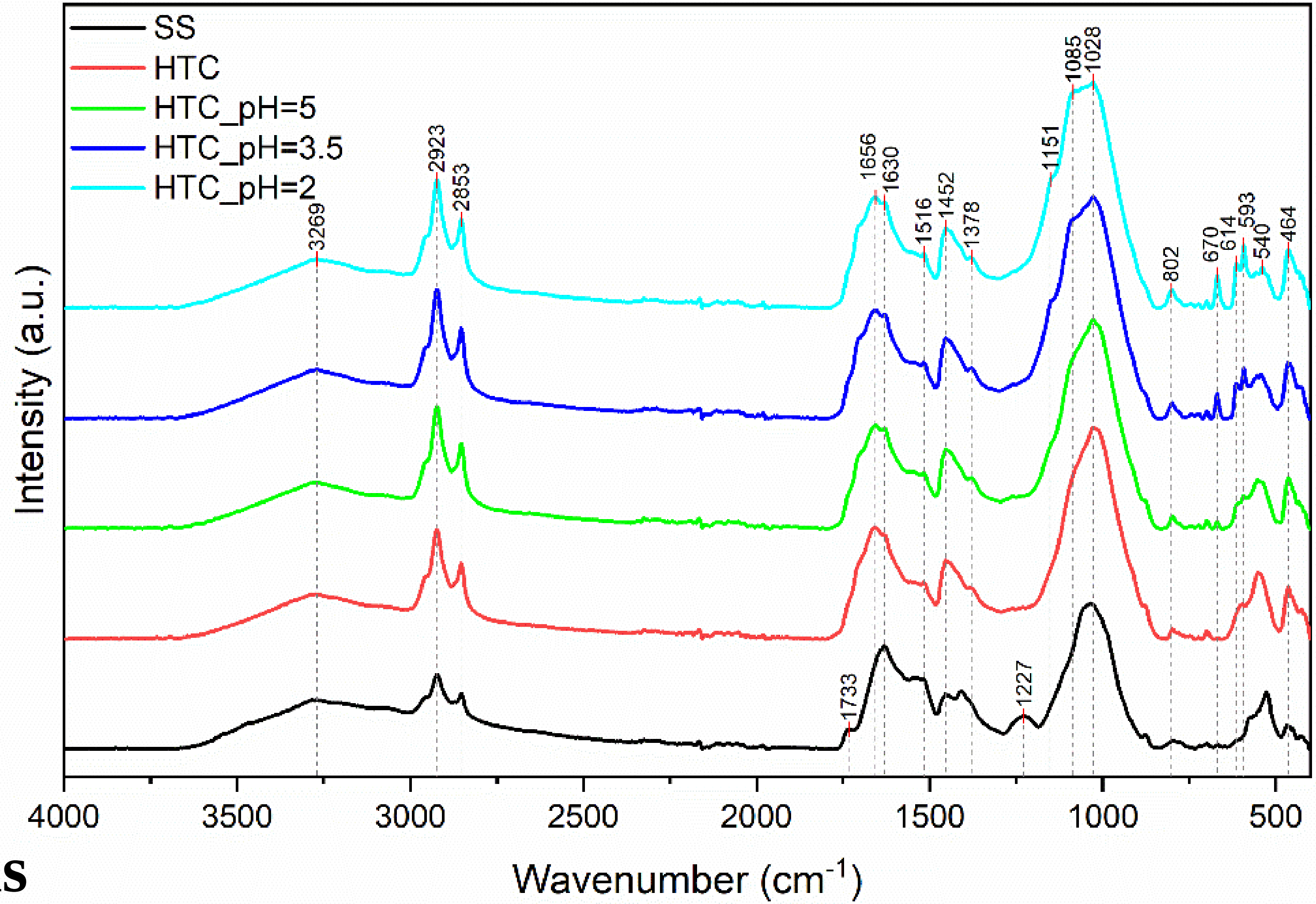
Gao, N.; Li, Z.; Quan, C.; Miskolczi, N.; Egedy, A. A new method combining hydrothermal carbonization and mechanical compression in-situ for sewage sludge dewatering: Bench-scale verification. J. Anal. Appl. Pyrolysis ***2019****, 139, 187–195.*

energies

PHYSICAL and CHEMICAL PROPERTIES

	Proximate analysis			Energy parameters				Product distribution		
	FC %	Ash %	VM %	HHV MJ/kg	EY %	MY %	EDR	Solid %	Liquid %	Gas and losses %
SS	10.76 ↓	22.78 ↓	66.45 ↑	17.7		-	-	-	-	-
HTC	12.21 ↓	36.58 ↓	51.21 ↑	19.0 ↑	45.9	43.4	1.06	4.4	90.6	5
HTC_pH=5	11.53	36.09	52.38	18.8 ↓	44.8	41.8	1.07	4.2	90.1	5.7
HTC_pH=3.5	10.04	35.09	54.87	18.9	66.7	61.4	1.09	6.2	89.3	4.5
HTC_pH=2	9.98	33.53	56.49	18.7	59.4	55.3	1.08	5.6	90.1	4.3

