Properties and beneficial uses of biochar from sewage sludge pyrolysis

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Abstract

Residual sludge disposal costs may constitute up, and sometimes above, 50% of the total cost of operation of a WWTP (Wastewater Treatment Plant) and contribute approximately 40% of the total greenhouse gas (GHG) emissions associated with its operation. Traditionally, wastewater sludges are processed for: a) reduction of total weight and volume to facilitate their transfer and subsequent treatments, b) stabilization of contained organic material and destruction of pathogenic microorganisms, elimination of noxious odors, reduction of putrefaction potential and, since a few decades, and at an increasing degree, c) value addition by developing economically viable recovery of energy and residual constituents.

Among several other processes, pyrolysis of sludge biomass was experimented by some researchers. From the process, oil with composition not dissimilar to that of biodiesels, syngas and a solid residue can be obtained. While the advantage of obtaining sludge-derived liquid and gaseous fuels is obvious to most, also the solid residue from the process, or biochar, may have several useful, initially unexpected applications. Recently, biochar is getting attention from the scientific community due to its potential to improve agricultural soils productivity, remediate contaminated soils, and supposed, possible mitigation effects on climate change. This paper first discusses sludge-pyrolysis derived biochar production fundamentals (including relationships between biochar, bio-oil and syngas fractions in different process operating conditions, general biochar properties and possible beneficial uses) then, based on current authors' experiments with microwave-assisted sludge pyrolysis aimed at maximization of liquid fuel extraction, evaluate specific produced biochar characteristics and production to define its properties and most appropriate beneficial use applications in this type of setting.

Keywords: wastewater sludge; pyrolysis; microwave-assisted pyrolysis; biochar; biodiesel; biochar applications

Introduction

Residual sludge disposal costs may constitute up, and sometimes above, 50% of the total cost of operation of a WWTP (Wastewater Treatment Plant) and contribute approximately 40% of the total greenhouse gas (GHG) emissions associated with its operation (Liu et al., 2013). The safe disposal of such sludge is literally a “big” issue in urban wastewater treatment: at the European Union level, the 2012 sludge production was estimated in 11 million tons dry weight, expected by year 2020, to have a further increase of more than 30%. Traditionally, wastewater sludges are processed for: a) reduction of total weight and volume to facilitate their transport and subsequent treatments; b) stabilization of contained organic material and destruction of pathogenic microorganisms, elimination of noxious odours, reduction of putrefaction potential; c) value addition by developing economically viable recovery of energy and residual constituents. After appropriate treatment, sludges are mostly disposed of in landfill, agriculture (including composting), or incinerated.

Landfill Directive 99/31/EC set restrictions (quantitative targets) for bio-degradable municipal wastes (such as sewage sludge) disposed in landfills; in addition, national legislations of some Member States have set very strict limits for organic matter or total organic carbon (TOC) contained in disposed sludge, prohibiting *de facto* its landfilling. According to recent Eurostat data, in fact, significant abandonment of sludge landfilling is occurring in most of Europe, except for Italy, Denmark, and Estonia.

Sewage Sludge Directive 86/278/EEC concerning beneficial use of sludge on soils, seeked to encourage safe use of sewage sludge in agriculture (composting is often included as a form of agricultural disposal in official reporting), regulating this form of disposal to prevent harmful effects. After concerns raised about possible harmful compounds accumulation in soils, 16 (out of 27) EU countries have set more stringent requirements for heavy metals in sludge, compared to the Directive's provisions, and 10 countries set stricter limit values for heavy metals in soil. Such restrictions are being strengthened periodically, while most EU countries have outright prohibited the disposal of untreated sludge in soil. Composting is applied more often in the new EU-12 countries, comparing to EU-15. According to Eurostat, increasing trend of overall agricultural uses (including composting) is observed in 7 (out of 15) old countries and 6 (out of 12) new countries. The most significant increases are observed in Portugal, Cyprus and Bulgaria, while significant decreasing trends are observed in Slovakia and Czech Republic, where direct agricultural disposal seemly is replaced by composting.

Finally, incineration is enforced in most EU-15 countries. Greece, Slovenia, Germany and Netherlands present the greatest increasing trends, even though the first two countries export sludge for incineration; Denmark, Austria, Belgium and Italy show instead decreasing incineration trends (Kelessidis and Stasinakis, 2012).

Thermal processing of sludge remains, however, a convenient and efficient approach for the disposal of waste urban sludge without causing excess secondary pollution, which is used as much as possible in many countries. Thermal utilization of sludge comes into play when the sludge does not comply, or is in excess, with requirements for disposal in agriculture, and allows forms of energetic recovery. Thermal processing of sludges can take several forms. Co-firing in power plants and heating plants with coal (approximately 5% sludge) does not significantly decrease the temperature of the combustion process and usually does not require extra investment costs for off-gas cleaning, as filters and separators can handle this component. Co-firing in cement kilns was considered the most convenient technology in terms of both sludge disposal and utilization: one ton of dried sludge can substitute up to 0.33 t of raw material and, since ash from sludge is bound to cement clinker, this can be considered a waste-less technology. This is actually considered a ‘‘waste-to-energy’’ system, and is acceptable if no other environmentally friendly technology can be applied (Capodaglio et al., 2016a). Incineration (with urban solid waste, or in special sludge incinerators) is another option, where the energy contained in the sludge contributes to the energy balance of the process.

An alternative option to classical sludge incineration is pyrolysis, which can achieve 50% or more reduction in waste volume, stabilization of organic matter, as well as recovery of valuable end products. Pyrolysis is the thermal degradation of organic material in an oxygen-deficient atmosphere, a second-generation alternative bioenergy production technology that is relatively simple, inexpensive, and robust, and can be used for transforming biomass into products such as bio-oil, biochar, and syngas. Among several other processes, microwave-assisted pyrolysis (MAP) of sludge biomass was experimented by some researchers (Menendez et al., 2002). MAP takes generally a much shorter time than conventional pyrolysis, where the process is induced by a furnace, as the heating of feedstock biomasses by microwave is more uniform. Obtained oil composition is not dissimilar to that of biodiesels obtained from common feedstock (food-) crops, although with a slightly lower calorific value.

