Stabilizate from Autoclaved Municipal Solid Waste as a Source of Valuable Humic Substances in a Waste Circular Economy

Dorota Kulikowska1 · Katarzyna Bernat1 · Irena Wojnowska-Baryła1 · Barbara Klik1 · Sylwia Michałowska1 · Sławomir Kasiński1

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Abstract
One of the solutions in unsorted municipal waste management is autoclaving, which maximize the amount of waste for recycling. After autoclaving, however, up to 30% of autoclaved waste, called organic remaining fraction (ORF) is still unsta-bilized and cannot be landfilled but must be subjected for further stabilization, e.g. in aerobic conditions. After this process waste meets standards for landfilling. However, as during aerobic stabilization humification of organic matter proceed, before landfilling humic substances (HS) could be recovered. High HS concentration in ORF means that before its landfilling HS can be recovered. The maximal recovering of valuable substances from waste is in line with the principles of sustainable development. Therefore, this study examined the humification of ORF from a full-scale mechanical-heat-treatment plant during composting in two-stage system (1st stage in 550 L reactor, 2nd stage in windrow). The rates of organics mineralization were 8.35–12.00 g OM/kg d.m. d. The rates of HS formation were lower, 3.31–3.92 mg/g OM d, and process proceeded most intensively up to 50 days. The maximum HS concentrations were 82–120 mg/g OM, similar to those in composts from different kinds of organic waste.

Keywords Autoclaved municipal waste · Aerobic stabilization · Humification kinetics · Fulvic fraction · Humic acids

Katarzyna Bernat
bernat@uwm.edu.pl

Extended author information available on the last page of the article
Statement of Novelty

So far, autoclaves were used mainly for treatment of medical waste. In last decade a few autoclaving installations (mechanical-heat-treatment plant, MHT plant) were established for municipal waste. However, after that process a large part of the autoclaved waste comprises the biodegradable fraction (ORF) that must be stabilized. However, the product of stabilization cannot be used in the environment, but needs to be only landfilled. If it was possible to extract useful substances from the stabilizate, e.g. humic substances, this would be consistent with the goals of a circular economy.

To the best our knowledge, humification process during aerobic stabilization of ORF from a full-scale MHT plant as well as humic substances content in stabilizate from ORF have not been analyzed. Humification have been the subject of many research but during composting, not municipal waste stabilization. We found that HS concentrations in stabilized ORF are high, which indicates that recovery of these substances can be profitable and that this waste can serve as a source of materials for new products in the circular economy.

Introduction

The constantly increasing amount of municipal solid waste and the implementation of directives regarding the reduction of the amount of waste that is landfilled has led to a search for new solutions that allow for maximal recovery and reuse of waste. One of the solutions may be autoclaving, which so far was applied mainly for medical waste [1–4]. In last decade a few autoclaving installations were established for municipal waste. The high temperatures and pressures during autoclaving hygienize pathogens, reduce water content, compact plastics, and disintegrate labels on cans, glass bottles and food packaging [5 as cited in 6]. Autoclaving is followed by mechanical post-treatment to maximize the amount of waste that is recycled (up to about 80% of the initial waste volume) at the mechanical-heat-treatment plant. One of the types of waste that remains after autoclaving and followed mechanical post-treatment is the biodegradable organic fraction (ORF), which, according to current regulations in Poland, cannot be landfilled. Thus, to comply regulations, further treatment of ORF must be applied, e.g. aerobic stabilization. It must be emphasized, however, that even the product of aerobic stabilization of ORF (aerobically stabilized ORF; AS_ORF) can only be landfilled or used in RDF production. According to polish law, it cannot be used directly in the environment.