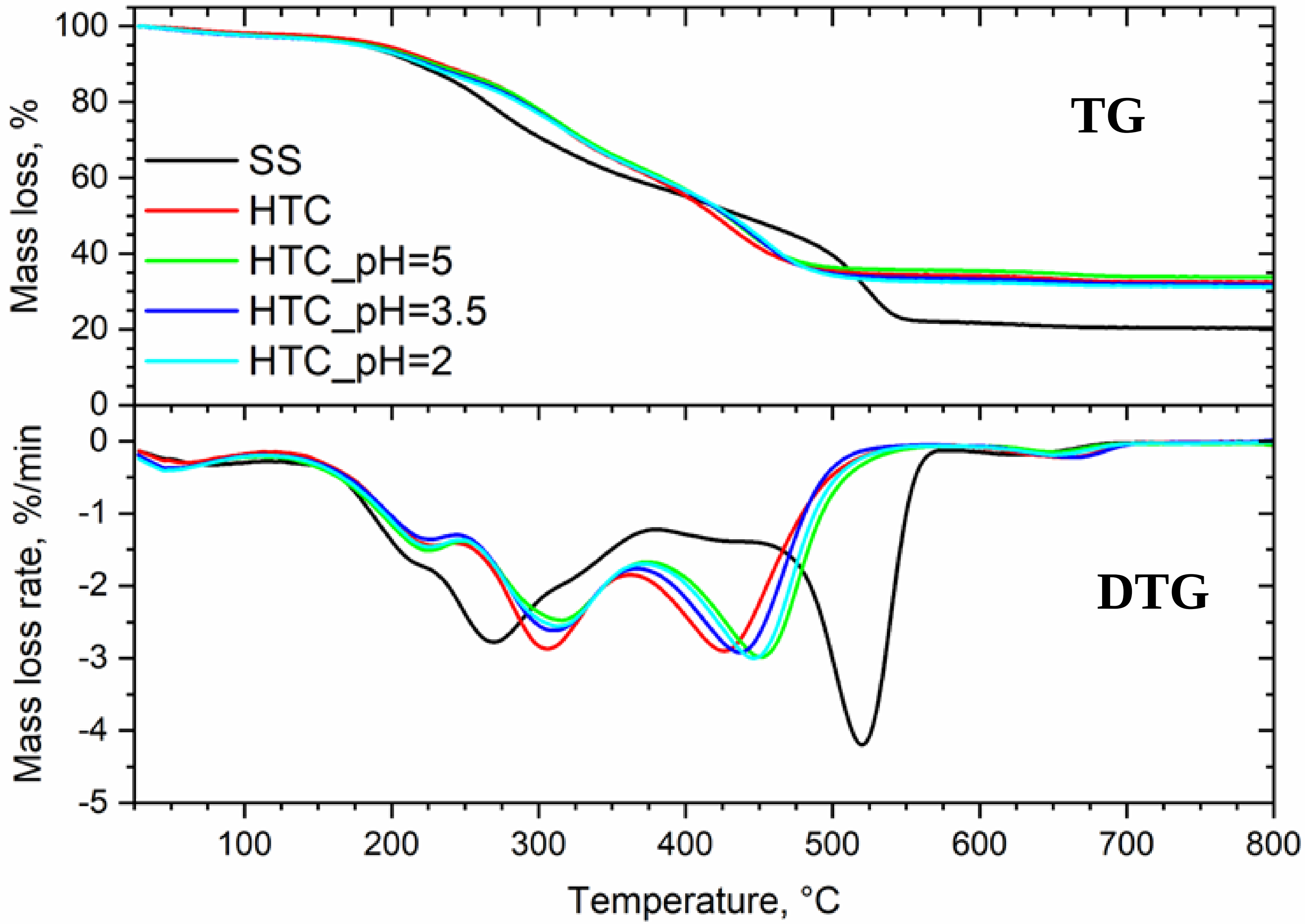
FTIR ANALYSIS



Sorptive analysis

	SS	HTC	HTC_pH=5	HTC_pH=3.5	HTC_pH=2
Specific Surface Area, m^2/g	0.4	3.6	5.5	5.8	6.2

