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Review

Municipal Sewage Sludge as a Resource in the Circular Economy

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Abstract: Municipal sewage sludge (MSS) is an inevitable byproduct of wastewater treatment, with increasing amounts year by year worldwide. The development of environmentally and economically acceptable methods for the sustainable management of MSS is a major environmental challenge. Nowadays, sludge management practices, besides the commonly used stabilization methods, focus attention on alternative sludge-disposal pathways, which encompass enhanced energy and valuable-resource recovery. This review presents the recent advances in the recovery of selected value-added products from sludge. Because of the high nitrogen and phosphorus concentrations, waste MSS can be a nutrient source (e.g., struvite). This paper discusses the conditions of and advances in the technology of struvite recovery. As in the extracellular polymeric substances (EPSs) of biological sludge, alginate-like exopolymers (ALEs) are present in MSS systems that treat municipal wastewater. The yields, dynamics in content, and characterization of ALEs and their possible applications were analyzed. MSS is an important source of humic substances. Their occurrence, characterization, and yields in various types of MSS (e.g., untreated, composted, and digested sludge) and main methods of application are presented. The important aspects and trends of MSS pyrolysis, including the thermochemical conversion to biochar, are discussed in this review. The characterization of biochar derived from MSS and the assessment of the environmental risks are also covered. This paper explores the potential use of biochar derived from MSS in various applications, including soil amendment, carbon sequestration, and environmental remediation.

Keywords: waste; struvite; alginate-like exopolymers; biopolymer; pyrolysis; biochar; value-added products

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1. Introduction

Municipal sewage sludge (MSS) is the primary byproduct resulting from municipal wastewater treatment processes. The amount of MSS generated worldwide is constantly increasing. For example, in 2017, the total production of MSS in municipal WWTPs in EU countries was over 6.6 million tons of dry solids (DSs). Among EU countries, the highest annual amounts of MSS are generated in Germany (1.78 million tons of DSs), Spain (1.19 million tons of DSs), and France (1.17 million tons of DSs). Together, these three countries generate nearly 63% of the total MSS produced in the EU. However, the MSS production per capita is the highest in Hungary, Finland, and Spain (Figure 1). For comparison, in Poland, the total MSS production is 2–3 times lower. As for other EU countries, the MSS production varies from 0.28 million tons of DSs (Romania) to 0.007 million tons of DSs (Cyprus). Based on these data, MSS is expected to remain a permanent waste problem requiring an appropriate solution.

MSS is a mixture of different sludges generated during municipal wastewater treatment, such as primary sludge, secondary sludge after biological wastewater treatment, chemical sludge after the chemical precipitation of phosphorous or coagulation processes, as well as sludge from digesters. Due to the different technologies used in wastewater treatment plants (WWTPs) and the varying characteristics of raw wastewater, the composition of MSS can vary. MSS can differ in terms of its contents of water, organics, nutrients, and

pollutants. In general, the structure of MSS is complex and heterogenous. In contrast to industrial sludge, MSS contains more organic matter (OM) and a substantial amount of nutrients, making it more suitable for resource recovery [1]. Dewatered MSS, depending on the stabilization processes, contains, on average, 50–70% OM, 30–50% mineral components (including 1–4% inorganic C), 3.4–4.0% nitrogen (N), 0.5–2.5% phosphorous (P), and significant amounts of other nutrients, including micronutrients (e.g., Mg, Ca) [2]. In addition, MSS contains a wide variety of substances and microorganisms (including pathogens) in suspended or dissolved form [3].

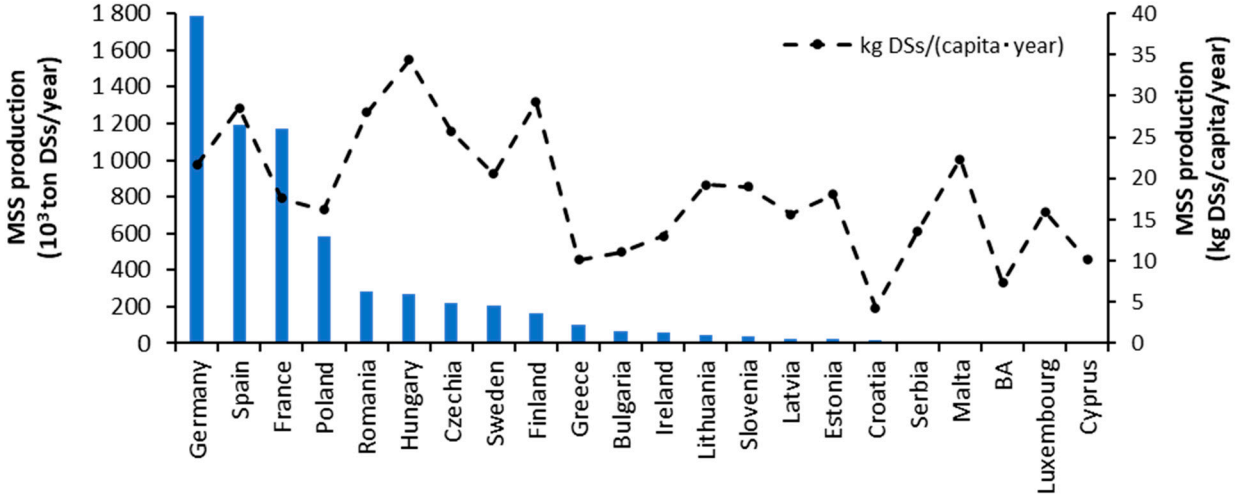


Figure 1. Production of MSS (total and per capita) in 2017 in WWTPs in selected EU countries (BA corresponds to Bosnia and Herzegovina) [4].

MSS can accumulate different potentially toxic and harmful inorganic and organic pollutants from wastewater (e.g., heavy metals, polycyclic aromatic hydrocarbons, pesticides, microplastics, nanoparticles, etc.). Among these pollutants, heavy metals are most commonly detected in raw MSS. It has been estimated that 80–90% of the heavy metals present in raw wastewater are retained and concentrated in MSS [5]. As a result, MSS can pose a potential risk to the environment, and the presence of various pollutants at different concentrations can limit the efficiency of MSS management [6].

Conventional methods of MSS disposal include direct use in agriculture, composting, incineration, and landfilling, but their application is limited due to legislation and pressure from environmental authorities and the public in different countries (Figure 2). In Germany, about 70% of the MSS is incinerated; in Spain, over 80% is used in agriculture; and in France, about 40% is used in agriculture and for composting. In Poland, over 36% of the MSS is used in agriculture or is incinerated, and other disposal methods (e.g., soil reclamation, anaerobic digestion, etc.) are used for over 50%.

Although MSS contains undesirable pollutants, it can serve as a source of valuable compounds with environmental, agricultural, and industrial potential that goes beyond what is typically obtained with conventional treatment methods. WWTPs could become sustainable biorefineries that are highly energy-efficient, enabling zero-waste operations and facilitating the long-term generation of environmentally beneficial materials [7]. All of the world's WWTPs treat large amounts of wastewater. Today, wastewater and MSS are used to produce biogas; in the future, WWTPs could have a broader function by being converted into biorefineries that recover and produce new materials. MSS, due to the presence of different resources (energy, nutrients, raw materials, and process byproducts), presents itself as a sustainable resource with substantial potential within the circular-economy concept. This approach aims to protect natural resources by reducing the dependence on primary resources and promoting the more sustainable management of secondary raw materials, particularly those derived from waste [8,9]. The proper use of these resources is essential for building and strengthening a virtuous circle based on wastewater. When integrated

into MSS management systems, circular-economy principles can significantly contribute to economic growth. The circular-economy value of MSS is considerable [10]. The European Union postulates a search for new ways of reusing MSS by its thermal treatment to produce energy, and by its transformation into new products, especially for agricultural use [11]. The principal organic compounds found in MSS are carbohydrates and proteins, with low contents of cellulose and lignin, and they may be used for producing high-value biopolymers [1]. The OM and nutrients (N, P, and K, as well as Ca, S, and Ca) can be recovered for agricultural use [3]. MSS contains more N than P, but because P resources are scarce, the recovery of this nutrient from MSS is currently the primary focus [12]. MSS is rich in various organic compounds, especially humic substances (HSs), which have great potential for use in soil remediation [13,14]. Methane derived from anaerobic sludge digestion or bio-oil from thermochemical processes can enhance energy self-sufficiency and reduce greenhouse gas emissions, and bio-hydrogen from sludge fermentation can be used as clean fuel [10]. Advances in MSS management technology have revealed that MSS has a relatively high calorific value and can be converted into energy via thermochemical processes. In comparison to biological processes, thermochemical treatments, such as pyrolysis and gasification, are generally regarded as more efficient from an energy perspective [15]. In addition to energy, the thermochemical conversion of MSS also produces biochar.

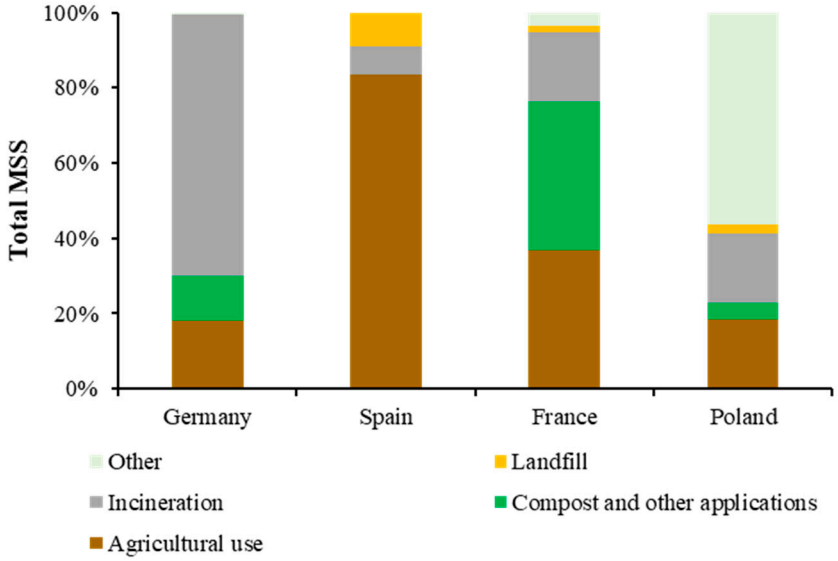


Figure 2. Methods of MSS management in selected EU countries [4].