In aerobic stabilization the unit processes are similar to those in composting, which means that humification takes place and humic substances (HS) are formed. Thus, the amount of HS increases during aerobic stabilization of ORF. HS are a source of nitrogen and phosphorus for plants and positively affect the activity of soil microflora. In addition, humus has an indirect effect on the assimilation of micronutrients and pesticides by plants [7]. Organic matter in compost with a high degree of humification can be a natural protective barrier against heavy metal pollution in soil and water environments [8–11]. Compost also increases the buffer capacity of soils by regulating and stabilizing the soil reaction [12, 13]. However, because stabilized waste cannot be used in the environment, the HS in stabilized ORF cannot be used in this way. It is not forbidden, however, the use of HS after extraction, e.g. as washing agent in remediation/phytoremediation of soils contaminated with heavy metals. The ability of HS to affect the mobility and bioavailability of heavy metals in soils is due to their amphiphilic nature. They have both hydrophobic and hydrophilic components, and their carboxyl and hydroxyl groups can form complexes with heavy metals [14]. In the last years intensively are developed research aimed at using dissolved HS or alkaline solutions of organic matter (DOM) as washing agents in remediation of soils contaminated with heavy metals [15–18]. Therefore, recovering of HS from AS_ORF, that could only be landfilled, seems to be an environmentally beneficial. Using HS from waste in soil remediation is in accordance with the principals of a circular economy, in which waste products serve as sources of a new products. In this context, the content of HS in AS_ORF must be established. Furthermore, the kinetics of humification during ORF stabilization need to be investigated to determine the time when the humification process is most intensive. To the best our knowledge, humification process during aerobic stabilization of ORF from a full-scale mechanical-heat-treatment plant as well as HS content in AS_ORF have not been analyzed. Humification have been the subject of many research but during composting, not municipal waste stabilization.

As is known that HS content depends mainly on feedstock composition, the concentration of HS in products also vary depending on the type of substrate (waste), and especially on the content of lignin. It is connected with the fact that lignin degradation products such as phenols, quinones and more complex compounds are the main precursors in the formation of HS by their polymerization and condensation with N-compounds. For example Kulikowska and Sindrewicz [19] proved that during sewage sludge composting the kind of amendments (barley straw, coniferous bark) influenced both kinetics of humification and HS concentration in compost. The time needed for intensive HS formation was longer with bark than with straw (140 days vs. 60 days). With bark, however, the increase in HS concentration during
composting was higher, and the fulvic fraction (FF) predominated in HS (80%), whereas with straw, humic acids (HA) predominated (82% of HS). The relationship between the content of lignocellulosic materials and HS formations has been studied also by other authors. For example, Zhou et al. [20] stated that, during co-composting of food waste, sawdust and Chinese medicinal herbal residues (CMHRs), high lignin content in CMHRs enhanced and accelerated the humification due to the high share of lignin, and of its derivatives that form the precursors for HA formation.

This study examined the humification of ORF during aerobic stabilization in a two-stage system, i.e. 1st stage in passively aerated reactor and 2nd stage in periodically turned windrow. During the process, temperature profiles, organic matter removal and humification progress were investigated. The concentrations of HS and their fractions, i.e., the FF and HA, were investigated, as were the kinetic parameters of HS and HA formation. On the basis of these results, the time at which humification proceeded most intensively was estimated. Finally, the concentrations of HS and HA in AS_ORF were compared to those in compost from different kinds of organic waste.

Materials and Methods

Waste Used in the Experiment

This paper analyzes the process of humification of the unstimulated biodegradable waste (so called the organic remaining fraction, ORF) that was separated from unsorted municipal waste, after the waste was autoclaved in a mechanical-heat-treatment plant (north-east of Poland) with a capacity of 40,000 Mg/year. During autoclaving the pre-prepared waste (after separation of large-scale waste from the mixed waste stream and mechanical homogenization) is treated under saturated steam conditions during 3 h, at 120–150 °C and pressure of 2–5 bar. The production and condensation of steam took place in a closed system. In this plant, during autoclaving, from each 1 ton of MSW 300 kg of the organic remaining fraction (ORF) is generated (ORF comprise ca. 30% of the waste). In previous study, we showed that ORF contained ca. 70% of organic matter, had a high calorific value of 10–12 MJ/kg; AT4 and GP21equaled ca. 25 g O₂/kg TS and 263 dm³/kg TS, respectively [21]. All above values clearly indicate that ORF needs further treatment to reduce its biodegradability.

Aerobic Stabilization of ORF

Two experimental runs were performed. In run 1, the feedstock for aerobic stabilization consisted entirely of ORF. In run 2, ORF was 90% (w/w) of the feedstock, however, 10% (w/w) was inoculum (I) in the form of stabilizate from run 1 (ORF+I). It was hypothesized that the use of this inoculum would accelerate stabilization. The product of aerobic stabilization of ORF was called AS_ORF, and that of ORF+I was called AS_ORF+I.