THERMAL ANALYSIS

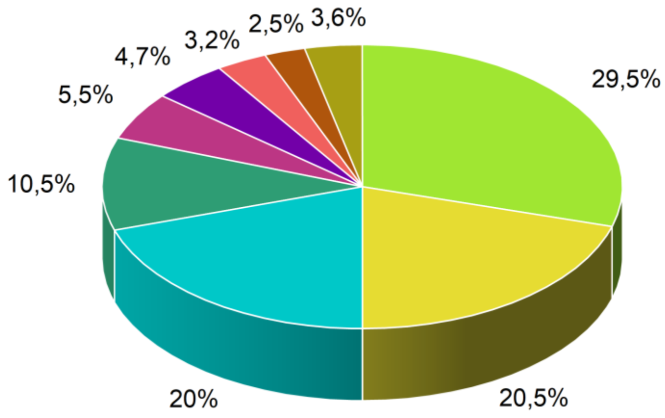


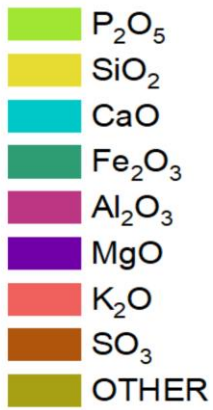
XRF ANALYSIS

Compounds, %	SS	HTC	HTC pH=5	HTC_pH=3.5	HTC_pH=2
Na_2O	0.8153	0.5066	0.4746	0.4443	0.4904
MgO	4.6777	4.8100	4.6763	4.4601	3.9290
Al_2O_3	5.4761	6.4932	6.4865	6.5979	6.3721
SiO_2	20.4600	21.3478	21.1093	21.2750	20.9872
P_2O_5	**29.5347**	**26.8832**	**26.6472**	**24.0831**	**22.3130**
SO_3	2.5372	2.8503	4.4213	8.9990	12.8801
Cl	0.0404	0.0245	0.0180	0.0111	0.0126
K_2O	3.1679	1.4399	1.2809	1.4090	1.5127
CaO	20.026	21.1726	20.4536	18.1619	17.9915
Fe_2O_3	10.5483	11.3501	11.3947	11.4543	10.5562
ZnO	0.3586	0.4320	0.4344	0.4362	0.4149
PbO	0.0526	0.0631	0.0613	0.0490	0.0563
Cr_2O_3	0.0809	0.0808	0.0646	0.0727	0.0848
NiO	0.0163	0.0132	0.0146	0.0130	0.0128
CuO	0.1568	0.1943	0.1806	0.1863	0.1978