The management of MSS presents a significant environmental challenge, requiring environmentally and economically acceptable methods for sustainable management. Changes in the level of knowledge and available technologies impact the limitations of the existing forms of MSS utilization, such as agricultural use and composting. This review aims to present recent advances in the recovery of value-added products from MSS, focusing on struvite recovery, alginate-like exopolymer (ALE) analysis, and HS extraction. Additionally, this review explores the importance and trends of MSS pyrolysis, specifically focusing on biochar production. This paper also discusses the characterization of biochar derived from MSS and assesses its environmental risks. Furthermore, it explores the potential applications of biochar derived from MSS in soil amendment, carbon sequestration, and environmental remediation. Methods that focus on resource and energy recovery are becoming increasingly preferable. With this review, we aim to contribute to the development of sustainable MSS management practices and the promotion of circular-economy principles in the field of wastewater treatment.

2. Recovery of P and N from MSS

The application of plant-available nutrients such as N and P to improve the fertility of agricultural soil is a common practice. N seems to be unlimited in its atmospheric form, but, in contrast, high-quality mineral reserves of P are quickly being exhausted and are expected to be depleted within a few hundred years [16]. It is known that P does not penetrate the soil but is prone to accumulate excessively in the soil and then is exposed to the risk of erosion into water courses when it is sorbed onto soil particles [17].

Nutrients, which are available both in the form of manufactured fertilizers (e.g., chemicals) and natural fertilizers (e.g., animal manure, MSS), are extensively used in agriculture. The production of manufactured fertilizers requires significant fossil energy inputs, resulting in gaseous emissions [18]. Therefore, more and more emphasis is placed on efficient methods for recycling existing nutrients. Notably, up to 30% of the N used for improving soil fertility ends up in municipal wastewaters [19], from where it could be recovered for re-use. The N and P loads in the influent to WWTPs are assimilated by the biomass of the activated sludge that is most used in the treatment process at conventional municipal WWTPs [20]. The P and N contents in the sludge depend on whether integrated processes of nutrient removal are used at the WWTP and on whether the P removal from the wastewater is supported by chemical precipitation [21]. As MSS contains undesired pollutants in addition to nutrients, its use as a soil fertilizer in agriculture is debated.

In MSS management, the sludge is often anaerobically digested. This reduces the weight and volume of the MSS and allows energy to be recovered, but it also re-solubilizes the biomass-bound P and N. After digested-sludge dewaterization, P and N are mostly present in the liquid fraction, which is commonly called reject water [20]. After anaerobic digestion, reject water from sludge dewatering, often with around 1 g NH_4-N/L and 0.5 g PO_4-P/L, is returned to the sewage treatment process, which can contribute up to 25% of the total N load to the process and, consequently, increase the energy demand and treatment costs. This unavoidably makes nutrient removal during the treatment process more difficult.

Many technological solutions for nutrient recovery from wastewater treatment streams are available on the market, several of which are suitable for applying to the reject water from digestate. One of the most used solution is struvite precipitation [22]. Struvite crystals are formed according to the following reaction:

$$Mg^{2+} + NH_4{}^{+} + HPO_4{}^{2-} + OH^{-} + 5H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \quad (1)$$

Struvite ($MgNH_4PO_4 \cdot 6H_2O$) recovery can be an alternative method of simultaneously reducing the internal load of P and N (at WWTPs) and recycling these nutrients as fertilizing materials. Struvite can be recovered either from reject water or directly from digested sludge. However, because reject water has a lower suspended solid (SS) content and viscosity than digested sludge, struvite can be more easily recovered from the liquid part of digestate. Fluidized bed reactors are commonly used to recover struvite from the liquid phase. However, direct struvite recovery from digested sludge has several advantages over recovery from the liquor [23]. Digested sludge contains soluble P, accounting for 15–30% of the total P, and, in addition, it contains struvite particles, typically accounting for 5–15% of the dry weight, which are both generated during anaerobic MSS treatment. Since soluble P and struvite particles are recoverable in a complete-mix reactor for recovering struvite from digested sludge, it can be expected that more P will be recovered from digested sludge than from the liquid phase alone. In the process of struvite recovery, the digestate is passed through a fine screen and fed to a crystallization reactor. Then, to promote crystallization, Mg hydroxide is added to the digestate as a source of magnesium. Struvite particles are separated from the mixture by centrifugation. A small portion of the particles of separated struvite are recycled to the reactor to serve as seed crystals. Struvite crystals are then sent to the scrubber several times per day. Recovered struvite is washed with water, dried, and stored for shipping. The remaining sludge is dewatered and incinerated by a mono-

incinerator. Typically, this process can recover more than 80% of the soluble P from digested sludge. The volume of dewatered sludge can typically be reduced by 3.3%, mainly due to the removal of struvite particles generated during sludge digestion [23].

Struvite is a relatively pure precipitate that contains large amounts of P and N, and a low content of impurities; thus, it can be considered a potential method for nutrient recycling and recovery from wastewater [24]. In contrast to precipitation processes that use coagulant agents, struvite formation requires low quantities of solids, which can be easily recovered via sedimentation, and avoids the formation of undesired compounds [25]. EC Regulation No. 1907/2006 (REACH) indicates that struvite has value as a commercial fertilizer [26]. Thus, in contemporary Europe, 15,000 tons of struvite are recovered in pilot and operational facilities each year. Substantial quantities of struvite are also produced in the USA, Japan, and China [24]. For example, to directly recover struvite from digested sludge, struvite precipitation was implemented at the full-scale Higashinada WWTP in Kobe City, which has a capacity of 241,500 m^3/day. Its capacity for treating digested sludge was 239 m^3/day, and it recovered 40 and 90% of the total P and soluble P, respectively [23].

Ammonium stripping is also a widely used method of chemical–physical treatment, and it has been successfully applied with ammonium-rich wastewater, such as the reject water from digested-sludge dewaterization. In this process, ammonium from the ammonium-rich solutions is transferred from soluble form to volatile form in the air flow. Then, it can be recovered as ammoniacal salts via absorption into acid solutions. Although this process is beneficial, it requires the adjustment of the pH to values of 11–12 and high air-flow rates [27].

Bioelectrochemical systems have gained popularity in recent years, especially in the context of N removal and recovery from reject waters [28,29]. In this process, anodic oxidation reactions are catalyzed by electroactive bacteria, which decreases the energy consumption. In contrast, electrochemical systems are based on purely electrochemical reactions. However, the driving force that ensures the migration of charged ions across ion-exchange membranes originates from the electricity that is generated in both cases. This can be utilized for concentrating ammonium. Desloover et al. found that a two-step system in a chamber with an anode and a cathode separated by a cation-exchange membrane allows the positively charged ammonium ions to be concentrated [30]. An alternative system with an anion-exchange membrane was proposed by Ledezma et al. for the recovery of nutrients from urine [31]. Koskue et al. optimized N recovery from reject water via bioelectroconcentration. The highest effectiveness of the ammonium recovery was 75.5 ± 4.6% (a recovery rate of 728 ± 117 g N/(m^3·d)) at a loading rate of 1.9 g NH_4-N/(L·d). At a loading rate of 2.9 g NH_4-N/(L·d), the ratio between the ammonium recovery efficiency (68.2 ± 11.6%) and recovery rate (965 ± 66 g N/(m^3·d)) was optimal, which ensured the concentration of ammonium almost 7.5-fold, up to values of 7483 ± 625 mg/L [29].

Traditionally, chemical addition is required to increase the pH to improve ammonium stripping. However, when bioelectrochemical processes are applied, cathodic reduction reactions release hydroxide (OH^-), which increases the pH. Thus, the ammonium concentrated from the anode to the cathode speciates into a gaseous form of ammonium that can be removed by stripping, followed by re-solubilization into an acidic solution that allows for its recovery [20].

The recovery of struvite from MSS can lead to environmental benefits, such as reducing P and N emissions to water bodies and improving the P- and N-use efficiency. However, it is important to note that the struvite recovery methods may vary in efficiency and cost-effectiveness, and the specific conditions of each WWTP should be considered.

3. MSS as a Source of Alginate-like Exopolymers (ALEs)

MSS, especially from aerobic granular sludge (AGS), has great potential for biopolymer recovery. AGS granules contain a high content of extracellular polymers (EPSs), which are characterized by a complex composition. EPSs consist mainly of polysaccharides, proteins, and other macromolecules, such as nucleic acids, lipids, and HSs [32]. One of the main

components of EPSs in sludge are ALEs. Chemically, an ALE is a polymer composed of linear polysaccharides comprising β-D-mannuronic acid (M-block) and α-L-guluronic acid (G-block) linked by 1–4 glycosidic bonds. The presence of both acids affects the properties of ALEs. Guluronic acid favors the formation of gels in the presence of multivalent cations such as Ca^{2+} and Mg^{2+}, and it affects gel properties such as the swelling, stiffness, and porosity [33]. In contrast, mannuronic acid supports chain elasticity and connects guluronic acids in the ALE chain, supporting its gelation [34]. The characteristics of recovered ALEs can be affected by the type of sludge [35]. The ALEs found in AGS granules have better chemical and mechanical properties (gel-forming capabilities) than ALEs in activated sludge flocs, presenting different blocks.

