Properties and beneficial uses of biochar from sewage sludge pyrolysis

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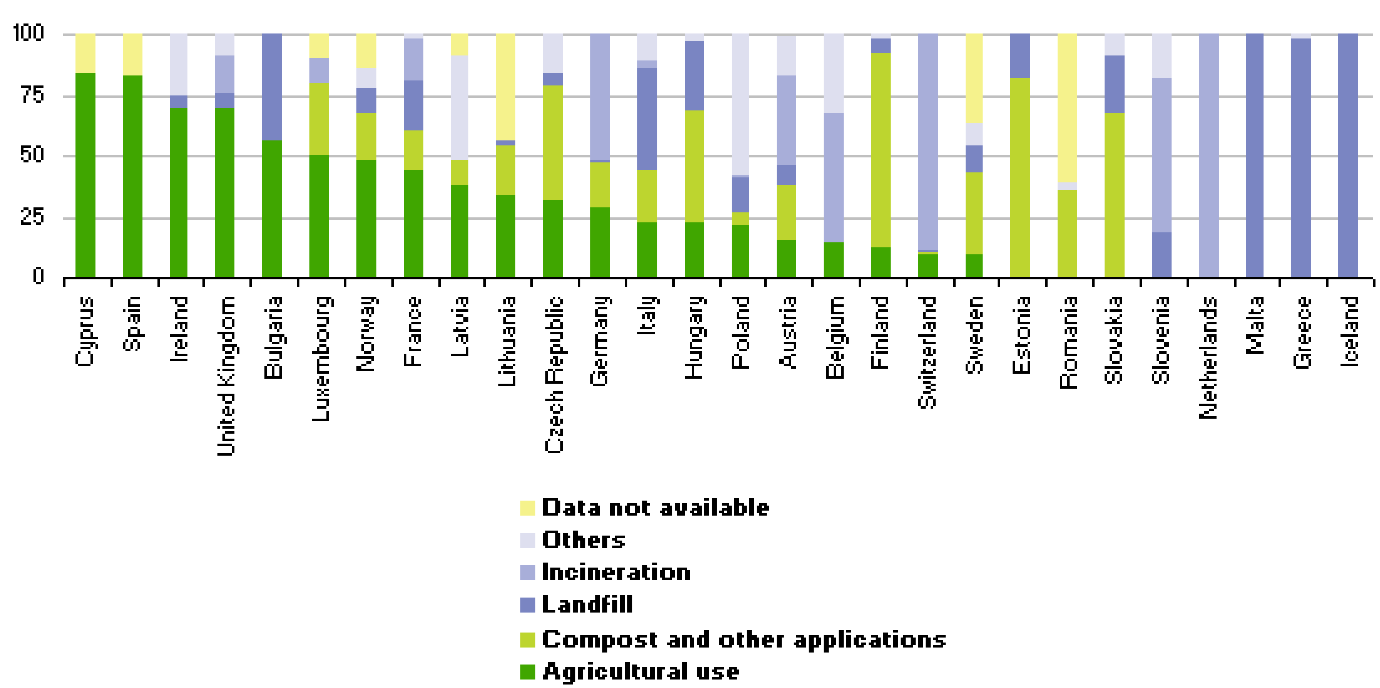
Residual sludge disposal costs may constitute up 50% of the total cost of operation of a WWTP, and contribute approximately 40% of the total greenhouse gas (GHG) emissions associated with it.

After appropriate treatment, sludges are mostly disposed of in landfill, agriculture (including composting), or incinerated.

Landfill Directive 99/31/EC set restrictions for bio-degradable municipal wastes disposed in landfills; in addition, national legislations of some EU Member States have set very strict limits for organic matter or total organic carbon (TOC) contained in disposed sludge, prohibiting *de facto* its landfilling.

Sewage Sludge Directive 86/278/EEC concerning beneficial use of sludge on soils, seeks to encourage safe use of sewage sludge in agriculture, regulating this form of disposal to prevent harmful effects. EU countries have set more stringent requirements for heavy metals in sludge.

Sewage sludge disposal by type (2009)



(1) Belgium, Germany, Luxembourg, Netherlands and Austria, 2008; Czech Republic, Ireland, Latvia and Slovakia, 2007;Greece and Switzerland, 2006; Italy, Cyprus and the United Kingdom, 2005; France and Hungary, 2004; Iceland, 2003; Sweden, 2002; Finland, 2000; Denmark and Portugal, not available.

Source: Eurostat (env_watq6)

Is incineration the best solution?