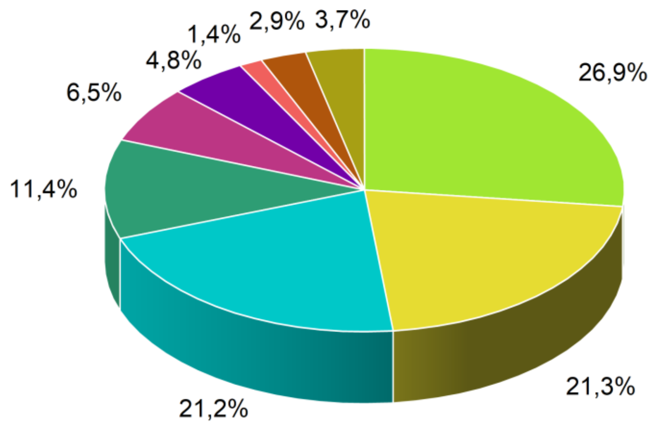
XRF RESULTS

SS

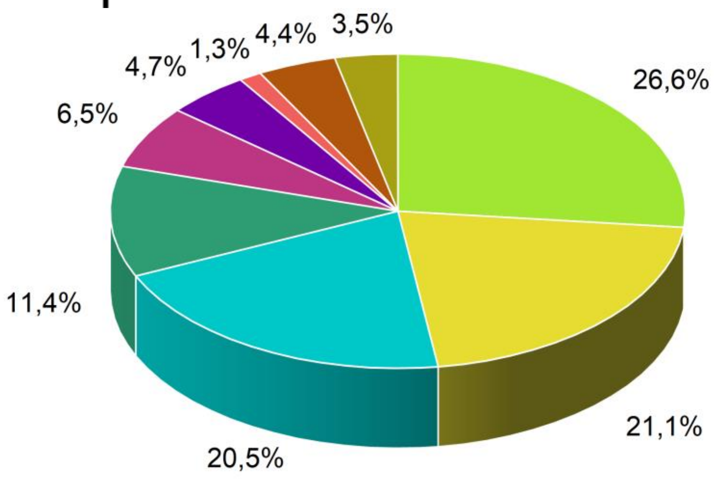




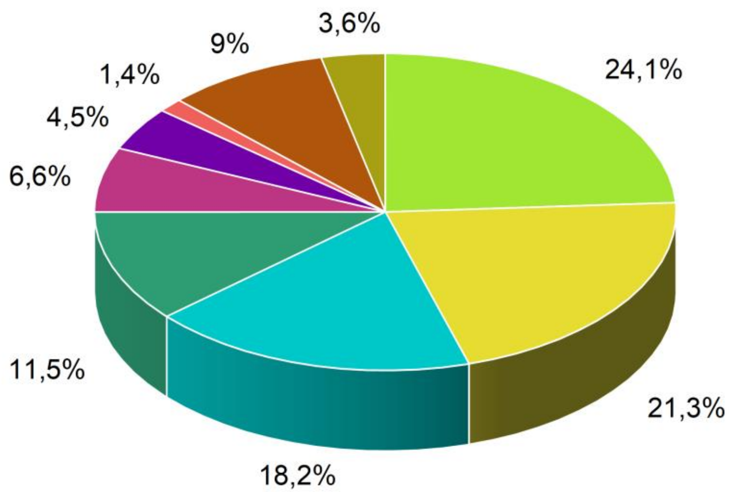
HTC



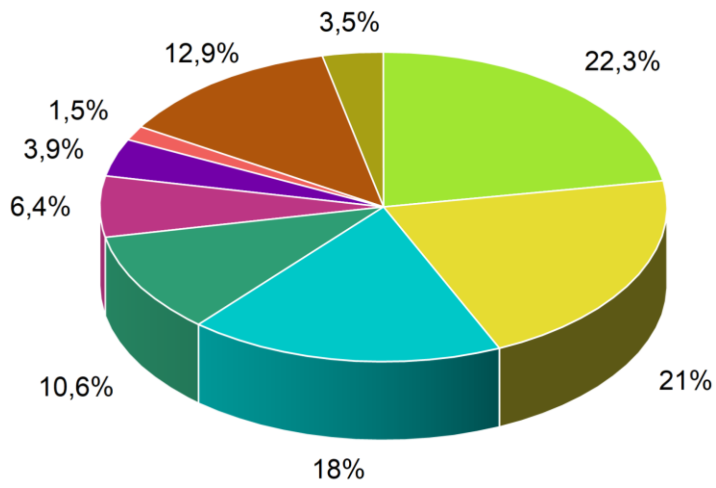
HTC_pH=5



HTC_pH=3.5



HTC_pH=2



METHODS for LIQUID SAMPLES

Type of analysis	Norm/method	Instrument
pH and conductivity	-	Multifunction Laboratory Meter CX-505 ELMETRON
Ultimate analysis CHNS	PKN-ISO/TS 12902:2007/combustion in oxygen 950 ^{o}C	Elemental Analyser Truespec Leco CHNS628
Heavy Metals (Cd, Cr, Cu, Fe, Pb, Hg, Ni, Zn) Alkali metals (Na) Alkali earth metals (Ca, Mg) Nonmetal (P)	PN-EN ISO 17294-2:2016-11/Inductively coupled plasma-mass spectrometry (ICP-MS) PN-EN ISO 11885:2009/ Inductively coupled plasma-optical emission spectrometry (ICP-OES)	iCAP RQ using the Thermo Fisher Scientific Spectrometer Optima 7300 dv Perkin Elmer Spectrometer

CHARACTERISTICS OF POST-PROCESSING WATER

	HTC	HTC_pH=5	HTC_pH=3.5	HTC_pH=2
Ultimate analysis				
C, %	2.84	2.76	2.56	2.59
H, %	10.10	9.66	9.72	9.40
N, %	0.58	0.57	0.56	0.57
pH	5.93	5.35	5.14	4.82
Conductivity, mS/cm	7.32	8.51	6.67	13.02

ICP-OES and ICP-MS analyses

Elements ml/g	Post-processing water HTC	HTC_pH=5	HTC_pH=3.5	HTC_pH=2
Cd	<0.0003	<0.0003	<0.0003	<0.0003
Cr	0.789	0.612	0.496	0.457
Cu	<0.001	<0.001	<0.001	<0.001
Fe	46.76	40.42	33.39	34.93
Pb	<0.0001	<0.0001	<0.0001	<0.0001
Hg	0.0016	0.0002	0.0002	0.0002
Ni	0.271	0.193	0.194	0.215
Na	103.3	91.1	96.2	108.1
Zn	0.349	0.342	0.512	0.838
Ca	106.1	275.2	467.2	592.7
Mg	91.9	101.2	149.7	243.9
P	452.2	487.4	698.8	862.2

CONCLUSIONS

Sulphuric acid as a catalyst in hydrothermal carbonization of sewage sludge caused:

- in hydrochars:

- modification of specific surface area (20 times higher than sewage sludge)
- an increase in ZnO and CuO and PbO
- a decrease in CrO and NiO
- did not affect combustion process and functional groups of hydrochars

- in post-processing water:

- a decrease in the heavy metals including Hg, Cr, and Ni contents
- an increase in P, Mg, Ca, and Zn

- Phosphorous recovery will be next step of investigation

Thank you for your attention

Acknowledgements

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