While the advantage of obtaining sludge-derived liquid fuels is easily obvious to most, also the solid fraction residue from the process (biochar) has been found to have several useful, unexpected applications. Biochar is a new technical term indicating “*the porous carbonaceous solid produced by the thermochemical conversion of organic materials in an oxygen depleted atmosphere that has physicochemical properties suitable for safe and long-term storage of carbon in the environment”* (Shackley et al. 2012). Biochar could also be used to generate energy, however recently, biochar is getting attention from the scientific community due to its potential to improve agricultural soils productivity, remediate contaminated soils, and supposed, possible mitigation effects on climate change. Process operational temperature has a substantial effect on the quality of biochar produced: biochar produced at low temperatures is most suitable for agricultural uses, due to carbon content and nutrient availability, while higher temperatures can improve its porosity and thus enhance its effectiveness in adsorbing contaminants present in soils (Agrafioti et al., 2013). Researchers have shown that the pyrolysis process can suppress heavy metal release by non-impregnated biochars, resulting in an extremely low environmental risk using sludge-derived biochar as soil ammendant (unlike the case of sludge as is). Biochars obtained under different processes significantly differ from one to another in their properties, depending on the type of biomass used to produce them, its growth conditions and also on pyrolysis operating conditions. Nevertheless, the concept of biochar production from sewage sludge has become increasingly popular in recent years.

This paper will first discuss sludge-pyrolysis derived biochar production fundamentals (including relationships between biochar, bio-oil and syngas fractions in different process operating conditions, general biochar properties and possible beneficial uses) then, based on current authors’ experiments with sludge pyrolysis aimed at maximization of liquid fuel extraction, evaluate specific produced biochar characteristics and production to define its properties and most appropriate beneficial use applications in this type of setting. Biochar obtained from wastewater treating microalgae or street-side grass clippings is also examined for relevant properties.

Fundamentals of sludge pyrolysis: technologies and final products

Pyrolysis is a thermochemical process that can be used to transform biomass and other waste materials (e.g. rubber tyres) into bio-oil (energy content ~17 MJ kg-1), biochar (energy content ~18 MJ kg-1), and syngas (energy content ~6 MJ kg-1). The process has been used to produce “charcoal” for thousands of years; initially, the volatile fraction was usually dispersed in air, giving these systems bad environmental reputation (causing deforestation, air pollution). In modern facilities, technology has been modified to avoid gross pollution and transform most of the biomass into renewable energy products. Four classes of traditional pyrolysis processes can be identified: slow pyrolysis, flash pyrolysis, gasification, and fast pyrolysis (Table 1).

Table 1 Classes of pyrolysis processes (elaborated from: Motasemi and Afzal; 2013 Zhang et al., 2017)

	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	$\Delta C < 1^{o}$C/sec	$\Delta C>1000$/s	$\Delta C < 1^{o}$C/sec	$10<\Delta C<300\ ^{o}$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.

Pyrolysis products

Syngas is primarily composed of H_2 and CO, with smaller quantities of CH_4, CO_2, H_2O, and other low molecular-weight volatile organics. While its heating value is low (~6 MJ kg-1) compared to natural gas (~54 MJ kg-1), it can provide fuel for hot water, drying or electricity. Some time ago, before widespread availability of natural gas, syngas was generated to provide energy for home heating, cooking, street lighting, etc (a.k.a. “town gas”).

Sanchez et al. (2009) studied pyrolysis oil composition with gas chromatography-mass spectroscopy (GC-MS) and found that pyrolysis oil was a complex mixture of organic compounds. Volatile oil (and gas) produced in the pyrolysis process showed high heat value, slightly lower than some fossil fuels; bio-oil consists of a wide range of oxygenated organic compounds including organic acids, aldehydes, alcohols, phenols, carbohydrates, and lignin-derived oligomers. Its chemistry and energy value are quite variable and vary substantially, depending on original feedstock, and processing conditions. Most bio-oils are acidic (pH ~2) and tend to solidify after being stored for prolonged periods of time, therefore their use as fuel oil in many desirable applications (i.e. home heating, diesel transportation fuel, exception made for industrial boilers) requires postprocessing to correct acidity and improve stability, or upgrade it to synthetic transportation fuels (biogasoline, biodiesel). Biooils can also be refined into ethanol and/or other chemical compounds. The European Union (EU) is currently pursuing an extended use of alternative liquid fuels in transportation uses, including biooils derived from biomasses (Raboni et al., 2015).

Biochar is the solid residue of the process, with high energy content, that can be therefore burned in systems fed with pulverized coal. NO_x emissions from biochar combustion are comparable to those of coal, requiring similar abatement technologies. Some types of feedstock (i.e. urban sludge) may contain relatively high levels of metals that concentrate in biochar after pyrolysis. Biochars, however, may also have many other attractive, high value uses, in fields such as chemistry, metallurgy, agriculture, waste treatment, etc., that will be analysed in a later section.

Pyrolysis technologies

In conventional biomass pyrolysis processes, energy production is the main target; in sewage sludge pyrolysis, the main purpose is its safe and economic disposal, with energy (oil, syngas) and material (biochar) recovery as an added benefit. Fundamentally, pyrolysis involves the heating of organic materials to high temperatures (usually greater than 400°C) in the absence of oxygen. In these conditions, organic materials thermally decompose releasing a vapor phase and a residual solid phase (biochar). Both oil and gas leave the pyrolysis furnace in volatile form. After cooling, polar and high molecular-weight compounds condense as liquid (bio-oil) from the vapor phase, while low-molecular-weight volatile compounds remain in gas phase (syngas). The main operating parameters in pyrolysis are heating rate, process temperature, and residence time, on which depend the physics and chemistry of the rather complex pyrolytic reactions.

Microwave technology has recently emerged as one of the most promising methods of enhancing and accelerating chemical reactions, due to effective heat transfer profiles. It is therefore being adopted as one of the best technologies available in pyrolytic processes, since it reduces residence time and brings significant energy savings (Motasemi and Azfal, 2013). Microwave-assisted pyrolysis (MAP) technology is an alternative heating method already in use in biomass pyrolysis for biofuels production presenting 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. The different heating mechanisms make MAP products retain different characteristics than those obtained with conventional heating.