Thermal processing of sludge is a convenient and efficient approach for the disposal of waste urban sludge. It can take different forms, for example:

- co-firing in power plants and heating plants with coal
- co-firing in cement kilns

Limitations

- large part of the energy recovery must occur locally (heat), only a fraction (20-25%) can be transferred easily (electricity)
- process residual (ashes) are hazardous wastes and must be disposed of accordingly

Pyrolysis can be a good alternative

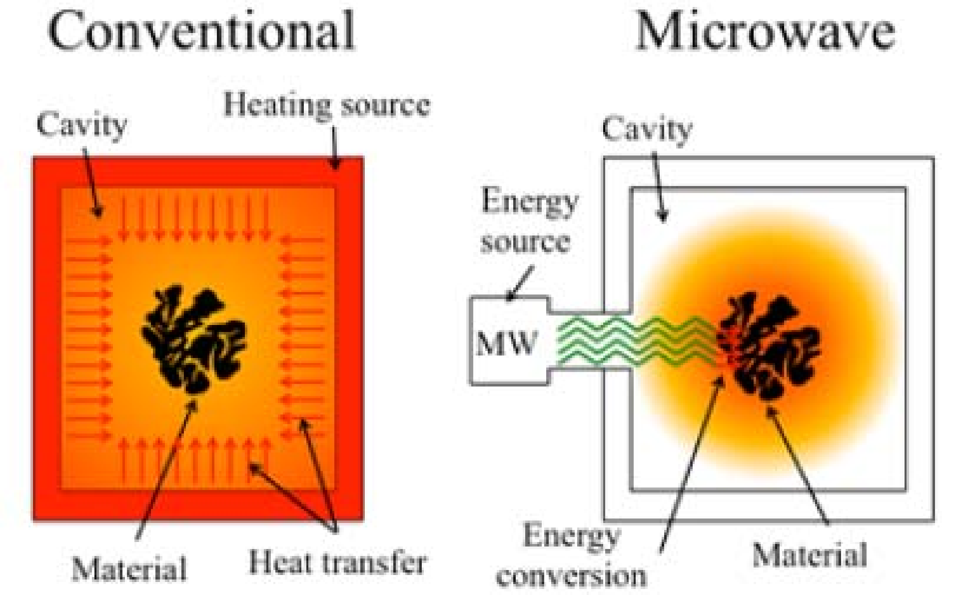
good alternative to classical incineration is pyrolysis, the thermal degradation of ganic material in oxygen-deficient atmosphere. It transforms biomass into oducts such as **bio-oil (~17 MJ/kg), syngas (~6 MJ/kg)** and **biochar (18 MJ/kg)**. l these sub-products have high energy content!

	Slow pyrolysis	**Flash pyrolysis**	**Gasification**	**Fast pyrolysis**
Temperature	>400^{o}C	800-1300^{o}C, under pressure	800-1200^{o}C	500-1200^{o}C
Heating rate	ΔC < 1^{o}C/sec	ΔC>1000/s	ΔC < 1^{o}C/sec	10<ΔC <300 ^{o}C/sec
Residence time	>7 min.	< 0.5 sec	>15-20 min.	< 20 sec
Products (by mass)	35% biochar 35% syngas 30% bio-oil	60% biochar 40% volatiles	85-95% syngas 5–15% char traces of bio-oil	50–70% bio-oil 10–30% biochar 15–20% syngas
Vapour separation	Usually not	Yes	No	Yes
Heat recovery	Usually not	Usually yes	Yes	Yes
Exhaust	To atmosphere, as is, or combusted	Controlled	Controlled	Controlled
Energy generation	From exhaust combustion	From volatiles	From syngas	From syngas
Use	Mostly developing countries (charcoal) Limited substrates applicability	Maximization of biochar production. Applicable to a wide variety of feedstocks	Maximization of syngas.	Maximization of biooil. Applicable to a wide variety of feedstocks.

Classes of pyrolysis processes (elaborated from: Motasemi and Afzal; 2013 Zhang et al., 2017)

But microwave-assisted pyrolysis could be a better alternative!

MAP technology presents several advantages over conventional pyrolysis, including:



- uniform internal heating for material particles, since electromagnetic energy is directly converted into heat at molecular level;
- ease of control due to its instantaneous response;
- simple set-up, facilitating its adaptation to large-scale industrial processes;
- reduced need for feedstock grinding;
- low cost, as microwave is a mature and energy-efficient technology.