Stabilization of ORF and ORF+I was proceeded in a two-stage system consisted of a passively aerated reactor (1st stage) and a periodically turned windrow (2nd stage). The reactor (with a capacity of 550 L) was equipped with devices for automatic monitoring of temperature and mass. A detailed description of the experimental material and the reactor is presented in Wojnowska-Baryla et al. [21].

The humidity during stabilization of ORF and ORF+I was maintained at ca. 40% by adding tap water when necessary. When the temperature in the reactor dropped to room temperature, the stabilized material was moved from the reactor to the windrow.

During stabilization of ORF and ORF+I the humification progress was investigated, including the humification kinetics and the concentrations of HS, FF and HA.

Analytical Methods

Analytical methods were carried out on representative samples of ca. 0.5 L that were taken from the top, middle and bottom of the reactor. After collection, the samples were mixed so that the mixture would represent the average characteristics of the waste. The samples were ground to a diameter of 0.5 mm using a Retsch SM100 mill. During the experiment on aerobically stabilized waste, the temperature in both runs was measured automatically using a PC THERM REM-84 m dual channel temperature sensor with ±0.1°C accuracy. Moisture content and total solids (TS) were determined by drying the samples at 105°C to a constant weight (PN-EN 12880:2004). OM content was determined by incineration at 550 °C (BS EN 12879: 2004). HS, FF, and HA were analyzed with a procedure that was presented in Kulikowska and Klimiuk [22] and in Kulikowska [23]. With this procedure, two fractions of HA were distinguished: labile humic acids (L-HA) (extracted with NaOH). The FF content was determined as the difference between the content of HA and that of HS. The content of TOC was determined using a Shimadzu Liquid TOC-VCSN analyzer.

Calculations

The mineralization of organic matter (g OM/kg d.m.) are described by pseudo 1. order kinetic equation:

\[ OM_{\text{mineralization}} = OM_{\text{max}} \cdot e^{-kt} + OM_{\text{final}} \]
where $OM_{\text{max}}$ is the maximal amount of OM mineralized during aerobic stabilization (g/kg d.m.), $k_{\text{OM}}$ is the rate constant of mineralization (day$^{-1}$), $t$ is the stabilization time (day), and $OM_{\text{final}}$ is the amount of OM after stabilization (g OM/kg d.m.).

The kinetics of HS and HA (including L-HA and S-HA) formation were calculated using a 1. Order kinetics equation:

$$C = C_{\text{max}} \cdot \left(1 - e^{-k \cdot t}\right) + C_0$$

where $C_{\text{max}}$ is the maximum concentration of HS, or HA, or L-HA, or S-HA (mg C/g OM), $k$ is the rate constant (day$^{-1}$), $t$ is stabilization time (day), $C_0$ is the initial concentration of HS, or HA, or L-HA, or S-HA (mg C/g OM).

The humification indexes, i.e., the percentage of HA ($P_{\text{HA}}$) and the degree of polymerization (DP), were calculated using the following formulas [24–26]:

$$P_{\text{HA}} = \frac{HA}{HS} \cdot 100\%$$

$$DP = \frac{HA}{FA}$$

Results and Discussion

Organic Matter Removal and Temperature Profiles

During aerobic stabilization of organic waste, the temperature increases; the temperature changes depend on the content of organic matter in the feedstock and their biodegradability. On the basis of the temperature changes, the process is divided into mesophilic, thermophilic and cooling phases. The temperature profiles during stabilization of ORF and ORF+I in the present study are shown in Fig. 1. Despite the fact that, in both runs, thermophilic conditions were reached very quickly, the duration of thermophilic conditions and the temperature profiles of the later phases of stabilization differed. The profile of stabilization of ORF had a more gradual temperature decrease, whereas that of ORF+I had a sharper decrease. In ORF, the temperature of the substrate reached maximum (70.9 °C) on the 9th day of stabilization, while in ORF+I, the maximum (76.1 °C) was reached on the 6th day. Thermophilic conditions were reached more quickly in ORF+I because this feedstock contained inoculum with microorganisms adapted to aerobic stabilization (stabilized ORF from previous series). In ORF, temperatures above 50 °C lasted until day 37 of the experiment; in ORF+I, they lasted until the 27th day. Subsequently, mesophilic conditions lasted until day 53 in ORF and until day 30 in ORF+I.