MAP of biomasses feedstock develops according to two stages: drying and pyrolysis. During the former, biomass temperature increases to 150~200 ^{o}C, with most of the moisture content evaporating with some volatile matter release. During actual pyrolysis, when process temperature can raise to almost 450 ^{o}C, dry feedstock is decomposed to form oil, gas components, and solid char. Since water has very good microwave absorbability, its biomass content results in high temperature rising rates during initial drying. As the temperature continues to increase, the biomass becomes less absorptive towards microwave irradiation, and temperature rising rates slow down (Budarin et al., 2015). Masek et al. (2013) showed that in case of MAP, pyrolysis of some feedstocks can occur even at lower temperatures (down to 200 $^{\circ}$C) than those reported for conventional heating.

Due to the properties of microwave heating, therefore, MAP provides faster heating, better efficiency, and a faster, more controllable process compared to conventional pyrolysis. Unfortunately, while other feedstocks behave well with this process, sewage sludge biosolids are poor absorbers of microwave irradiation (Brodie et al., 2014); therefore, dielectric materials, able to better absorb microwave energy, are often added to the sludge to reach temperatures required for pyrolysis. These work as “hot spots”, absorbing microwave energy and conductively transferring it as heat to the surrounding material. Carbon-based materials, including biochar, are often selected as microwave absorbers because of their effectiveness, and relatively low cost.

Despite these and other advantages of microwave over conventional heating methods, only a few studies have been conducted on sewage sludge pyrolysis with microwave technology, and the effects of catalysts on the process.

MAP applied to bio-oil production from sewage sludge was reported by Tian et al. (2011) as a feasible method to obtain maximum yields from the process. It was shown that by adjusting exit power, it was possible to select the desired gas, bio-oil and solid fraction yields. The maximum bio-oil yield of 49.8% was obtained at 400W microwave exit power for 6 min, while increasing power from 200W to 1200W, the solid fraction yield decreased from 77.3 wt% to 32.6wt%, and bio-gas yield increased from 4.4wt% to 60.21 wt%, respectively. Bio-oil production from sewage sludge by MAP was also tested by Lin et al. (2012), who studied the effects of reaction parameters and chemical additives on produced oil yield, and quality. Five types of additives (KOH,H_2SO_4, H_3BO_3, $ZnCl_2$, and $FeSO_4$) were tested. All catalysts decreased the quantity of bio-oil produced, while KOH, H_2SO_4, H_3BO_3, and$FeSO_4$ improved its quality (calorific value, density, viscosity, carbon content). $ZnCl_2$ had instead a negative effect on product′s quality. Dominguez et al. (2003) compared bio-oil characteristics obtained from MAP and conventional pyrolysis. Three types of sewage sludge (two from urban WWTPs and one from a dairy factory) enriched with graphite (0.5g-3g/kg) were used as feedstock. Results showed that oil produced using a conventional furnace at high temperatures was of considerable environmental concern, containing “dirty” compounds such as PAHs in high quantity, while the one obtained from MAP had a higher calorific value, and lower proportion of PAHs. The same group of researchers (Domingues et al., 2006) later investigated MAP of sewage sludge for bio-fuel preparation using single-mode and multimode microwave cavities at constant input power, duplicating tests in an electric oven and applying graphite and char as microwave absorbers. The conclusion was that MAP improved the quality of gases produced (up to 38% increase in H_2), in comparison with conventional method, also improving char production and decreasing reaction time by over 51% to 10 min. Single-mode MAP was recognized as a better microwave source for gas production, while multimode yielded higher char production in the tests.

Using monomodal microwave synthetizers (MMSs) instead of multimodal ones, the need for preliminary dry sludge mixing with microwaves receptors additives is eliminated, and the process temperature needed for process completion is lowered (as low as 270^{o}C) (Capodaglio et al., 2016b). Monomodal Microwave assisted Pyrolysis (MMAP) is a MAP-alternative process, that occurs when microwaves produced by a magnetron travel through special wave guides to a circulator, that diverts reflected microwave power into an electromagnetically matched load. A microwave directional coupler, which allows measurement of forward and reflected power, and a three-stub tuner, matching the impedance of the wave-guide segments to the load, directs the microwaves into the single-mode chamber. (Antunes et al., 2017). A similar system was used by Capodaglio et al. (2016a).

Sewage Sludge Biochar characteristics

Excess (waste) 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. Most studies on sewage sludge pyrolysis refer to fuel recovery, however, the effects of sewage sludge biochar on soil, plant nutrients, and bioavailability of heavy metals in plants have seldom been studied (Liu et al., 2014).

Perhaps one of the most comprehensive studies on systematic evaluation of the properties of biochars produced from different sewage sludges at different temperatures is the one that was carried out by Zielinska et al. (2015). In this study, sewage sludge samples were subject to (traditional) pyrolysis in a laboratory furnace at temperatures of 500, 600 and 700 ˚C, with heating rate of 25 ˚C/min, in oxygen-free atmosphere maintained by constant flow of nitrogen gas. The results from the study are compared with results obtained from other authors on biochar obtained from traditional and microwave-assisted sludge pyrolysis (Table 2).

Yield

From the results reported in Table 2 some considerations can be drawn considering sewage sludge biochar characteristics. First, an increase in pyrolysis temperature generally results in a decrease in biochar yield (as % dry weight), due to the volatilization of some organic fractions.

pH

Based on available literature, pH of biochars produced at a low temperatures (≤500 ◦C) mostly depend on sludge pH, resulting in biochars with neutral pH (≈ 7.3). Higher pyrolysis temperatures (≥550 ◦C), on the other hand, promote the formation of biochar with alkaline pH, regardless of the sludge pH. pH increase with increasing pyrolysis temperature is typically observed for biochars derived from sewage sludge and other feedstocks. The phenomenon can be significant: biochars produced from sludge at neutral pH, at high temperatures (up to 700 ◦C), were characterized by pH's ranging from 12.0 to 13.0 (Zieliska et al., 2015). Such increases could be due to polymerization/condensation reactions of aliphatic compounds, dehydration associated with decrease of acidic surface groups during thermal treatment and to the concentration of inorganic constituents in the biochar resulting from the separation of metal salts from the organic matrix at increasing temperatures (Gascò et al., 2005).

Carbon and inorganic constitutents

The carbon percentage in sewage sludges investigated by literature summarized in Table 2, ranged from 21.6 to 33.2%. Generally, sludge pyrolysis does not have significant effect on C percentual changes in the produced biochars, although most studies on sewage sludge pyrolysis show a reduction of this relative to the original feedstock. C losses are likely due to increased volatility of C during pyrolysis.