Sewage Sludge Biochar characteristics

Sewage sludge contains valuable nutrients such as nitrogen, phosphorus, organic matter and essential trace elements that can improve soil physical properties and, as fertilizers, increase crop yields.

The concomitant contents of heavy metals and other toxic/ dangerous compounds (micropollutants, pharmaceutical compounds), however, may affect soil-plant systems and threaten human health.

It has been shown that pyrolytic conversion of sewage sludge is advantageous over conventional incineration concerning fuel economy, nutrient recovery, and control of heavy-metal emissions.

Characteristics of biochars produced from different sewage sludges at different temperatures:

Source	Zielinska et al., 2015				Lu et al., 2013			Agrafioti et al., 2013			Antunes et al., 2013			Authors		
Type of sludge	Municipal WWTPs (4)				municipal WWTPs (3)			municipal WWTP			Municipal WWTP			municipal WWTP		
Pyrolysis process	Traditional slow				Traditional slow			Traditional			MAP			Monomodal Microwave-assisted		
Sample/ Temp. °C	Orig.	500	600	700	Orig.	300	600	Orig.	300	500	Orig.	300	800	Orig	270	500
Yield (% dry w.)	-	45-54	43-51	40-49	-	n.d.	n.d.	-	58.1-64	27-31	-	91	77	-	-	-
Ash content (%)	55.8-61.3	64-73	63-77	68-79	n.d.	n.d.	n.d.	25.9	n.d	n.d.	55.5	55.8	63.3	52-55	54-57	58-61
Carbon (C, %)	21.6-26.2	18.9-26.6	18.4-27.7	18.1-27.8	23.8-33.2	21.7-31.5	15.2-26	37.9	39.7	9.8	19.9			22-25	20-22	17-21
(O+N)/C	0.32-0.66	0.25-0.29	0.15-0.28	0.09-0.21	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1			-	-	-
S_{micro} (m^2g^{-1}) (Micropore surf.)	-	7.1-19.4	2.8-7.7	1.4-27.7	-	4-6.7	6.3-18.2	-	0.5-18	4-90	16.64	50.06	64.67	-	-	-
pH	7.01-7.39	7.08-7.25	80.5-11.4	12.2-13.1	6.08	6.2	9.6	5.9	6.0	11.6	6.13	6.42	6.6	7.2-7.45	7.3-7.55	7.5-7.88

Yield

An increase in pyrolysis temperature generally results in a decrease in biochar yield (as % dry weight), due to the volatilization of organic fractions.

pH

pH increase with increasing pyrolysis temperature is typically observed for biochars derived from sewage sludge and other feedstocks.

Carbon and inorganic constitutents

Most studies on sewage sludge pyrolysis show a reduction C percentual changes in the produced biochars compared to the original feedstock. C losses are likely due to increased volatility of C during pyrolysis.

Sewage sludge susually contain high concentrations of silica, although it is difficult to exactly predict ash content in biochars, based on the mineral components content of original sewage sludge. Regardless of pyrolysis temperature, the percentage of ash in biochar is higher than in the feedstock, and moreover an increase in temperature will cause an increase in the percentage of ash in pyrolyzed sewage sludge.

Phosphorus, Nitrogen

The P content of sewage sludge is further concentrated (by about 40-100%) when pyrolysed at temperatures above 600ºC. This indicates that phosphorus is associated with the inorganic fraction of the sludge.

N content of the sludge is decreased in biochar when process temperature is increased, due to volatilisation of nitrogen during pyrolysis through loss of the NH_4-N and NO_3-N fractions, as well as the loss of volatile matter containing N groups.

Porosity

Sewage sludges are practically nonporous. As a result of pyrolysis, a material with a more developed surface is obtained from the feedstock. The increase in surface area can vary widely, between 6 to almost 40 times.

Metals

Sewage sludge contain high concentrations of metals, which accumulate in the biochar with the increase of pyrolytic temperature. Also the stability of heavy metals in biochar increases with pyrolysis process temperature, therefore their leaching potential is greatly reduced.