Until now, the commercial production of ALEs has been exclusively from brown alga genera, such as *Ascophyllum*, *Laminaria*, and *Macrocystis*, found in coastal regions of North America, Europe, Asia, and Australia [36]. To a lesser extent, ALEs can be produced by the bacterial genera *Azotobacter* and *Pseudomonas* under controlled conditions [37]. AGS can be considered as a serious source of ALEs, but the biosynthesis of ALEs in AGS systems depends on many operational parameters, such as the organic load rate (OLR), carbon (COD)-to-nitrogen (N) ratio, salinity, granule size, and sludge retention time (SRT). The most beneficial for ALE synthesis are fluctuations in the OLR, a high COD/N ratio (from 10 to 20), moderate salinity (ca. 1% NaCl), mature granules of AGS with significant size (diameters between 400 and 600 µm), and an SRT between 10 and 20 days [36]. About 15–25% of the AGS granule dry weight is composed of ALEs, which makes the recovery of this high-added-value resource reasonable [38]. Currently, more research on ALE recovery and characterization is being performed in lab- and pilot-scale studies. The yields of ALEs using ALE granules and synthetic wastewater in lab-scale studies vary between 0.11 and 0.23 g ALEs/g VSS [39–41]. For comparison, the ALE yields in pilot-scale studies using municipal wastewater are 0.21–0.24 g ALEs/g VSS [39,40]. The difference in the ALE yields can also be caused by the extraction methods for ALE recovery. Only the alkaline extraction method using sodium carbonate (Na_2CO_3) at high temperatures forms a gelatinous matrix, proving to be the most suitable technique for ALE recovery [36].

The resource recovery in full-scale AGS reactors is still at the beginning. The first full-scale ALE extraction was performed in 2019 from excess Nereda® sludge in Zutphen (The Netherlands). In a field test, it was demonstrated that 18 kg of ALEs can be produced from 80 kg of Nereda granular sludge, with an ALE production expectation of about 400 tons per year [42]. A second plant was opened in 2020 in Epe (the Netherlands). The plant was designed to produce 50 tons of neo-alginate, called Kaumera, with the possibility of an increase in the ALE production of up to 100 tons per year, according to the market demand [36].

An economic analysis of recovered ALE (after extraction and refining costs) revealed that 1 ton of the biopolymer generates a final revenue of EUR 1000–2000. These results show that a WWTP with AGS technology-treated domestic wastewater (COD ≈ 600 mg/L) with a flow rate of approximately 3.0 m^3/s would be able to produce approximately 1 ton of ALEs/day, generating a revenue of approximately EUR 365,000–730,000/year [43]. Therefore, ALE recovery from excess AGS from full-scale AGS plants is not only economically proven but also has possibilities for further application.

Although ALEs are currently obtained mainly from brown seaweed, their composition varies due to seasonal and environmental changes. The recovery of ALEs from waste AGS as biomaterial not only reduces the amount of waste sludge but also avoids the synthetic ALE production processes [44]. Based on ALE characterization, including their non-toxicity, biocompatibility, and ability to form crosslinks with cations, ALEs have wide application, including in the pharmaceutical, cosmetic, paper, textile, and food industries, as well as the potential to be used in medical, environmental, and agricultural applications (Figure 3). Thus, the ALE recovery process shows promising economic prospects and potential applications across industries.

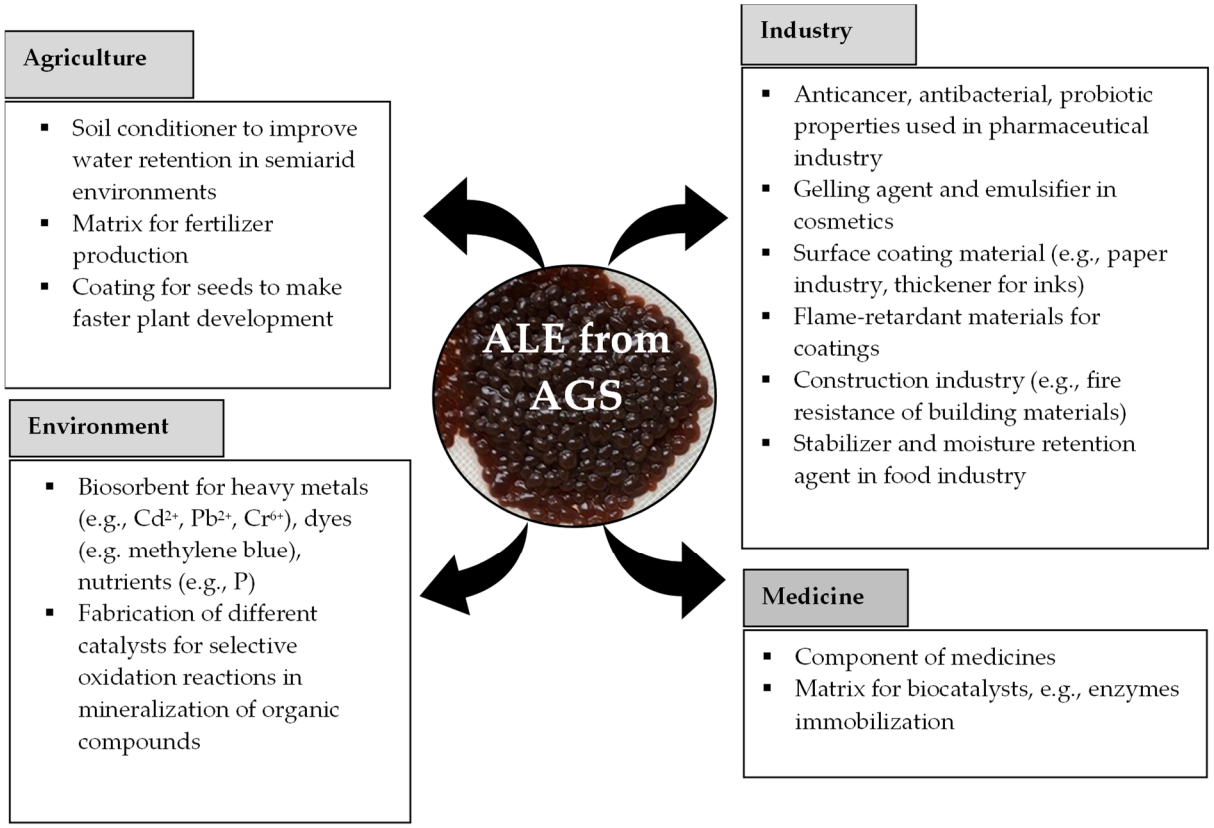


Figure 3. Possible applications of ALEs recovered from waste AGS (based on [43,45–47]).

4. MSS as a Source of Humic Substances (HSs)

4.1. HS Contents in Raw and Processed MSS

MSS is an important source of HSs. Their occurrence, characterization, and yields depend mainly on the type of MSS (e.g., untreated, composted, or digested) [48]. Raw MSS may contain humus-like materials because, during municipal wastewater treatment, the OM mineralization is accompanied or closely followed by humification, making MSS rich in intermediate products of decomposition, mostly "raw" humus. According to Feng et al., HSs are generally non-degradable or difficult-to-degrade during wastewater treatment, and they are removed from wastewater by biosorption on activated sludge instead of biodegradation [44,49,50]. Some HSs are also precipitated with flocculants and then removed in primary clarifiers; however, HSs are difficult to remove totally. HSs can be utilized by microorganisms as a supplementary source of nutrients [51]. Additionally, HSs may be produced by microbial activities during sludge storage and treatment [50,52]. HSs are natural polymers with a highly heterogeneous structure and are traditionally classified as humic acids (HAs), fulvic acids (FAs), and humins according to their solubility.

According to many authors, depending on the type of sludge, the contents of HSs range from 2% to 7%, and the ratio of HA to FA ranges from 0.3 to 3.0 [53,54]. For example, Réveillé et al. showed that, in unstabilized MSS, the respective concentrations of HA and FA were 83.5 mg/g OM and 84.8 mg/g OM, and in the sludge after anaerobic stabilization, they were 79.5 mg/g OM and 77.4 mg/g OM [55]. In unstabilized sludge, FA and HA together account for 56.8% of the total organic carbon (TOC), and in sludge after anaerobic stabilization, they constitute 83.1% of the TOC. In MSS after anaerobic treatment, the HA content equaled 12.53% of d.m. [56]. Kulikowska et al. provided the quantitative characteristics of HSs, including the fulvic fractions (FFs) and HAs, from five different municipal WWTPs. The HS concentration was highest in anaerobically stabilized sludge (227.5 mg/g OM). In a mixture of primary and biological sludge that had not been stabilized, the HS concentrations were from 1.6 to 1.9 times lower (118.7–144.3 mg/g OM). In all the

sludges, the FF constituted the largest share of HSs; the percentage of HAs in the HSs ranged from 35.7% to 48.2% [57]. The HA/FF ratio ranged from 0.55 to 0.93, which was within the range given by other authors.

Li et al. monitored the evolution of HSs during anaerobic sludge digestion [50]. HAs were the main component of the HSs, whereas the FA content was only one-fifth that of the HA content in both raw MSS and digested sludge. After anaerobic digestion, the average HA content changed from 87.7 mg/g TSs in raw sludge to 73.4 mg/g TSs in digested sludge, and the average FA content went from 17.2 mg/g TSs to 13.6 mg/g TSs. The FAs were more degradable than the HAs: during digestion, 16.3% of the HAs and 27.0% of the FAs were degraded. However, the HAs and FAs were more difficult to degrade than other organic substances in the sludge, as the overall degradation percent of the sludge volatile solids was 34.6%.

The concentrations of HSs increase substantially during MSS composting because, during the second phase of composting (cooling and maturation), the degradation of more complex proteins, hemicellulose, cellulose, and lignin leads to the formation of carbohydrates, amino acids, simple peptides, and phenols of low structural complexity, which can either be degraded by microorganisms as a source of C and energy or serve as building blocks for humus formation. The products of lignin degradation, such as phenols, quinones, and more complex compounds, are the main precursors that form HSs via polymerization and condensation with N compounds. HSs can be created from lignin degradation products because, in the feedstock for composting, lignocellulosic materials must be added to the MSS. Bulking agents and amendments, which are mainly lignocellulosic materials, are added to MSS because the sludge cannot be composted alone due to its low porosity, high moisture content, and low C/N ratio. Although the overall concentration of HSs increases during composting, it is generally accepted that, while the concentration of HA increases during this process, that of the FF decreases [58–60]. However, more recent works have indicated an increase in both the FA and HA concentrations during composting [61,62], and that the HS content in compost can vary as a result of adding different types and amounts of amendment(s) (the content of lignocellulose in the amendment(s) is particularly important). In mature compost, the concentrations of HSs vary widely, from ca. 150–180 mg C/g OM up to even ca. 300 mg C/g OM [62–64].