Both sewage sludges and biochars analysed in Table 2 show high ash content, ranging from 55.8 to 61.3% in sewage sludges and from 64.1 to 79.1% in biochars, showing increase in ash content compared to the feedstock with increasing pyrolysis temperature. Such increase is a typical tendency for sewage sludge (and other feedstock's) biochars, due to concentration of the non-volatile mineral constituents that form the ash, and removal of volatile organic decomposition products. Mineral fractions are, in fact, dominant fractions both in the untreated sewage sludges and in biochars, usually are much higher than in biochars derived from other materials. This seems to be the result of the complexity of sewage sludge, and the diversity of its components. Sewage sludges, in fact, usually contain high concentrations of silica (19–58% in sewage sludge before pyrolysis), although it is difficult to exactly predict ash content in biochars, based on the mineral components content of original sewage sludge. It is however obvious that, regardless of pyrolysis temperature, the percentage of ash in biochar will be higher than in the feedstock, and moreover an increase in temperature will cause an increase in the percentage of ash in pyrolyzed sewage sludge (Novak et al., 2009).

Phosphorus, Nitrogen

The original P content of sewage sludge depends on wastewater treatment processes adopted, an is further concentrated (by about 40-100%) when pyrolysed at temperatures above 600^{o}C. This indicates that phosphorus is associated with the inorganic fraction of the sludge. On the other hand, 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 (Zielinska et al., 2015), although it is difficult to define a straightforward relationship between specific surface area of the initial sewage sludges and surface area of the biochars produced. Increase in surface area with increasing temperature up to 600 ◦C and then its decrease at higher temperatures were observed by Zelinska et al., (2015) and Lu et al. (2013).

Kinetic sorption mechanisms onto biochar from aqueous solutions were investigated by several researchers on samples obtained from traditional sludge pyrolysis. Biochar exhibited significant ability in adsorbing Cr(III), with removal at equilibrium at approximately 70%, while it was not as effective in removing As(V), for which maximum removal capacity (under equilibrium) was approximately 30%. The high differences observed in metal removal could be attributed to favourable electrostatic interactions between the biochar negative surface charge and metal Cations, contrary to Anions (Agrafioti et al., 2013). In terms of phosphorus adsorption, biochar exhibits similar capacity of biosolids, about 15 mg/g, which is almost seven times higher than activated carbon.

Metals in biochar

The composition of sewage sludges is naturally varied and heterogeneous, however, analysis of total heavy metals concentrations in samples from different WWTP feedstocks has been found surprisingly consistent (Table 3). Organic wastes, like sewage sludge, are known to generally contain high concentrations of metals, which accumulate in the biochar with the increase of pyrolytic temperature. Data shown therein demonstrate that metal concentrations are usually less than regulatory limits stipulated in the European Union Council Directive 86/278/EEC (The Sewage Sludge Directive). However, some metals (e.g. Zn and Cu exceed Chinese GB4284-84 standard, which is more stringent than those set in the Sewage Sludge Directive 86/278/EEC. In addition to their concentration, also the stability of heavy metals in biochar increases with pyrolysis process temperature, therefore their leaching potential is greatly reduced.

DTPA extractable fraction has been used to estimate bioavailability of metals in soils and sludge, due to its capacity to chelate a wide range of metallic elements (Halim et al, 2003). To assess the environmental impact of sludge-derived biochar application to soil, heavy metal solubility, mobility and fate in soil. Many researchers who dealt with this issue concluded that heavy metals are practically immobile in biochar, and that the pyrolysis process itself acts to reduce their potential release.

	Pb	Zn	Cu	Cd	Fe	Mn	Source
Total (mg/kg)							
Original	137.5	629-900	401-611	2.28-3.39	14250-20280	253-476.6	Lu et al. 2013
300	198.5-242	849-1493	479-1034	3.30-5.68	24350-28000	425-654.7	
500	211.8-299	1014-1798	565-1257	4.25-6.44	30850-33650	545-783.6	
Extractable (mg/kg)							
Original	21.5-32.5	324-740	63.7-265	0.28-1.84	842-1715	86.9-311.6	
300	n.d.	1.3-8.6	1.28-2.07	n.d.	18.6-116.7	n.d.-8.45	
500	2.5-7.5	18-92.6	15.9-23	n.d.	64.2-281.7	2.52-34.9	

Table 4. Total and extractable (DTPA) heavy metals in sludges

Advantages of biochar vs. dewatered sludge handling

In biologic wastewater treatment processes, sorption to biosolids is one of the primary removal pathways for many hydrophobic, and especially for persistent, bioaccumulative toxic organic chemicals (Cecconet et al, 2017). Even volatile organics, such as benzene, are commonly found in sewage sludges as a result of sorption to organics in the sludge matrix. Land application of sewage sludge was widely used in the past (and still is in some countries) in view of its fertilizer and 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. Industrial and non-domestic effluents may also cause the sludge to contain many toxics in addition to organic material. Uninformed sludge soil-amendment may disturb soil properties, especially when containing high concentrations of metals and toxic constituents, which may accumulate in agricultural soil due to long term uses. Once accumulated, heavy metals are highly persistent in topsoil and may cause potential problems and/or transfer into the food chain. This, in turn, may pose serious risks to human health. Much of the existing literature on organic contaminants was focused on past use chemicals such as PCBs, chlorinated pesticides, and chlorophenols, whose importance as inputs to sewage collection systems, however, declined in the last decade. The biggest scientific interest relating to pollutants concentrations in sewage sludge currently includes endocrine-disrupting substances or other common-use potential toxicants such as linear alkyl benzenesulfonates.

Very few countries have rules limiting the concentration of any organic chemicals in sewage sludges. While accumulation of heavy metals in plants and their effects has been assessed in sludge amended soil, no extensive evaluation has been conducted for xenobiotic organics (XOCs). Giger et al, (2003) investigated occurrence and fate of antibiotics in wastewaters and sewage sludge in Switzerland. Mass balance studies on antibiotics for human use show that, while wastewater treatment as a whole resulted in reduction compounds mass flow of about 90%, approximately 84% was due to sorption on sewage sludge, without further significant removal under methanogenic conditions in sludge digesters. Jelic et al, (2011) observed the presence of 32 target pharmaceutical compounds in three WWTPs influents and 29 in their effluents, in concentrations ranging from low ng/L to a few mg/L. An analysis of sludge samples showed that 21 pharmaceuticals accumulated in sewage sludge from all three 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.