Source	**Zielinska et al., 2015**				**Lu et al., 2013 (note different data units)**			**Authors**		
Sample/Temp °C	Original	500	600	700	Original	300	600	Original	270	500
Fe (% d.w.)	1.1-6.8	2.4-11.5	2.37-12.5	2.6-13.2	0.8-23.2*	18.6-37.6*	0.06-43.2*	2.2-4.9	2.8-7.3	3.68-9.4
Si (% d.w.)	2.5-5.8	4.8-9.1	5.1-9.4	5.5-97	-	-	-	2.8-5.3	3.6-8.6	4.6-10.2
P (% d.w.)	3.4-4.9	5.4-9.6	5.3-9.2	5.6-9.5	20-28.4*	29.5-42.6*	35.5-57.6*	3.6-4.5	4.72-7.18	5.2-9.82
S (% d.w.)	1.5-3.8	1.37-4.6	1.2-3.97	1.37-5.2	0.7-1.1	0.5-0.67	0.43-0.57	1.65-4.02	1.88-4.5	1.85-4.3
Al (% d.w.)	1.8-2.5	2.3-3.3	2.6-3.7	2.7-3.9	26.2-31*	38.1-52*	50.8-55.2*	1.98-2.75	2.17-2.94	2.15-3.33
Mg (% d.w.)	0.57-2	0.9-3.3	1.08-2.6	1.1-2.4	4.1-6.3*	8.2-11*	9.3-14.5*	0.8-2.3	0.85-2.87	1.03-3.06
K (% d.w.)	0.5-0.8	0.9-1.4	1.0-1.55	1.1-1.64	0.8-1.2*	1.6-2.1*	2.6-2.8*	0.6-0.95	0.7-1.1	0.69-1.6

*results in g/kg

Beneficial uses of biochar: current and potential applications

In biologic wastewater treatment processes, sorption to biosolids is one of the primary removal pathways for many hydrophobic chemicals.

Industrial and non-domestic effluents may also cause the sludge to contain many toxics in addition to organic material.

Land application of sewage sludge was widely used in view of its soil conditioning properties. Macronutrients in sewage sludge serve as a source of plant nutrients and the organic constituents provide beneficial soil conditioning properties.

Its heterogeneous nature and variability, however, require knowledge of its composition prior to such applications. Uninformed sludge soil-amendment may disturb soil properties, especially when containing high concentrations of metals and toxic constituents, which may accumulate

Beneficial uses of biochar: current and potential applications

Mass balance studies on antibiotics show that, while wastewater treatment as a whole results in reduction of compounds mass of about 90%, approximately 84% is due to sorption on sewage sludge, without further significant removal under methanogenic conditions in sludge digesters.

Analysis of sludge samples shows that pharmaceuticals accumulate in sewage sludge from WWTPs in concentrations up to 100 ng/g. This indicates that even good removal rates obtained in the aqueous phase (i.e. determined by comparison of influent and effluent wastewater concentrations) do not actually imply degradation of the compounds to the same extent.

Beneficial uses of biochar: current and potential applications

Soil amendment with biochar eliminates these problems, as:

- Inorganic compounds (incl. metals) are deeply adsorbed into biochar granules, and are only minimally leached, in addition biochar may have the capacity of adsorbing additional metals present in the soil;
- Organic compounds (incl. pharmaceuticals and other CECs) are mostly destroyed during the pyrolysis process, so they are not transferred to the soil by the biochar.

SOME SPECIFIC APPLICATIONS OF BIOCHARS:

Agricultural uses

Biochar improves:

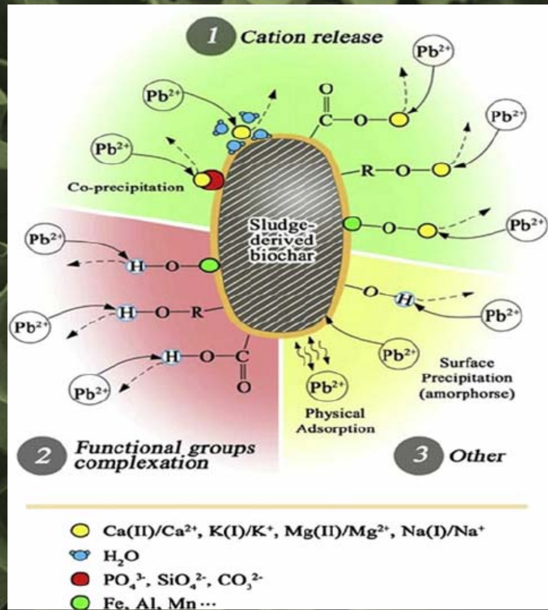
- **the yield of some crops**
- **nitrogen fertilisers use efficiency by improving the chemical properties of soil**
- **soil cation exchange capacity (CEC) by up to 40% and soil pH by up to one pH unit, with improvement of plant available nutrients, and carbon sequestration**
- **soil quality, as it enhances soil aeration, increasing water holding capacity and environmental conditions for the growth and development of plant root systems**

Difference between plants grown in regular and biochar-amended soil (darker soil on the right).