![Fig. 1 Temperature profiles and changes in the values OM content in waste during aerobic stabilization of ORF and ORF+I](image-url)
The organic matter (OM) content in the ORF feedstock was ca. 70% (686 g OM/kg d.m.); it was slightly lower in the ORF+I feedstock, ca. 60% (597 g OM/kg d.m.). The profiles of changes in OM content showed that after ca. 55 days of stabilization of ORF, the organic content had decreased by 253 g OM/kg d.m., whereas it had decreased by 177 g OM/kg d.m. after ca. 30 days of ORF+I stabilization. However, the final OM content in both ORF and ORF+I was ca. 420 g OM/kg d.m. In windrows, no changes in OM content were observed.

Mineralization of OM during aerobic stabilization can be described by pseudo 1. order equations. The rate constant of mineralization \( k_{\text{OM}} \) in ORF+I (0.068 day\(^{-1}\)) was 2 times higher than that in ORF (0.033 day\(^{-1}\)) (Fig. 1). The initial rates of OM mineralization \( r_{\text{OM}} \) were 8.4 and 12.0 g OM/kg d.m. d in ORF and ORF+I, respectively.

It must be emphasized that difference in OM content in the feedstocks and differences in temperature profiles and time needed for OM stabilization in both series may resulted from two reasons: (i) the use of the inoculum in form of stabilized ORF, and (ii) high heterogeneity of mixed municipal waste subjected to autoclaving.

**Humification Progress**

**Kinetics of Humification**

It is known that during composting humification take place [27–29]. To date, most studies only measured the concentration of HS, HA and FF in the feedstocks and the final product and the studies on process kinetics are very scarce. However, it is important because kinetics allows determination of the time at which the humification process proceeds most intensively.

In this study, the concentrations of HS, FF and HA, (including both stable humic acids, HA-S, and labile humic acids, HA-L) were measured over time. The changes in the concentrations of HS, HA and FF are shown in Fig. 2.

In the ORF and ORF+I feedstocks, the concentrations of HS were 70.6 mg C/g OM and 61.9 mg C/g OM, respectively. During the first days of the experiment, there was a decrease in HS concentration that lasted until day 22 (ORF) or day 6 (ORF+I). After that time, the concentrations of HS were 56.8 mg C/g OM and 42.9 mg C/g OM, respectively.

The same trend was observed with FF and HA concentrations. The concentrations of FF and HA in the ORF feedstock were 39.6 mg C/g OM and 31 mg C/g OM, respectively. After the initial decrease, these concentrations were 32 mg C/g OM and 21 mg C/g OM, respectively. After the initial decrease, these concentrations were slightly lower (30.6 mg C/g OM and 29.5 mg C/g OM, respectively). After the initial decrease, these concentrations were ca. 27 mg C/g OM.

A decrease in the concentration of HS during aerobic stabilization, and especially a decrease in HA concentration, are not typical phenomena, but Kulikowska [30] has already reported decreases in HS and HA concentrations during the first phase of sewage sludge composting. Other researchers have reported that some species of fungi and actinomycetes have the ability to decompose both natural soil HA and synthetic HA [31–33]. Most of these studies were carried out at laboratory scale with commercially-available HA. Blondeau [31] showed that biodegradation of natural and synthetic (melanoidin) HA by *Phanerochaete chrysosporium* BKF-1767 occurred during secondary metabolism in nitrogen-limited cultures. These authors based their conclusions about HA biodegradation mainly on decolorization in batch culture, reduction in molecular weight and CO\(_2\) production. However, *P. chrysosporium* was not able to degrade HA when these acids were the only source of organic carbon. In contrast, the process was effective in the presence of readily biodegradable compounds, e.g. glucose. Steffen et al. [33] showed that *Collybia dryophila* K209 has the ability to degrade both natural HA isolated from pine-forest litter and synthetic HA to low molecular weight fulvic acids and carbon dioxide. Those authors indicated that the enzyme responsible for HA degradation is manganese-dependent peroxidase (MnP). HA decomposition was considerably increased in the presence of Mn\(^{2+}\), leading to 75% conversion of HA and 50% mineralization of these acids. In the absence of Mn\(^{2+}\), only 60% of HA was converted and only 20% was mineralized. Blondeau [31] and Steffen et al. [33] reported that the main enzyme responsible for HA conversion is peroxidase. In contrast, Zavarzina et al. [34] reported that transformations of soil and peat-derived humic acids were carried out by laccase from the white-rot basidiomycete *Panus tigrinus* 8/18. Those authors showed that purified laccase alone is capable of both polymerizing and depolymerizing HA in vitro.