This, and the heavy metal accumulation issue, certainly pose considerable potential public health risks issues when urban waste sludge is disposed of in agriculture. The very process of biochar production, by destroying most of the organic contaminants contained in the sludge is alone capable of eliminating such risks.

Beneficial uses of biochar: current and potential applications

In the introductory section a brief review of the existing methods of excess sewage sludge disposal was presented. This section analyses in greater detail the beneficial uses by which biochar can be disposed of, since the reuse pathways for bio-oils and syngas should be obvious enough. The most appealing feature of biochar is the fact that it is an inexpensive, sustainable and easily-produced material with potentially extensive applications. It has a much lower cost than materials from petrochemical or other chemical processes. In fact, biochar from sewage sludge (a waste material) should be available at a cost very close to the cost of simple disposal of wastewater sludge with current technologies. Even though most applications are still in infancy, biochar has already a number of identifies applications with potentially extraordinary effects, including soil amendment, catalysis, water purification, and many others still to be invented. As mentioned in the introductory section, biochar is the final solid residue of the pyrolysis process. Biochar has a higher energy content than the original feedstock (sludge), therefore, as sludge is, it could be therefore burned in systems fed with pulverized coal, with emissions issues comparable to those of coal, thus requiring similar abatement technologies. In reality, biochars have many other much more attractive, high value, uses, that will be herein analysed.

Agricultural uses

The beneficial effects of biochar produced from various feedstocks on agricultural crops yield and properties of soil have been studies, with findings that biochar significantly improves the yield of some crops (Chan et al., 2008). Biochar addition is also known to improve nitrogen fertilisers use efficiency by improving the chemical properties of soil. Wastewater sludge biochar application was specifically found to increase soil cation exchange capacity (CEC) by up to 40% and soil pH by up to one pH unit (Hossain et al, 2010), with improvement of plant available nutrients, and carbon sequestration. It should be noted that biochar itself will not contribute meaningful amounts of nutrients, given its high stability, but due to its chemical characteristics it will make the ones already present more available.

The accumulation of heavy metals, particularly arsenic, cadmium, chromium, copper, lead, nickel, selenium and zinc, are of great concern in agriculture due to potential threat for human and animal health, and one of the principal reasons for the existing limitations on continuing sludge disposal practices. Hossain et al. (2010) identified 16 metals and trace elements in the biochar applied to a cherry tomato cultivated plot at dose of 10 t/ha to a soil with low agricultural properties due to the poor nutrient availability.

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. ^{o}C	Original	500	600	700	Original	300	600	Original	300	500	Original	300	800	Original	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

Table 2. Characteristics of biochar derived from sewage sludges with traditional and microwave-assisted pyrolysis

Source	Zielinska et al., 2015				Lu et al., 2013 (note different data units)			Authors		
Sample/Temp ^{o}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

Table 3. Main ash components for some reported biomass feedstocks. Zhang et al

The results of produce analysis showed that all elements are uptaken by fruits, but in amounts that are not significant: selenium, lead and tin were all below detection limits, as well as arsenic and chromium. Copper and zinc showed the lowest bioavailability and that of other trace elements was very low, while improving the yield of cherry tomato production by 64%. Their study confirmed that biochar improves availability of phosphorus, total nitrogen and major cations, and has positive liming effect when applied to low pH soils, increasing soil pH and enhancing nutrients use efficiency.

The study also detected insignificant bioaccumulation in the fruit of the metals present in the wastewater sludge biochar. In addition, biochar is known to have positive effects on soil quality, as it enhances soil aeration, increasing water holding capacity and environmental conditions for the growth and development of plant root systems. Biochar significantly increases soil C, and although it may increase its total nitrogen, this does not imply that lesser amounts of N fertilizers may be needed. Studies found that N in biochar is not directly available to plants, but it is fused in the C matrix. Nonetheless, evidence show that soil application of biochar often affects crop productivity and can be beneficial in some situations. One consistent effect of biochar amendment is the change in soil pH(most frequently raising it), implying crop productivity improvements. Therefore, biochar may be considered a potential substitute for agricultural lime, especially in regions with acidic soils. (Collins, 2008).

Remediation and restoration of contaminated soils

Regulators are now starting to be concerned with contaminant bioavailability and mobility effects on environmental risk, rather than just their total concentration. Biochar has shown great potential for managing waste streams originated by animals or plants while decreasing their associated pollution loading to the environment. Soils amendment is a long standing remediation procedure, aimed at reducing the risk of pollutants transfer to ground or surface waters, or receptor organisms. Biochars have demonstrated potential for reducing a variety of organic and inorganic contaminants present in soils in mobile forms: from the study of environmental pollutants fate, in fact, it is well known that by increasing the organic fraction content of soil, its pollutants adsorption properties are increased, and therefore it capacity to reduce their bioavailability. Carbon-rich amendments, such as activated carbon, have in fact been employed for soil and sediment remediation purposes for some time, due to their ability to reduce contaminant bioavailability and risk (Brändli et al., 2008).

In recent literature, benefits associated with applying biochars to soils, such as their conditioning properties, have been reported (Beesley et al, 2011). Biochars are capable to complex metal ions present in the soil on their surfaces and therefore reduce their bioavailability, resulting in a reduced risk. Furthermore, it was shown earlier that increasing the pyrolysis temperature of biochars increases their degree of carbonisation, surface area , and reduces the abundance of amorphous organic matter. This has been shown to increase biochars' capability to also adsorb organic contaminants (Yu et al., 2009). Chen et al. (2008) compared biochar surface areas processed at different pyrolysis temperatures and found that those pyrolysed at 700^{o}C had half the surface area of activated carbon. This indicates that biochars obtained at high temperatures ("activated") will have the highest organic contaminant remediation potential. In a study comparing activated carbon to low-temperatures biochars, these showed to linearly absorb atrazine (Cao et al., 2009), suggesting possible advantages in the remediation of soils with organic and inorganic contaminants competing for sorption sites.