Remediation and restoration of contaminated soils

Demonstrated potential for reducing organic and inorganic contaminants present in soils in mobile forms: increasing the organic fraction content of soil, its pollutants adsorption properties are increased, and therefore its capacity to reduce their bioavailability, resulting in a reduced risk.

Biochars obtained at high temperatures ("activated") will have the highest organic contaminant remediation potential.



Conceptual illustration of the possible mechanisms of Pb adsorption on biochar (from Lu et al. 2012).

Water and wastewater treatment

Likewise biochar can be a proper adsorbent to remove pollutants from aqueous solutions. Adsorption efficiency of biochar is influenced by its properties, dosage, competitive anions, and solution temperature and pH.

Carbon sequestration

Biochar contains a considerable fraction (roughly 1/4 to 1/3) of the carbon initially contained in sewage sludge.

The half-life of C in soils is in excess of 1000 yr, indicating that soil-applied biochar will make not only a lasting contribution to soil properties and quality, but also that it will be removed from the atmosphere and sequestered in the soil for millennia!

Substitution of fossil fuels with crop-derived bio-oils could raise some ethical and sustainability issues (i.e. foodcrops use competition), waste sludge is by all means an available and obligatorily disposable by-product of wastewater treatment, that may itself constitute, if not properly disposed of, an environmental problem.

Processing of urban sludge with pyrolysis not only allows recovery of valuable products, but also improves the characteristics of environmental compatibility of the final resulting solid fraction.

OTHER USES

Biochar for catalyst production

Biochar can also work as catalyst for conversion of syngas into liquid hydrocarbons by Fischer–Tropsch synthesis and be a good precursor for producing heterogeneous acid catalysts (solid acid catalyst) for esterification/transesterification of vegetable oils/animal fats for biodiesel production.

Biochar as gas adsorbent

CO_2 capture and storage is a promising strategy to reduce GHG-CO_2 emissions. For effective capture and removal, high CO_2 selectivity and adsorption capacity are required, in addition to adsorbent medium long life, ease of regeneration, and low cost. Biochar-based activated carbons have shown adsorption capacity similar to the highest reported for carbon materials.

Biochar in microbial fuel cell (MFC) systems

Biochar can also be used as low-cost anode material in microbial fuel cells (MFC), a technology that can simultaneously remove organic matter from wastewater and soil, with direct generation of electricity. Electrode materials used in MFCs are normally granular activated carbon or graphite granules, which average cost ranges from $500 to $2500 per ton. Biochar was found to be a promising alternative source material for MFC construction.

Biochar-based supercapacitors

Supercapacitors are energy storage devices that can store energy from renewable sources, due to high-power densities, long cycle lifes, and quick charge/discharge capabilities. The preferred raw materials for making supercapacitors is carbon material with high specific surface area and porous structure. Recently, biochar was used for fabrication os supercapacitors, indicating that its use of biochar is promising thanks to low cost and satisfactory performance.

Conclusions

Sewage sludge pyrolysis biochar may be an additional important resource for reuse in agricultural and many other environmental or industrial applications.

Feedstocks utilized for biochar production, as well as the production process itself, influence biochar characteristics.

Literature shows that pyrolysis processes affect quality and quantity of the produced biochar, and thus its environmental behavior. Among these, *pyrolysis temperature* has the largest effect on biochar quality, as its increase decreases biochar yield, N content, increasing at the same time biochar's pH, specific surface area, carbon content, available nutrients and heavy metal stability.

Generally speaking, biochar produced at low temperatures is suitable for agricultural uses, while the one produced at higher temperatures has greater effectiveness in adsorbing contaminants present in soils.

Increased sewage sludge biochar exploitation can provide new incentives for agriculture improvement and investment development, offer farmers additional sources of income, help in carbon sequestration, increase crop and land yield and productivity, improve sustainable land use in agriculture, and provide new incentives for municipal solid waste (MSW) and sludge treatment research and development as well.

The use of waste biomass for biochar production is not only economical but also highly beneficial. Initially, expected benefits mainly included soil improvements, energy production and climate change mitigation, however, as research on possible uses picks up momentum, their range seems to expand exponentially. Despite this justified optimism, however, a number of research gaps and uncertainties still exist that need more specific, relevant investigations.

Biochar characteristics vary widely according to original, individual feedstock types and pyrolysis processing conditions.

Definition of a stanardized protocol for biochars properties characterization would help researchers in matching best specific uses and production processes.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