4.2. Characteristics of HSs

Elemental analysis. HA and FA can be described and compared based on their elemental compositions (C, H, N, and O contents). The elemental compositions of HA and FA from raw MSS and processed MSS (e.g., digestate, compost) are often compared with the compositions of the soil HA and FA. In soil, FA contains less C than HA but more oxygen (O), which is present in numerous -COOH groups. Kononowa found that the content of C (40–49%) in FA is similar to that of O (44–49%), and the shares of hydrogen (H) and N are 3.5–5% and 2–4%, respectively [65]. Jouraphy et al. found that, in FA extracted from compost from MSS and green waste, the C content was lower (31.2%) and the N content was higher (4.2%) than in FA from soil (C, 45.7%; N, 2.1%). However, the FA from the compost and the soil had similar contents of H (4.6% and 5.4%, respectively) and O (44.3% and 44.8%, respectively) [59]. Kalsom et al. reported that the elemental composition of HA from MSS compost was similar to that of HA from soils [66]. Amir et al. obtained similar results with mature compost from MSS and straw: C, 50.1%; O, 39.3%; H, 5.9%; and N, 4.8% [67]. A slightly lower C content (47.5%) and higher N content (7.3%) were reported in compost from MSS and green waste [68]. Finally, Droussi et al. found that compost from waste generated during olive oil pressing had higher contents of C (58.47%), H (6.34%), N (5.43%), and S (7.04%) and a lower content of O (22.72%) than MSS compost [69]. In HA extracted from MSS, C predominated in the HA (by weight), comprising just over 50% of the total, which is similar to the C content in HA extracted from compost and soils. The content of N in the HA extracted from the MSS ranged from 7.63% to 9.90%, and the S content was relatively high, particularly in comparison with that of the soil HA [57].

Li et al. compared the elemental compositions of FA and HA in raw and digested MSS. They showed that the FA had a lower C content and higher O content than the HA in both raw MSS and digested sludge. In anaerobically digested sludge, the C content decreased and the O content increased, and there was also a relative increase in the N content in both the FA and HA [50]. HA derived from aerobically digested sludge had a lower H/C ratio than anaerobically digested sludge, which indicates that aerobic digestion makes sludge more aromatic and condensed. The digested sludge is still far from full maturation compared with organic materials like sludge compost [70].

Changes in the elemental composition are accompanied by changes in the atomic ratios (H/C, N/C, O/C, O/H). These ratios provide information about the structure of the HA molecules in terms of the degree of condensation of the aromatic rings (H/C ratio) and the degree of HA maturity (N/C, O/C, O/H ratios). In soil HA, H/C values of ca. 0.3 are characteristic of compounds with highly condensed aromatic rings; values of about 0.7 indicate monocyclic aromatic hydrocarbons; values of 0.7–1.5 indicate aromatic rings with aliphatic chains of up to 10 carbon atoms; values of 1.5–1.7 indicate alicyclic hydrocarbons; and values of about 2 indicate paraffin [71]. The values of the H/C atomic ratio of HA extracted from MSS ranged from 1.55 to 1.85 [57]. The process of OM humification is connected with an increase in the O content and a decrease in the H content, which changes the O/H and O/C atomic ratios. The values of the O/H and O/C ratios are an indicator of the degree of oxidation of HA [72], and the O/H value is also related to the degree of humification of HA molecules. The higher the O/H ratio, the higher the humification of the HA molecules [72]. The O/H ratio of HA from MSS was lower than that of soil HA, indicating that the HA from the MSS had a lower degree of humification [57]. Li et al. found that, after anaerobic digestion, the O/C ratio of HA increased from 0.32 to 0.39, and the C/N ratio decreased from 9.06 to 6.41 [50].

Molecular-weight distribution. The molecular-weight distribution of HSs reflects their degree of humification. These weights typically range between 5 and 100 kDa for HA and are less than 10 kDa for FA [56,73]. Li et al. reported the molecular weights of HAs and FAs in MSS collected from a full-scale municipal WWTP. The excess sludge was mixed with primary sludge and then mechanically dewatered [52]. The authors found that most of the FAs belonged to the 30–50 kDa fraction, while most of the HAs had molecular weights higher than 100 kDa. In general, sludge HAs have a larger molecular size than sludge FAs. In a more recent paper, Li et al. reported the molecular-weight distribution in raw and digested MSS [50]. They found that most of the FAs in the raw MSS were in the 30–50 kDa and 10–30 kDa fractions. In terms of the TOCs in the FA fractions, sludge anaerobic digestion caused the fractions with MWs lower than 50 kDa to decrease from 85.35% to 61.49% of the total FAs, while those with MWs higher than 50 kDa increased from 14.65% to 38.51%. These changes demonstrated the evolution of sludge FA. The HA underwent similar changes: while the TOC contents of the fractions with MWs higher than 100 kDa were the highest before and after the anaerobic digestion of the sludge, the percentage of HA in this fraction increased from 65.31% to 85.49% after digestion. The increase in the proportion of FA and HA demonstrated that the sludge HSs became more aromatic and condensed, and that humification processes took place during the sludge anaerobic digestion.

4.3. Application of MSS and HSs

An important strategy for recycling the OM and nutrients in MSS is using them as fertilizer and as an organic amendment in agriculture. The contents of OM in European soils are decreasing, which is reducing the soil productivity. The OM contents can be maintained or increased by adding organic soil amendments or organic fertilizers. Preferably, organic fertilizers/soil amendments should contain a high proportion of stable OM that is recalcitrant to biodegradation (i.e., HSs), which can be stored in the soil for a long time and thereby contribute to long-term soil fertility and C sequestration. Although MSS contains HSs, most of the organics are low-molecular-weight compounds that are easily biodegrad-

able, especially in raw MSS. These compounds may be problematic after application to soil due to the O consumption by these organic substances. Therefore, prior to using MSS as an organic fertilizer, it should be stabilized and sanitized. The main biological stabilization process for the agricultural use of MSS is composting. Fertilization with sludge compost improves the chemical properties of the soil. These improvements include increases in the concentrations of OM, nutrients, and microbial biomass, as well as improved physical properties, such as the water-holding capacity. Soil OM, which includes HSs, is important for improving the soil tilth, buffering the pH, and improving the air–water conditions in soil, and it serves as a large pool of carbon and other essential nutrients for plants. Even small increases in the organic carbon content in soil, if achieved over very large areas, will substantially reduce net CO_2 emissions. For this reduction to be long-lasting, the OM has to be in the more stable or resistant fractions (e.g., HAs). HSs are often defined as "the black gold of agriculture" [56,74] due to their beneficial effects on soil quality and plant growth.

Compost, including MSS compost, has also been used in the remediation of soils that are contaminated with heavy metals. These soils pose the potential risk of groundwater contamination, which increases when the metals are in mobile and potentially mobile fractions. Thus, one of the main goals of soil remediation should be to decrease the concentration of metals in bioavailable and mobile fractions (stabilization). Although this process does not decrease the total metal concentration in soil, decreasing metal mobility does substantially decrease the environmental risk. In heavy-metal stabilization, compost acts as an organic amendment that contributes to the immobilization of metals in the soil [75–77].

A new trend is using MSS or compost simply as a source of HSs, which are used as natural biosurfactants for the remediation of soils contaminated with heavy metals. After they are extracted from a suitable source, HSs are effective washing agents for the removal of heavy metals from polluted soils (mobilization). It should be emphasized that HSs for soil washing can be recovered even from MSS or compost/stabilizate with elevated concentrations of HM that would make the sludge unsuitable for agricultural use and composting. To use compost in agriculture (as a fertilizer, a soil amendment, or for metal stabilization), it must not only meet sanitary requirements but also contain less than the maximum allowable concentrations of heavy metals. If the concentrations of heavy metals are higher than permitted, the compost can only be landfilled. However, these composts contain high concentrations of valuable HSs. Thus, the recovery of HSs from compost before landfilling is beneficial because waste products become the source of bioproducts (HSs).

HSs substantially influence the mobility and bioavailability of heavy metals in soils because they are amphiphilic, with both hydrophobic and hydrophilic components, and their carboxyl and hydroxyl groups can form complexes and chelates with heavy metals. For soil washing/soil flushing, HS-rich materials like sludge or other waste can serve as sources of HSs, which are extracted and used as washing agents. It has been shown that these HSs extracted from MSS or compost are very effective for removing heavy metals from highly contaminated soils [14,78–81]. HSs, with their ability to form complexes and chelates with heavy metals, play a crucial role in soil improvement and remediation, making them a valuable resource from MSS.

5. MSS as Feedstock for Thermochemical Conversion to Biochar

Thermochemical technology is considered a promising approach for MSS treatment, as it offers a volume reduction in MSS, the destruction of pathogens, and energy recovery simultaneously [82–85]. The main thermochemical technologies include incineration, pyrolysis, gasification, and hydrothermal liquefaction. The choice of a specific technology depends mainly on the target product. In incineration, MSS is burned at high temperatures (800–900 °C) in the presence of oxygen, producing heat and electricity instead of biochar and ash as the main byproducts. In pyrolysis, the MSS is heated in the absence of oxygen (300–700 °C), resulting in the decomposition of the organic matter into biochar (for resource

recovery) and gases and liquids (for energy recovery). Gasification also takes place in the absence of oxygen, but at higher temperatures than pyrolysis (750–900 °C), and it is mainly aimed at obtaining syngas products (85% on average), rather than biochar (10% on average), that can be used directly for heating or for further processing into hydrocarbon fuels. Hydrothermal carbonization uses elevated temperatures (180–300 °C) and high pressures (5–20 MPa) in a water-rich environment, producing hydrochar (as opposed to products from dry processes such as pyrolysis) and bio-oil, as well as traces of gases [85,86]. Although hydrothermal carbonization also has its own advantages, such as the ability to process wet MSS without drying, pyrolysis is often preferred for biochar production from MSS due to its higher carbon content, elimination of pathogen contents, flexibility in operating conditions, energy recovery, and established technology.