Care must be taken as biochar can have different effects on the mobility of metals in soils, compared to that in water: in a study where biochar was applied to multi-element (As, Cu, Cd, and Zn) contaminated soil, Cd and Zn were immobilized, as expected, in soils amended with biochar, however, Cu and As were mobilized. This phenomenon was associated with soil's increased pH resulting from biochar application (Beesley et al. 2010). Mobility of As can also be increased by biochar soil amendments, as it can cause reduction of As(V) to As(III) (more environmentally mobile) (Zhang X. et al, 2013).

Currently, little information is available concerning biochar application in treatment of contaminated sediment, however, considering biochar's excellent adsorption capabilities for many pollutants in solution, all the elements suggest that biochar could be used as a new, in-situ potential amendment sorbent for remediation and management of contaminated sediment sites, with advantages both for both carbon sequestration and sediment remediation opportunities.

Water and wastewater treatment

The specific properties of biochar, including a large specific surface area, porous structure, enriched surface functional groups and mineral components make it possible to use this material as a proper adsorbent to remove pollutants from aqueous solutions. Compared to activated carbon, biochar can be considered a potential low-cost and effective new adsorbent. Activated carbon is charcoal treated (*activated*) with oxygen to increase its microporosity and surface area, and is the most commonly used carbonaceous sorbent. Its production needs high temperatures and the additional activation processes, therefore, comparatively, the production of biochar is cheaper since it has lower initial energy requirements, in addition, its feedstock is abundant and low-cost, especially when biochar is obtained from urban sludge. Studies report that biochar showed excellent ability to remove contaminants, such as heavy metals, organic and other pollutants from aqueous solutions, and some biochars exhibit comparable or better adsorption capacity than commercially activated carbon (Zhang et al., 2013).

In available literatures about biochar application in water treatment, 46% of the studies concern its removal ability of heavy metals, 39% of organic pollutants, 13% of ferilizers NP, and 2% other pollutants. Both Langmuir and Freundlich isotherm models fit very well data to describe heavy metals equilibrium adsorption by biochars. Since these also show high affinity for organic pollutants (dyes, pesticides, herbicides, antibiotics, and others) perfect fit of the experimental data with Langmuir or Freundlich models was also demonstrated.

Ahmad et al (2014) covered an extended overview of biochar use as sorbent for contaminant management in soil and water. Sorption of organic contaminants from water onto biochar occurs due to the latter's high surface area and microporosity; electrostatic attraction/repulsion between organic contaminants and biochar has been indicated as another possible adsorption mechanism. Biochar surfaces, in fact, are normally negatively charged, facilitating electrostatic attraction of cationic organic compounds.

Adsorption efficiency of biochar is influenced by its properties, dosage, competitive anions, and solution temperature and pH.

Dosage of adsorbent has significant influence on adsorption efficiency (Aliverti et al., 2010). Applying an optimum biochar-to-contaminants ratio is essential for cost-effective application. Chen et al. (2011) reported that increase of biochar concentration decreased adsorption effectiveness, although increasing adsorbent concentration may result in increased total removal efficiency of heavy metals due to the increase of active sites.

Co-existence and interaction of pollutants ions have a significant influence on equilibrium adsorption capacity, especially for applications of biochar in real water systems. Studies on biochar adsorption capacity for co-existing contaminants (e.g. atrazine and simazine, phenanthrene and Hg(II)) showed that adsorption of two contaminants decreased when they co-existed in solution (Zheng et al., 2010). Presence of heavy metals had different effects on oxytetracycline adsorption onto biochar, ranging from insignificant (Cd^{2+}), slight facilitation (Zn^{2+}), slight inhibition (Pb^{2+}), and facilitation (Cu^{2+}), regardless of solution pH value (Jia et al., 2013).

Adsorption of contaminants onto biochars appears to be an endothermic process, with capacity increasing with increasing temperature: increase in the absolute values of ΔG_0 with temperature suggests that adsorption is more favorable at higher temperatures (Meng et al., 2014).

The solution's pH is one of the most relevant parameters for adsorption process, and depends on biochar type and target contaminants, affecting not only the adsorbent surface charge, but also the degree of speciation of the adsorbate. Surface functional groups (e.g. carboxylate, -COOH; and hydroxyl, -OH) which behavior changes with solution pH are present on biochar. At low pH most of these groups are in positively charged form, favoring anion adsorption. The biochar surface negatively charged in the higher pH range, when $pH > pH_0$ (point of zero charge), then, cations can be easily captured. Solution pH also significantly affects metal speciation, in turn also influencing their adsorption. Researchers have also studied the effect of pH on organic and inorganic contaminants adsorption: results show that this adsorption is also highly pH-dependent due to variations of biochar surface charge and contaminants properties with solution pH.

All published adsorption studies so far, however, were conducted on simulation wastewater, in order to simplify the underlying hypotheses. This is a normal procedure, which however presents wide gaps with an actual situation. Application of biochar for actual wastewater treatment is still unpublished, probably due to the complex pollutants-and-ions combinations that usually co-exist in real systems, which could have significant influence on equilibrium adsorption capacity.

Since application of biochar for removal of pollutants from aqueous solutions is mainly dealing with toxic pollutants (organic or inorganic), the final disposal of spent biochar becomes an important issue. Biochar loaded with ammonium, nitrate, phosphate, and without toxic pollutants, can be used as slow-release fertilizer to enhance soil fertility; however, biochars used to adsorb toxic pollutants need appropriate handling, following standards of hazardous wastes treatment. Biochars desorption/regeneration properties have been investigated to determine the feasibility of economical reuse of an adsorbent. Results indicate that food waste biochar could be used repeatedly without much loss of total adsorption capacity, however, the wide source of waste biomass for its production and increasingly limited usage cycles may render a recovery process economically un-effective. At the present time, little information is available about disposal of spent biochar: its stability, risks of secondary pollution, effect on carbon sequestration, and economical feasibility are still unclear and require further investigation (Tan et al., 2015).

Soil properties amelioration

Biochar from urban sludges has been proven a strong adsorbent; when spread into soils it not only increases their capacity to better adsorb plant nutrients and agricultural chemicals, reducing the leaching potential of those chemicals to surface and ground water, but also contains itself significant quantities of carbon and plant nutrients, that are slowly released to growing plants. Last, biochar has a relatively low density, that helps improving soils' properties: lowering bulk density, improving drainage, aeration, and root penetration properties of clay soils, and increasing water and nutrients retention ability of sandy ones by increasing their carbon content. The following list summarizes some of the positive effects of biochar soil amelioration.