In this study, after the initial decrease in HS concentrations, which involved decreases in both HA and FF concentrations, the concentrations of all these substances increased. HS and HA formation started after 20 days (in ORF) and 5–6 days (in ORF+I) when the temperature in the reactor decreased below 60°C. The most intensive humification in ORF and ORF+I lasted for the next 4–5 weeks of the process. The concentrations of HS were 120 mg C/g OM (ORF), and 82 mg C/g OM (ORF+I), with the share of HA at ca. 60%. After that, the concentrations of HS did not change, but HA concentrations increased while FF concentrations decreased.

On the basis of the changes in HS and HA concentrations over time, the kinetic parameters of humification were calculated. Both HS and HA formation proceeded according to 1. Order kinetic equations (Fig. 2). The kinetic constants of HS formation in ORF and ORF+I were 0.066 day\(^{-1}\) and...
0.078 day\(^{-1}\) (Fig. 2), respectively, whereas those of HA formation were 0.060 day\(^{-1}\) and 0.071 day\(^{-1}\), respectively. The rates of HS formation were 3.92 mg C/g OM d (ORF) and 3.31 mg C/g OM d (ORF+I), respectively, and those of HA formation equaled 2.97 and 1.55 mg C/g OM d, respectively. Although in the literature data on the humification kinetics are scarce, our earlier studies also found that humification during sewage sludge composting proceeded with 1. order kinetics \[19\]. The kinetic constants of HS and HA formation were 0.047 day\(^{-1}\) (\(k_{\text{HS}}\)) and 0.044 day\(^{-1}\) (\(k_{\text{HA}}\)) during sewage sludge composting with barley straw and 0.025 day\(^{-1}\) (\(k_{\text{HS}}\)) and 0.022 day\(^{-1}\) (\(k_{\text{HA}}\)) when bark was used instead of barley straw. The rates of HS formation were 3.95 mg C/g OM d (barley straw) and 4.45 mg C/g OM d (bark), and those of HA formation were 3.04 mg C/g OM d and 0.77 mg C/g OM d, respectively. The low rate of HA formation during composting of sewage sludge with bark resulted from the low concentration of HA (polymerization of FF to HA did not take place).

In this study, it was not possible to describe the changes in FF concentrations with a kinetic model, and kinetic constants were not determined due to the fluctuations in FF concentration in time. The maximum concentrations of FF in ORF and ORF+I were ca. 60 mg C/g OM and ca. 34 mg C/g OM on days ca. 45 and ca. 16 of stabilization, respectively; after this time, the concentrations decreased. This was

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**Fig. 2** Changes in the concentration of HS, HA, and FF in waste during aerobic stabilization of ORF and ORF+I; the table presents the kinetics of HS and HA formation

| Kinetic parameters | ORF | ORF+I |
|-------------------|-----|-------|
| HS formation      | \(k_{\text{HS}}\) [d\(^{-1}\)] | 0.066 | 0.078 |
|                   | \(r_{\text{HS}}\) [mg/g OM·d] | 3.92  | 3.31  |
| HA formation      | \(k_{\text{HA}}\) [d\(^{-1}\)] | 0.060 | 0.071 |
|                   | \(r_{\text{HA}}\) [mg/g OM·d] | 2.97  | 1.55  |
probably due to the polymerization of low molecular-weight FF, creating high molecular-weight HA.

In the AS_ORF and AS_ORF+I, HA predominated slightly in HS. It is known that the share of HA and FF in the final product (compost, stabilizate) depends on both the maturation time and the feedstock composition. Kulikowska and Sindrewicz [19] showed that, during composting of sewage sludge with barley straw, HA was the predominant fraction in HS; after 160 days of composting, the concentration of HA was 129.3 mg/g OM, whereas that of FF was 81.9 mg/g OM. When barley straw was replaced by bark, FF predominated in mature compost (HA 90.8 mg/g OM, FF 221.9 mg/g OM). Many studies have reported that higher amounts of FF may indicate the immaturity of the compost and suggest the need to elongate the maturation time. Earlier research has shown that the elongation of maturation time had a greater effect on changes within HS (i.e. polymerization of FA to HA) than on the amount of HS [23].