The yield of biochar depends on whether fast or slow pyrolysis is used. Fast pyrolysis (residence time: 0.1–0.3 s; heating rate: 10–200 °C/s) gives a biochar yield between 15 and 25 wt.%, while slow pyrolysis (residence time: 5–30 min; heating rate: 0.1–1 °C/s) gives a biochar yield of 35 wt.% [87]. Thus, slow pyrolysis is more efficient for the biochar yield than fast pyrolysis. Higher pyrolysis temperatures result in lower biochar yields due to water loss, the destruction of OM, and the development of aromatic structures [83]. In general, lower pyrolysis temperatures and longer residence times favor biochar production [87].

5.1. Properties of MSS-Derived Biochar

The properties of MSS-derived biochar affect its suitability for further applications, and they depend on many factors, such as the temperature of the pyrolysis, the properties of the MSS (e.g., moisture content, particle size), the heating rate and residence time, as well as the reactor type.

Porosity and surface area. The porous structure and specific surface area of biochar play an important role in the adsorption processes of different substances. In general, the greater the proportion of micropores in biochar, the higher its adsorption properties. Chen et al. reported the presence of numerous mesopores in biochar prepared from MSS, with an average pore size of 11.3 nm [88]. The porous structure of biochar obtained from MSS at 600 °C was not well developed and had small specific, micropore, and external surface areas. The sizes of the pores in this biochar were concentrated mostly in the ranges of < 2 nm (micropores) and 10–20 nm (mesopores), and the respective percentages of micropores and mesopores were 25.8% and 74.2%. The total volume of the pores was 0.14 cm^3/g, while the volume of the micropores was 0.0034 cm^3/g [89].

Raw MSS has a low surface area of 11 m^2/g, on average. Yuan et al. found that increasing the temperature of pyrolysis from 300 to 700 °C only gradually increased the surface area of MSS-derived biochar, from 14.3 to 26.9 m^2/g, as a result of the removal of volatile organics from the biochar and the opening of the pores [90]. However, surface area values can vary because the source of the MSS influences the content of OM. The other study shows that when the pyrolysis temperature was increased from 500 to 700 °C, the surface area of the biochar obtained from MSS increased from 69.7 to 89.2 m^2/g [91]. In addition, the moisture present in the MSS affects the surface area of the biochar that is produced. Biochar prepared from wet sludge had a higher surface area (41.4 m^2/g) than biochar prepared from dried sludge (34.3 m^2/g) [88].

Biochar pH and electrical conductivity (EC). The pH of MSS-derived biochars produced at 300–400 °C is near neutral, whereas the pH of biochars produced at higher temperatures is alkaline (pH 8.0–12.4) [91–93]. The EC can be used as a proxy for the salinity, and, like the pH, it is affected by the temperature of the pyrolysis. The increases in the pH and EC as the temperature of pyrolysis is increased result from the loss of volatile materials and acidic groups, and from the concentration of alkali metal salts in the ash fraction. Raising the temperature from 500 to 700 °C increased the pH (9.4–12.4) and EC (2.3–9.0 mS/cm) of MSS-derived biochar [91].

Ash. The ash content in biochar reflects the inorganic content of the original feedstock and increases with an increasing pyrolysis temperature. MSS-derived biochar has a rela-

tively high amount of ash, ranging from about 40% at a lower temperature of pyrolysis to 80% at a higher temperature (Table 1). This is because MSS has a high content of inorganic matter, which is concentrated and retained in biochar during pyrolysis. The main components of the ash in raw MSS are Al_2O_3 (13.1%), SiO_2 (21.0%), P_2O_5 (5.2%), Fe_2O_3 (4.3%), and CaO (2.2%) [88]. For comparison, biochars produced from agricultural biomass contain from 8 to 24% ash. The high ash content in MSS-derived biochar can make it unattractive for use as a solid biofuel [94].

Cation-exchange capacity (CEC). The CEC is an indicator of the ability to exchange cations, such as Ca^{2+}, Mg^{2+}, K^+, and Na^+. The CEC is important when biochar is used as a soil amendment. The CEC of MSS was 67.3 cmol/kg and it increased to 113.7 cmol/kg in MSS-derived biochar at 300 °C [95]. The CEC for this biochar was higher than that of compost made from municipal solid wastes (72.2 cmol/kg). With a higher pyrolysis temperature, the CEC in biochar decreases [96].

Volatile matter (VM) and fixed carbon (FC). The VM includes compounds released as volatiles during heating, while the FC is the solid combustible residue left after the sample is completely burned and its volatiles are released. The content of VM in MSS is high, ranging from 51 to 72%, whereas the biochar that is produced from it has a lower VM content (9–26%) (Table 1). Usually, with an increase in the pyrolysis temperature, the contents of ash and FC increase, while the VM decreases, which is due to the degradation of volatiles during pyrolysis. With an increase in the pyrolysis temperature from 500 to 700 °C, the content of VM in MSS-derived biochar decreased from 63% to 18.2%, while the content of FC increased from 12.1% to 24.8% [97]. The greater degree of MSS carbonization and higher amount of FC in biochar produced at a higher pyrolysis temperature indicate a higher thermal stability and higher HHV value of the biochar.

Elemental composition. This property provides information about the nature of the biochar in terms of its recalcitrance and aromaticity. Biochar from MSS is a heterogenous material and contains a significant inorganic pool, which makes it difficult to define its exact chemical composition [11].

An increase in the pyrolysis temperature decreases the C, H, N, O, and S contents in biochar. The total C content in MSS-derived biochar can vary widely, from 21.2% to 45.4% for biochars produced at 300 °C and from 9.8% to 40.5% for biochars produced at 500 °C (Table 1). With an increase in the temperature of pyrolysis, the content of organic carbon (C_{org}) also decreases. Lu et al. analyzed MSS-derived biochar from three WWTPs in China at temperatures of 300–600 °C [98]. The content of C_{org} decreased on average from 9.5 to 5.4%. The average shares of the C_{org} in relation to the total C were 35% for biochar produced at 300–500 °C and 25% for biochar produced at 600 °C. The degree of the C stability in biochar can be expressed by the H/C_{org} molar ratio. The molar H/C_{org} ratio correlates with the degree of thermochemical alteration, by which fused aromatic-ring structures are produced in the material. The presence of these structures is an intrinsic measure of the stability of the material [99]. The lower the H/C_{org} ratio (below 0.7), the greater the stability of the C. The H/C_{org} ratios for MSS-derived biochar are usually lower than 0.7 at different pyrolysis temperatures, which indicates that MSS is a material that is easily thermochemically converted and that contains a large proportion of fused aromatic-ring structures. The H/C_{org} ratio for MSS-derived biochar produced at temperatures between 300 and 600 °C fluctuates between 0.32 and 0.22 [98], which indicates a high degree of aromatic condensation. The hydrophilic nature of MSS-derived biochar, like that of biochars produced from other types of biomass, decreases as the temperature of pyrolysis increases.

The C/N ratio is commonly used as an indicator of the capacity of the biochar to release inorganic N when incorporated into soil. In most cases, the content of N in biochar decreases with an increase in the pyrolysis temperature. As a result, the C/N ratio increases, reflecting the greater loss of N at higher pyrolysis temperatures. Yuan et al. observed an increase in the C/N ratio of MSB from 6.7 (300 °C) to 17.7 (600 °C) [90]. Lu et al. found that the C/N ratio in biochar from MSS increased in a narrow range, on average from 5.0 (300 °C) to 6.4 (600 °C) [98]. Nevertheless, MSS-derived biochar produced at higher

temperatures (e.g., 500 °C) could be used with the environmental function of storing C in soil, whereas biochars produced at lower temperatures (e.g., 300 °C) may be more appropriate for providing labile organic material to the soil, thereby providing nutrients to plants.

Table 1. Chemical characterization of MSS and MSS-derived biochars (MSS-B).

Characteristics	[100]			[101]		[82]			[92]			[102]	
	MSS	MSS-B		MSS	MSS-B	MSS	MSS-B	MSS-B	MSS	MSS-B	MSS-B	MSS	MSS-B
		300 °C	500 °C		500 °C		300 °C	500 °C		300 °C	500 °C		500 °C
pH	-	-	-	-	-	-	-	-	6.82	7.02	7.70	-	-
Moisture (%)	7.0	2.6	3.0	6.30	-	84.5	-	-	85.2	-	-	12.3	2.3
VM (%)	72.1	49.8	26.0	54.1	26.6	73.7	-	-	-	-	-	50.9	8.9
FC (%)	11.9	11.9	23.7	7.8	22.6	0.4	-	-	-	-	-	9.1	-
Ash (%)	16.0	38.3	50.4	31.8	50.9	25.9	-	-	46.6	63.9	77.4	35.5	59.6
C (%)	38.3	45.4	40.5	35.2	35.1	37.9	39.7	9.8	24.7	21.2	15.6	37.9	27.4
H (%)	5.0	4.2	2.0	5.4	3.4	5.5	4.1	0.4	4.6	2.3	0.9	4.5	0.9
O (%)	37.3	7.3	0.7	15.6	5.8	-	-	-	18.6	8.2	3.3	54.1	69.9
N (%)	3.4	4.9	5.7	5.6	4.8	7.1	7.1	2.1	4.5	3.3	2.2	2.7	1.3
S (%)	<0.05	<0.05	0.7	-	-	-	-	-	0.9	1.0	0.6	0.7	0.5

Pyrolysis conditions: a heating rate of 10 °C/min, a residence time of 30 min, and the values are given on a dry basis [100]; spiral continuous pyrolysis reactor with a residence time of 23 min [101]; a muffle furnace with a heating rate of 17 °C/min and a residence time of 30–90 min [82]; a pyrolysis apparatus with a heating rate of 15 °C/min and a residence time of 40 min [92]; a fixed-bed cylindrical glass reactor with a heating rate of 10 °C/min [102].

Nutritive elements. MSS is a rich source of macro- and micronutrients (especially N, P, K, Mg, and Ca). The pyrolysis of MSS has an important effect on the levels of these elements in the resulting biochar (Figure 4).