-Enhance soil properties and plant growth. Biochar could raise and sustain crop yields, improve problematic nutrient-poor soils, including acidic tropical humid and drier environment soils. Having a nutrient affinity, it can retain plant nutrients, notably N in permeable soils under rainy conditions. Reduces soil acidity, raising its pH and improving productivity of many crops. Supporting nitrogen fixation, it can also reduce needs for fertilizers, reduce dependency of farmers on suppliers. Increases cation exchange capacity. By improving soil characteristics, it also enhances moisture retention, reducing irrigation demand and make cropping more resilient. Can increase soil microbial biomass, supporting beneficial organisms like earthworms and arbuscular mycorrhizal fungi in soil.

-Help reduce agrochemical pollution. Biochar may bind agrochemicals, and help reduce phosphate and nitrate pollution of streams and groundwater, resolving major problems hindering intensive agriculture. As a consequence it could help reduce pressures for new forest clearances (biodiversity conservation benefits). It can also reduce plant uptake of pesticides from contaminated soils, which is a form of bioremediation. Reduces aluminum toxicity. In periurban/urban agriculture biochar may counter harmful compounds like heavy metals, dioxins, PAHs (polycyclic aromatic hydrocarbons) present in raw sewage or refuse inputs.

-Help compensate GHG emissions associated with agricultural development. Biochar store carbon in soil for long time, while compost and manures are subject to rapid microbial breakdown. Sequestration in biochar is likely to last for centuries, possibly thousands of years. Suppresses methane and N_2O (nitrous oxide gas) emissions from cultivated soil: a laboratory study in Japan found that soils amended with 10 wt.% of biochar suppressed 89% of N_2O emissions (Yanai et al., 2008). Ash (metals) tends to be lost by wind and water erosion out of soils in non-bioavailable form.

-Combat climate change. Biochar applied to soils offers effective, long-term carbon storage. It can increase adaptability to environmental change by improving soil moisture retention, increasing agricultural resilience against climatic change effects like increased drought and floods. Supporting biofuel production (by-product of the process) its carbon footprint may even be completely carbon neutral.

Carbon sequestration by biochar

Biochar is emerging as not only as an ameliorant to reduce bioavailability of contaminants, with additional benefits of soil fertilization, but also as a possible mitigation agent of climate change, in the sense that it can act as an efficient and economic carbon sequestration means. Biochar contains a considerable fraction (roughly ¼ to 1/3) of the carbon initially contained in sewage sludge (or in any other feedstock used for its production). It has been shown that the half-life of C in soils is in excess of 1000 yr (Glaser et al., 2002), 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, at a lower cost than some of the Carbon Capture and Storage (CCS) technologies commonly used today (i.e. storage in geologic traps). It has been estimated that a US-wide system of pyrolyzers for processing biomass into bio-oil and charcoal, replacing fossil fuels with bio-oil and returning biochar to soils, could reduce that nation's demand for fossil oil by 25% and its C emissions by 10%, all the while strengthening its rural economy. If extrapolated to the global scale, such strategy could make a major contribution to world energy supply and solution to global warming.

It should be noted that, while 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 obligatory disposable by-product of wastewater treatment, that may constitute itself, if not properly disposed of, an environmental problem. As indicated in prior sections of this paper, 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

Biochar as raw material for activated carbon production

Activated carbon is produced according to two main steps: (a) carbonization of raw material, such as agricultural residues, under an inert or limited oxygen atmosphere to produce char, and (b) char activation through chemical or physical means, at a temperature that usually ranges between 600-1200^{o}C. Physical activation occurs in the presence of oxidizing gases (carbon dioxide, steam and air) and does not involve any chemicals. Chemical activation, on the other hand, uses chemicals as activating agents in one-step or two-step activation. The most common agents are $ZnCl2$, KOH ,H_3PO_4 and K_2CO_3. Physical activation offers advantages over chemical activation since due to the lack of chemicals involved, however two-step chemical activation has the advantage of producing highly microporous activated carbon with high specific surface. Test on activating biochar for use as an activated carbon substitute have met with positive results (Azargohar and Dalai, 2008).

Biochar for catalyst production

Syngas from gasification/pyrolysis of biomass contains considerable amounts of tars, that are detrimental to highest value downstream uses, requiring subsequent treatment, such as water/oil scrubbing, thermal (typically at $T>1000^oC$) and catalytic cracking. The latter is considered the most promising technology for syngas cleaning, requiring low temperatures ($<700^oC$) and less energy to achieve high tar removal (>90%) by using appropriate catalysts. Marin (2011) showed that biochar can be used as gas catalyst for this purpose with and without active metal loading.

Biochar can also work as catalyst for conversion of syngas into liquid hydrocarbons by Fischer–Tropsch synthesis as shown by Yan et al. (2013), and be a good precursor for producing heterogeneous acid catalysts (solid acid catalyst) for esterification/transesterification of vegetable oils/animal fats for biodiesel production (Dehkhoda and Ellis, 2013). Three biochar-based solid acid catalysts from peanut shells, pine residues and woodchips were tested to this end by Kastner et al. (2012), achieving 90–100% conversion within 30–60 min and high reusability (up to 7 cycles with no significant loss in esterification).

Biochar as gas adsorbent

CO_2 capture and storage is a promising strategy to reduce GHG-CO_2 emissions, which main challenges are high flow rates of flue gases, and low partial pressure of CO_2, hence 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 (Gonzales et al., 2013).

Zhang et al. (2013) developed a corncob biochar-based activated carbon using KOH chemical activation that created high surface area(up to 3500 m^2/g) and large pore volume (1.3–1.94 cm^3/g), that could play an important role in adsorbing hydrogen. One of the technical obstacles in deploying hydrogen-based fuel technologies is the difficulty in safely storing hydrogen, considered a promising clean energy carrier, with potential to play a major role in future transportation. The small pore activated carbon exhibited the highest hydrogen uptake capacity so far with > 2.85 wt% at1.0 bar and 196^oC.

Biochar in fuel cell systems

A direct carbon fuel cell (DCFC) was recently developed, converting molten carbonaceous solid fuel directly into electricity without the need of previously converting solid into gas fuel (Ahn et al., 2013). Results showed the feasibility of using biochar as renewable, low cost fuel for DCFC despite its relatively low carbon and high ash contents, with fuel cell power density about 60–70% of a coal-based fuel cell. In a comparison of nine carbonaceous fuels for DCFCs (commercial graphite, carbon black, two commercial coals, five biochars) on cell performance, commercial biochar had the second highest current(64.2 mA/cm^2) and power densities (32.8 mW/cm^2) (Kacprzak et al., 2014).

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 (Capodaglio et al., 2013, 2016c). Electrode materials used in MFCs are normally granular activated carbon or graphite granules, which average cost ranges from \$500 to \$2500 per ton, making costs prohibitive at the large scale.. Biochar was found to be a promising alternative source material for MFC construction: comparing cost and power output of wood-based biochar electrodes with activated carbon and graphite electrodes, it was found that power output of biochar (532–457 mW/m^2) was comparable to that of activated carbon (674 mW/m^2) and graphite (566 mW/m^2), at a speficic cost about 90% lower than the other materials (biochar \$17–\$35/W, activated carbon \$402/W, graphite \$392/W) (Huggins et al., 2014).

Finally, biochar was also used as catalyst in MFCs with carbon cloth air cathode and biochar catalytic layer coating both sides of the wet-proofed membrane. The catalytic layer made of sewage sludge-derived biochar was compared with a hugely more expensive Pt/C layer. Power density of the biochar-coated cathode reached 500 mW/m^2, comparable to that of Pt/C coated cathode. This showed that sewage sludge biochar was active in catalyzing redox reactions in MFCs, and could become an alternative to more expensive Pt catalysts, with even better stability than the latter (Yuan et al., 2013).

Biochar-based supercapacitors

Supercapacitors are energy storage devices that are indispensable to store energy from renewable sources, due to high-power densities, long cycle lifes, and quick charge/discharge capabilities. They can store 10 to 100 times more energy per unit volume other capacitor types, and can accept and deliver charge much faster than batteries, tolerating many more charge/discharge cycles than rechargeable batteries. They can be used as uninterruptible power sources in electric vehicles like cars, buses, trains, cranes and elevators, can be used for regenerative braking, short-term energy storage or burst-mode power delivery. The electrodes' microstructure of these devices has a great influence on their performance.

The preferred raw materials for making supercapacitors is carbon material with high specific surface area and porous structure, due to its wide availability, relatively low cost and environmental impacts. Recently, biochar from different biomass feedstocks (paper cardboard and woody biomass) was used for fabrication os supercapacitors, indicating that its use of biochar is promising thanks to low cost and satisfactory performance. Supercapacitor electrodes made from biochar showed potential of about 1.3 V and fast charging–discharging behaviour with gravimetric capacitance of about 14F/g, that could be increased by activating the biochar with nitric acid to115F/g (Liu et al., 2012).

Discussion

Sewage sludge is a material that is very diverse in terms of physico-chemical properties, depending on its origin. It is therefore a huge simplification to try to generalize conclusions on biochar based on results only from one or a few types of sludge, as this may lead to wrong assumptions. Unfortunately, although there is some literature information on the evaluation of biochars produced from sewage sludges of varying properties, with different processes and at different temperatures, systematic guidelines on investigation of physical and chemical properties of biochars still do not exist, mainly because of poor focus towards a myriad of final uses. Relating how the initial properties of a generic sewage sludge determine the properties of derived biochar for aspecific application (and how the other variables such as process and process conditions influence these properties) is of key importance in a situation where interest in sewage sludge-originated biochar is becoming highly relevant.

Biochars could virtually be a panacea for un-numerable environmental and industrial uses: for example, activated biochar could replace activated carbon in most of its current applications, as it has equivalent or even greater sorption efficiency for various contaminants due to its cost-effective production from waste resources,that make biochar less expensive compared to activated carbon. In fact, estimated break-even price for biochar is US $246/ton, which is approximately 1/6 of commercially available activated carbon (US $1500/t) (McCarl, 2009).

As discussed above, biochar has been applied to the most various applications, with others that undoubtedly will be proposed in the near future. A still missing, thorough understanding of biochar properties will be critical in mitigating its possible undesired impacts, while harnessing its benefits. Research on in-depth characterization of its properties and relationships to reaction conditions in its production are critical to optimize and tailoring properties for maximum effectiveness in any application (Qian et al., 2015).

In catalysis uses, biochar has potential roles in different applications, such as syngas reforming and conditioning, and bio-oils upgrading; its use will increase net sustainability of bioenergy refinery systems by reducing the need for external materials. Use in fuel cells and supercapacitors also suggests economic and environmental benefits, however, properties of biochar-based, novel functional materials depend highly on biomass precursors, and have still space for substantial improvement. For example, capacitance of Co_3O_4 nanotube-based supercapacitors can reach 500 F/g while the maximum of biochar-based ones is only 250F/g, so far.

In the introduction, it was stated that biochar is one of the products of biomass (and specifically sewage sludge pyrolysis), and that often product preference is given to bio-oils development. Optimum reaction conditions for producing each fraction are not, however, the same, therefore conditions of biomass (sludge) processing should be optimized based on the target products aimed at specific applications, perhaps with the help of an overall Life Cycle Assessment (LCA) analysis to suggest the most appropriate option in each case, minimizing environmental impacts and costs.

Conclusions

Sewage sludge pyrolysis biochar may be an additional important resource for reuse in agricultural and many other environmental or industrial applications, and its additional contribution in the selection of a final strategy for wastewater sludge disposal must be carefully evaluated.

Feedstocks utilized for biochar production, as well as the production process itself, influence biochar characteristics. Optimizing biochar for a specific end-uses may require feedstock selection as well as pyrolysis production technique and conditions. Several studies address these relationships. Literature shows that pyrolysis process parameters (temperature, residence time, heating rate, feedstock particle size) 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. As different sludges have different characteristics, it becomes evident that optimum pyrolysis temperature depends not only on feedstock source, but also on biochar intended application. Generally speaking, however, biochar produced at low temperatures is suitable for agricultural uses, while the one produced at higher temperatures has a 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

This paper discussed initially how sewage sludge biochar characteristics are developed during its production process, then existing and prospective environmental and technological uses of this by-product. 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 as partly identified in the previous discussion, that need more specific, relevant investigations.

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