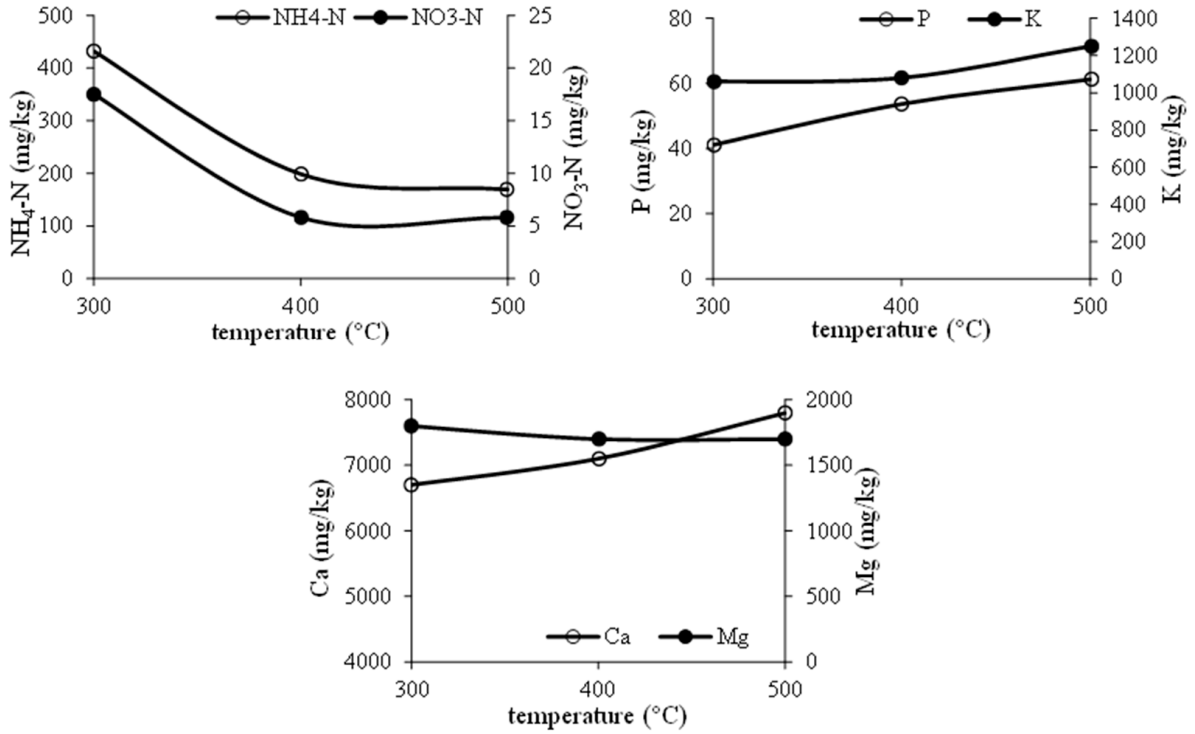


Figure 4. The effect of the pyrolysis temperature on the enrichment in nutritive elements of MSS-derived biochar (based on [103]).

Pyrolysis decreases the concentrations of mineral N forms (i.e., ammonium (NH_4-N) and nitrate (NO_3-N)) in MSS because of the N gas losses during the process. A considerable decrease in N in MSS-derived biochar was observed as the pyrolysis temperature was

increased from 300 to 700 °C [90]. The N loss (expressed as the residue ratio (i.e., the ratio of N content in biochar to that in MSS)) changed from 84 to 18%.

In contrast, the pyrolysis of MSS enriches the levels of other nutrients (K, P, Ca, Mg) in biochar. This is because these elements are present in the inorganic fraction, and they are not volatilized during pyrolysis. High concentrations of elements such as K, P, N, Mg, Ca, and S make MSS-derived biochar suitable for soil fertilization.

5.2. Potential Environmental Concerns Regarding MSS-Derived Biochar

Pyrolysis may be a promising strategy for immobilizing inorganic pollutants, decomposing organic pollutants, and inactivating pathogens present in MSS. The effects of pyrolysis on the various pollutants present in MSS depend on the temperature of the process.

5.2.1. *Heavy Metals*

As a result of pyrolysis, the concentrations of heavy metals are higher in biochar than in the original MSS [104]. When comparing individual heavy metals in MSS and MSS-derived biochar, their concentrations are usually in the following order: Zn > Cu > Cr > Pb > Ni > Cd (Figure 5). The concentrations of individual heavy metals in MSS can vary widely, depending on the type of WWTP and the quality of the treated wastewater. As the temperature of pyrolysis is increased, the average concentrations of most heavy metals in MSS-derived biochar increase within the following ranges: 1430–2694 mg Zn/kg; 647–1113 mg Cu/kg; 123–803 mg Cr/kg; 60–153 mg Ni/kg; and 5.5–14 mg Cd/kg (Figure 5). For good-quality biochar, the International Biochar Initiative (IBI) and European Biochar Certificate (EBC) guidelines state that the concentrations of selected heavy metals should be within the following ranges: 400–416 mg Zn/kg; 100–143 mg Cu/kg; 90–93 mg Cr/kg; 120–121 mg Pb/kg; 30–47 mg Ni/kg; and 1–1.4 mg Cd/kg [99,105]. As can be seen, the heavy-metal concentrations in MSS-derived biochars very often exceed the stated limits.

The total metal concentrations indicate the overall level of pollution in biochar. The environmental impact of biochar always depends on the concentration of bioavailable and leachable metals. The mobility of metals in biochar and their environmental risk can be assessed based on metal fractionation using a suitable sequential extraction protocol (e.g., BCR sequential extraction) or the leachable-heavy-metal concentration (e.g., the Toxicity Characteristic Leaching Test (TCLP)).

Although increases in the temperature of pyrolysis increase the total metal concentration in MSS-derived biochar, this process makes it more difficult to leach most mobile metals out of the resulting biochar. For example, Raj et al. used the TCLP test and found that the leachable concentrations of Ni, Pb, Cd, Cu, and Zn (in mg/kg) in MSS were 1.5, 5.2, 2.6, 2.4, and 14.0, respectively [106]. After pyrolysis (350–500 °C), the concentrations of leachable metals decreased, except for that of the Cd. After pyrolysis, the metal leaching from the MSS-derived biochar was 70% lower than that from the original MSS [107].

Pyrolysis has a considerable effect on the metal distribution in the resulting MSS-derived biochar. In MSS before pyrolysis, Cu, Zn, Pb, Cr, and Ni were predominantly found in the reducible fraction (metals bound to oxides), which contained 57–88% of the total metal concentration [104]. In the most mobile fraction (i.e., exchangeable and soluble in acid), the percent concentrations were 28% Ni, 27% Zn, and 11% Cu (Figure 6a).

In MSS-derived biochar, the shares of metals in the exchangeable and acid-soluble fraction and in the reducible fraction decrease, while the shares in the stable fraction (i.e., oxidizable and residual) increase, especially at 600 °C. The stability of metals in MSS-derived biochar can be estimated using the reduced partition index (I_r), which is based on the metal distribution in MSS-derived biochar [108] (Figure 6b).

When the pyrolysis temperature is increased, the metal stability increases in MSS-derived biochar, as shown by the redistribution of metals from the mobile and potentially mobile fractions to the stable fractions. Based on the I_r, the stability of the metals in MSS-derived biochar change in this order: Cr > Ni ≈ Pb > Cu > Zn. These results confirm that the

pyrolysis of MSS to produce MSS-derived biochar significantly reduces the environmental risk from heavy metals in MSS.

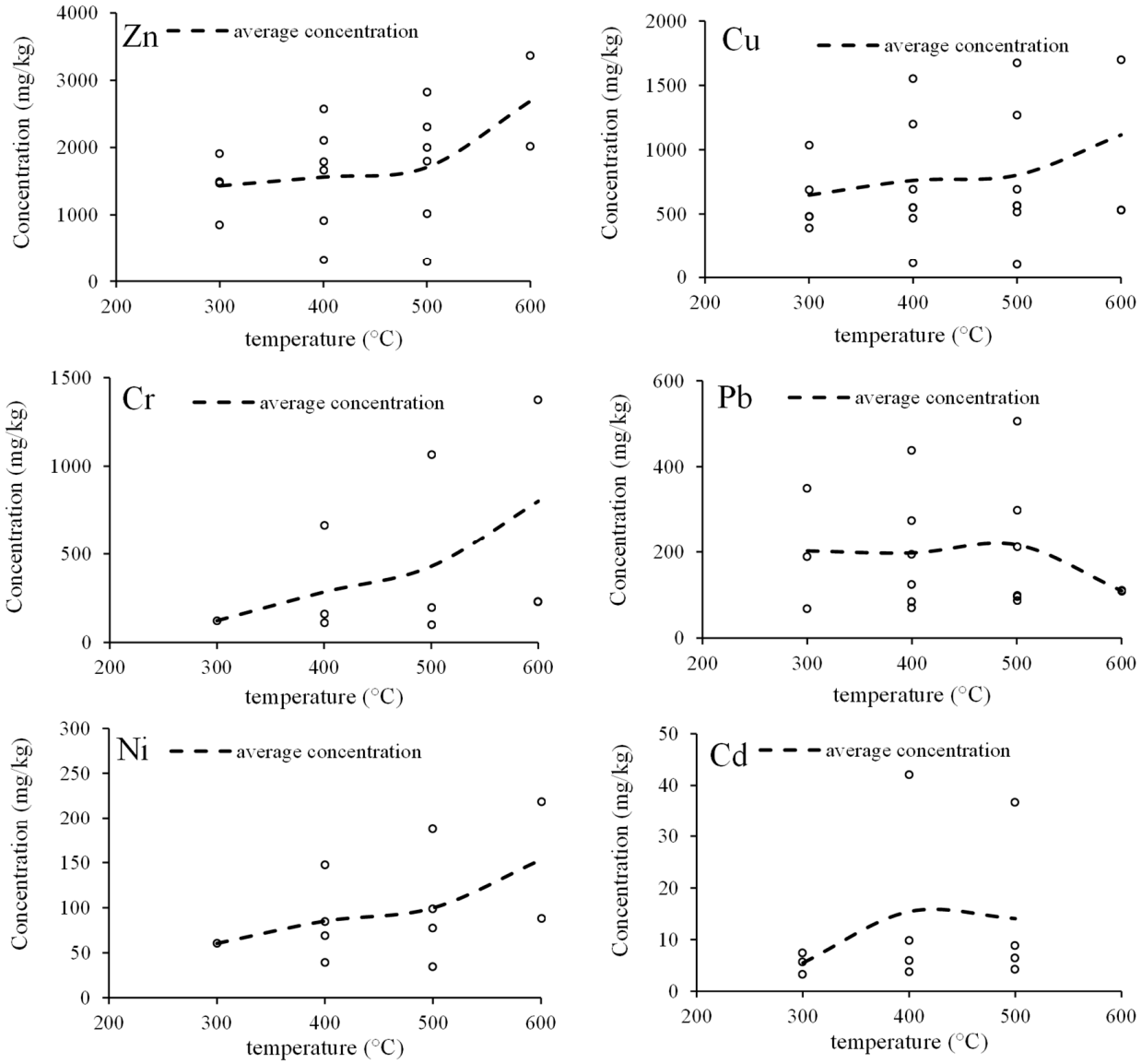


Figure 5. The ranges and averages of heavy-metal concentrations in MSS-derived biochars produced at different temperatures of pyrolysis (based on [93,98,104,106]).

5.2.2. *Organic Pollutants*

MSS may contain various organic pollutants depending on the type of wastewater being treated. Among them, polycyclic aromatic hydrocarbons (PAHs) are frequently analyzed in both MSS and MSS-derived biochars due to their toxicity and carcinogenicity. These molecules differ in their hydrophobicity and degree of sorption to MSS particles. Based on their chemical structure, PAHs can be classified as low-molecular-weight (two- and three-ring), medium-molecular-weight (four-ring), and high-molecular-weight (six-ring) PAHs. After classifying PAHs by the number of rings, Raj et al. found that their abundances decreased in this order: four-ring PAHs (38.8%) > three-ring PAHs (35.5%) > five-ring PAHs (13.7%) > two-ring PAHs (9.1%) > six-ring PAHs (3.4%) [106].

The total PAH content in MSS was 1347.28 µg/kg and was lower in biochar. Depending on the pyrolysis temperature, the total PAH content in biochar was 393.8 µg/kg (350 °C), 258.7 µg/kg (400 °C), 138.3 µg/kg (450 °C), and 741.8 µg/kg (500 °C). Pyrolysis removes most PAHs from MSS, especially low-molecular-weight PAHs, which are thermally

degraded or converted to gaseous and liquid products. However, the contents of some PAHs (e.g., pyrene, benzo[a]pyrene, or chrysene) may be higher in the resulting biochar than in the original MSS [106]. In general, the total content of PAH in MSS-derived biochar is within the permissible limits (i.e., 4 mg/kg [105] or 6 mg/kg) [99]. However, some concern is warranted due to the presence of highly toxic PAHs in MSS-derived biochar (e.g., benzo[a]pyrene).

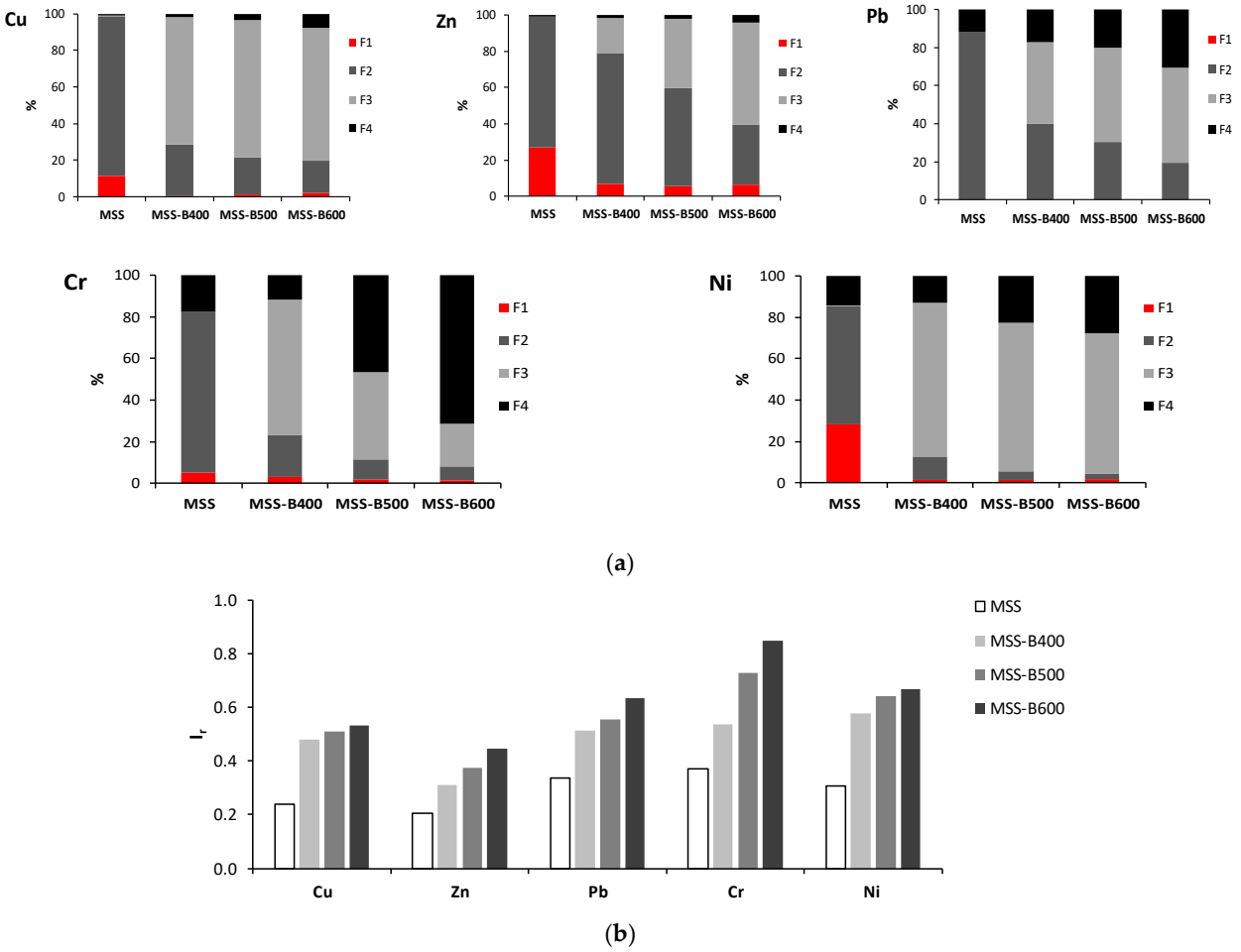


Figure 6. Metal distribution (**a**) and stability (**b**) in MSS and MSS-biochar (MSS-B) produced at different temperatures. F1 is the exchangeable and acid-soluble fraction; F2 is the reducible fraction; F3 is the oxidizable fraction; F4 is the residual fraction. Metal stability (as I_r) was calculated based on metal distribution given in [104].

To improve the physicochemical properties of MSS-derived biochar (e.g., surface area, pore volume, CEC), it can be modified by various methods, such as physical and chemical activation [109]. An interesting approach to improve the quality and quantity of products from MSS pyrolysis is to add other raw materials to the MSS for co-processing. Various co-substrates have been used, such as pine sawdust, microalgae, straw, and wood waste [110]. The co-pyrolysis of MSS with other biomasses could be beneficial not only for improving the biochar properties but also for solving the problem of the presence of pollutants in MSS-derived biochar, especially heavy metals. This is because the mixing of MSS with other biomasses can dilute inorganic and toxic compounds [111].

6. Main Applications of MSS Biochar

Biochar derived from MSS is considered one of the most interesting end products in the wastewater-based circular economy, as shown by the variety of uses that have been tested in different applications. One of the most attractive characteristics of biochar is that

its production is simple, inexpensive, and sustainable. It is estimated that the average price of MSS-derived biochar is about 246 USD/ton, while the price of commercial activated carbon is up to 1500 USD/ton [109]. Although most applications are still in their infancies, MSS-derived biochar already has numerous applications with potentially extraordinary effects in agriculture, the environment, catalysis, etc. [112]. The possible main applications of MSS-derived biochar are summarized in Figure 7. MSS-derived biochar definitely offers many benefits and eliminates the environmental risk associated with the direct use of MSS.

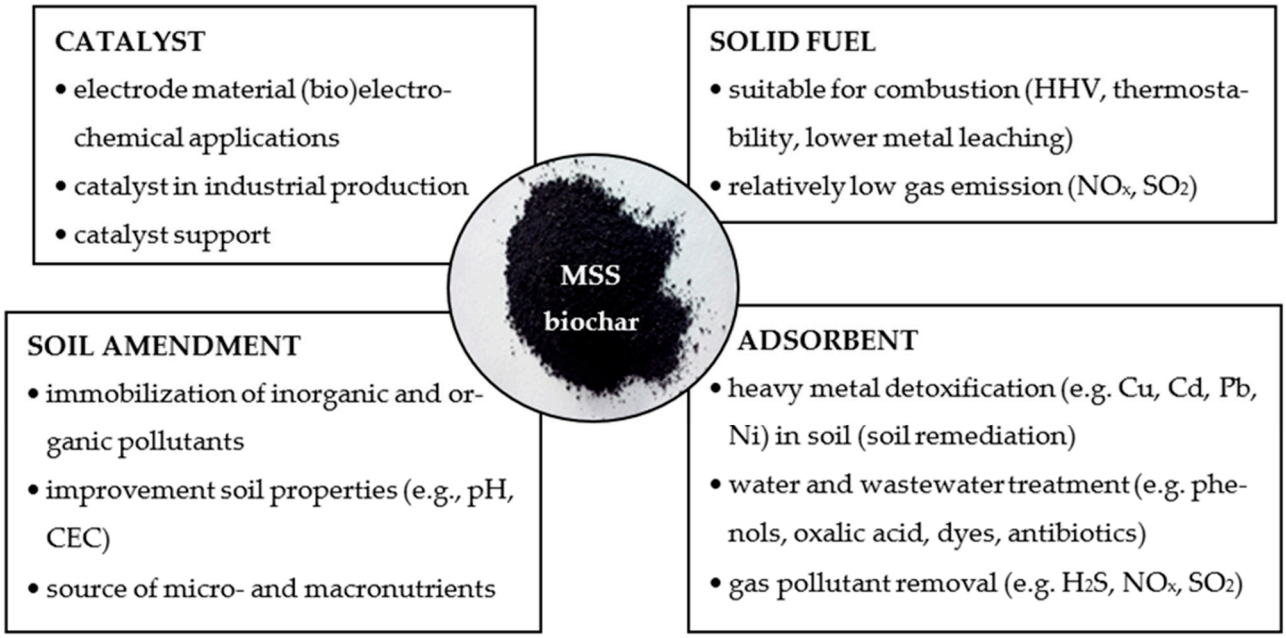


Figure 7. Main applications of MSS-derived biochar (based on [109]).

MSS biochar has attracted a lot of attention as a promising catalyst for various applications, such as wastewater treatment, pollutant removal, and biomass conversion. It can catalyze reactions such as tar removal, biodiesel production, and organic-pollutant conversion. The porous structure and relatively high surface area of MSS biochar provide abundant active sites for catalytic reactions, resulting in improved efficiency [113,114]. When the MSS constituents are not sufficient for the properties of pure MSS biochar catalysts, doping with metals and heteroatoms (Fe, Mn, Co, N) provides catalytic sites. For example, Fe-doped catalysts based on MSS biochar are commonly used in Fenton-like or sulfate-based advanced oxidation processes (AOPs). The N doping of MSS biochar-based catalysts, especially pyridinic and graphitic N, increases the catalytic activity by promoting non-radical pathways in sulfate-based AOPs. In addition, N doping improves the electron shuttle capacity and promotes the formation of graphitic carbon nitride in photocatalytic systems, significantly increasing the photocatalytic capacity of the catalyst. However, excessive N doping can change the nature of the catalyst and introduce new pollutants [113]. MSS biochar can be used as a catalyst in energy storage devices, especially as an electrode material. And the performance of these electrodes is comparable to that of other electrodes based on biochar and graphene [115].

MSS biochar has potential as a solid fuel, although its energy content varies depending on the type of sludge. Digested and dry sludge can have calorific values between 8.5 and 17 MJ/kg, while undigested sludge can reach values of up to 23 MJ/kg. The calorific value of biochar after pyrolysis is typically between 5 and 21 MJ/kg. Although values close to 5 MJ/kg may not be suitable for combustion or energy use, MSS biochar with higher heating values could offer significant opportunities for energy utilization [11]. However, MSS biochar produced by torrefaction shows significant differences compared to biochar produced from other feedstocks. While the torrefaction temperature influences the decrease

in organic matter in MSS biochar, it also has an influence on the ash and sulfur contents. In contrast to biochar from sawdust, an increase in the torrefaction temperature does not lead to an increase in the calorific value of MSS biochar. Instead, the ash and sulfur contents increase, which can lead to problems with ash disposal and SOx emissions during thermal utilization. High ash and sulfur contents could limit the use of MSS biochar as a fuel [116]. Although MSS biochar can be used as a solid fuel, challenges such as the high ash and sulfur contents, lower calorific value, and potential presence of toxic metals need to be addressed for its effective utilization as a solid fuel.

MSS biochar has been investigated as an effective and low-cost adsorbent for the removal of various organic and inorganic pollutants from water and wastewater, such as dyes, heavy metals and metalloids, antibiotics, and others [83,87]. The ability to remove a variety of pollutants simultaneously is related to some particular physicochemical properties of MSS biochar, such as its surface area, pore size, and functional groups. Depending on the type of MSS biochar, different mechanisms are involved in the adsorption of organic and inorganic pollutants (pore filling, hydrophobic interaction, electrostatic attraction, hydrogen bonding, co-precipitation, complex formation, or ion exchange) [117]. MSS biochar can also be used as an adsorbent for odorous and toxic gases. This is mainly due to the alkalinity of biochar and the presence of minerals that can play an important role in gas sorption (e.g., H_2S sorption and sulfur conversion) [118].

The use of MSS biochar as a pollutant adsorbent offers numerous advantages, including a high adsorption capacity, cost efficiency, environmental friendliness, versatility in pollutant removal, and sustainability. The physicochemical properties of MSS biochar together with its diverse adsorption capabilities and potential for modification make it a promising material for environmental remediation. These results support the potential of MSS biochar as an effective and sustainable solution for the adsorption of pollutants in various industrial and environmental applications. While MSS biochar offers promising catalytic and adsorption capabilities, the presence of potentially toxic substances, such as heavy metals, and their possible leaching require careful consideration of its environmental impact and application limitations.

The use of MSS biochar as a soil amendment should be carefully managed to ensure that it does not contain harmful pollutants, such as heavy metals or pathogens. In addition, proper application rates and practices should be followed to maximize the benefits of biochar while minimizing the potential risks. Biochar can help buffer the pH of the soil. Biochar has a high surface area and a porous structure that allows it to hold water and nutrients in the soil, making them available to plants over a longer period of time. In addition, biochar can improve the soil structure by increasing the aggregation, porosity, and water infiltration, thereby improving the soil aeration and root penetration. The addition of biochar to soil can reduce greenhouse gas emissions by stabilizing the organic matter and reducing the decomposition of organic materials in the soil. It can help sequester carbon and mitigate climate change by storing carbon in the soil for hundreds–thousands of years [119]. Good results have been achieved in acidic soils, for example. The application of 2% MSS biochar resulted in higher biomass yields in winter wheat and spinach compared to the 1% biochar-amended soils and the unamended control. In addition, the 2% biochar significantly improved the stability of the soil aggregates and neutralized the soil acidity, resulting in a pH of 6.5, compared to 5.8 in the control and 5.5 in the 1% biochar treatment. However, no effect of the MSS biochar on the biological properties of the soil was observed [120].

7. Limitations and Future Prospects

While the use of MSS as a resource in the circular economy offers significant opportunities, there are also some challenges that need to be addressed in order to fully exploit its potential. Future research and innovation efforts should focus on overcoming these challenges and on developing cost-effective, environmentally friendly, and sustainable technologies to recover valuable resources from MSS. The main limitations and prospects for selected MSS resources are listed in Table 2.

Table 2. Limitations of and future prospects for selected MSS resources.

MSS Resources	Criteria	Limitations and Future Prospects
Struvite	Recovery	Further optimization of the operating parameters is necessary for maximum efficiency and minimum recovery costs.
	Cost	A comprehensive economic analysis is needed to evaluate the cost-efficiency of struvite recovery compared to conventional methods.
	Quality	A more detailed characterization of recovered struvite is necessary to ensure its suitability as a commercial fertilizer (analysis of impurities, nutrient contents, and compliance with fertilizer quality standards).
	Scale	The struvite recovery process should be scaled up to full-scale municipal wastewater treatment.
	Environmental impact	A comprehensive lifecycle assessment (LCA) is needed to evaluate the environmental impact of the struvite recovery process.
ALEs	Operating parameters	Further research is needed to optimize the operating parameters (e.g., organic loading rate, COD/N, retention time) to maximize ALE synthesis in MSS.
	Recovery	Investigation, optimization, and standardization of the extraction methods for ALE recovery is necessary to maximize the yield and quality of the recovered biopolymer not only at the laboratory/pilot scale but also at full scale.
	Quality	Further characterization of the recovered ALEs is necessary to ensure their quality and suitability for various applications (pharmaceutical, environmental, agricultural, etc.).
HSs	Synthesis	Identification of pathways for the synthesis of HS during municipal wastewater treatment is needed.
	Recovery	Research into more efficient and cost-effective extraction techniques is needed to make the process more economically viable.
	Quality	Sewage sludge can contain various impurities that can interfere with the extraction and purification process. The analysis of the HS quality enables further HS use. Creating a clear framework for the use of recovered HSs in various applications will provide certainty for producers and consumers.

Table 2. *Cont.*

MSS Resources	Criteria	Limitations and Future Prospects
Biochar	Production	Research into the optimization of the pyrolysis process is needed, including the use of catalysts, additives, and novel reactor designs, to help improve the efficiency and cost-effectiveness of biochar production from MSS.
	Quality	MSS biochar may contain impurities such as heavy metals and organic pollutants, which must be removed or reduced to ensure the safety and quality of the product. The relationship between the WWTP equivalence population and the quality of MSS biochar should be analyzed. Research into strategies to improve the properties of biochar (pre-treatment, co-pyrolysis, post-treatment) is necessary.
	Scale	The commercialization and scaling of MSS biochar should be undertaken.

8. Conclusions

In recent years, the view of wastewater treatment plants has changed from pure environmental protection and their use as sanitation facilities to their potential as biorefineries. This change opens up opportunities for the valorization of MSS as a valuable resource for energy and material recovery. Technologies such as struvite precipitation to recover phosphorus, the extraction of alginate-like polymers and humic substances from MSS, and pyrolysis to produce biochar offer promising avenues for resource recovery and environmental improvement. The recovered phosphorus can be used for the production of slow-release fertilizers, contributing to both environmental sustainability and agricultural productivity. Alginate-like polymers are a cost-effective alternative to alginate from marine algae. Exploring and exploiting the potential applications of these polymers could lead to significant economic and environmental benefits. The extracted humic substances can be used as soil conditioners, contributing to sustainable agricultural practices and environmental remediation. The pyrolysis of MSS is an effective method for reducing the sludge volume and producing biochar-based adsorbents. With appropriate modification, these biochar-based adsorbents can compete with other commercial adsorbents. However, further research is required to optimize the process and ensure the economic viability.

Technologies for the recovery of value-added products from MSS are in line with the principles of the circular economy and bioeconomy. However, these technologies are not yet fully commercially viable and require further scientific, regulatory, and economic development to realize their full potential. Due to the different characteristics of MSS, it is important to carefully select the final disposal strategy. Tailored approaches for the disposal of MSS can optimize the recovery of resources and minimize the impact on the environment, thereby contributing to the overall sustainability of wastewater treatment processes.

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