If organic waste after stabilization (which could be, for example, selectively collected organic waste, waste from the agri-food industry or sewage sludge) is introduced into soils as a fertilizer, it is important that the carbon is present in the most stable form, i.e., in the form of humic acids. This prevents excessive mineralization and the creation of an oxygen deficit in the soil. However, if waste is considered as a source of HS that could be recovered and then used, then even waste containing a high concentration of FF is valuable as FF contributed considerably to binding some metals (i.e. Fe, Zn, Cu) [35]. Similar observations were made by Borůvka and Drábek [36] in heavily polluted soil (Fluvisol type). In their study, 98, 82, and 96% of organically bound Cd, Pb, and Zn, respectively, were in the FF. Donisa et al. [37] reported that 11 different elements (including Cu and Cd) were more abundant in the FF than in the HA in all analysed soils (andosol, podzol, cambisol). All these reports show that FF are generally the main fraction of HS that reacts with metals. The FF has a high capacity for metal binding because it contains higher number of reactive groups. However, mainly due to their lower molecular weight and higher content of functional groups, FF are thought to form more soluble, mobile and bioavailable metal complexes than HA. Therefore, FF can act as metal carriers. Thus, there is no need to extend the stabilization time, including maturation, to obtain HA as the dominant fraction in HS (by polymerization of FF to HA).

HA consists of labile L-HA and stable S-HA. It is thought that L-HA bind weakly to mineral surfaces via cation bridges, and that they are more similar to fulvic acids in nature. S-HA are more stable and bind strongly to the mineral fraction in soil. Whereas L-HA have low to medium molecular weights and are aromatic in nature, S-HA have higher molecular weights and are more aliphatic. In this study, in stabilizat of ORF, the share of L-HA was slightly lower than that of S-HA (ca 46% of HA vs. ca 54% of HA). In stabilizat of ORF+I, the shares of L-HA and S-HA of HA was similar as in ORF, however, their concentrations were lower (ca 23 mg C/g OM, L-HA, and ca 25.6 mg C/g OM, S-HA, vs ca. 31 mg C/g OM, L-HA, and 36 mg C/g OM, S-HA).

On the basis of changes in the concentrations L-HA and S-HA during humification in ORF and ORF+I, the rates of the formation of these forms of HA and the kinetic constants of the process were determined. L-HA and S-HA formation followed a 1. Order kinetic model. Such a detailed characterization of the kinetics of L-HA and S-HA formation is lacking in the literature. The kinetic constants of L-HA and S-HA formation were similar to those obtained for total HA formation, ranging from 0.059 to 0.063 day⁻¹. The rates of L-HA and S-HA formation in ORF were lower than those in ORF+I (Fig. 3).

In this study, the share of L-HA in HA was high. This is not typical phenomenon, as earlier research concerning humification during sewage sludge composting showed that, in mature compost, L-HA in HA did not exceed 10–20% [22, 23, 30].

In the present study, the degree of polymerization (DP) and the percentage of HA (P_HA) were used as humification indexes (Fig. 4). Other authors have also indicated that these indexes are useful for assessing humification [25, 28, 38]. In the present study, P_HA increased from 44% to 65.3% during stabilization of ORF and from 47.7% to 60% during stabilization of ORF+I.

The DP, which is an indicator of the formation of complex molecules of HA from simpler molecules of FF, increased from 0.78 to 1.88 in ORF stabilization and from 0.90 to 1.71 in ORF+I stabilization. It should be noted that the most intensive polymerization took place in the last days of stabilization. However, the maximum concentration of HS was obtained within ca. 60 days (ORF) and ca. 35 days (ORF+I) days (Fig. 2), and a higher concentration of HA did not need to be obtained because AS_ORF or AS_ORF+I have to be landfilled and not introduced to soil. Thus, a stabilization time of ca. 50 days is sufficient to produce the maximum amount of HS, and the process does not need to be continued further.

After 50 days of ORF stabilization, the HS concentration reached a maximum of ca. 120 mg C/g OM. During stabilization of ORF+I, the maximum concentration of HS was lower by a factor of 0.68 (ca. 82 mg C/g OM). However, the maximum concentration was obtained faster than with ORF, after ca. 35 days. In ORF and ORF+I, the concentration of FF was ca. 60 mg C/g OM and ca. 30 mg C/g OM, respectively. These concentrations comprised 50% and 37% of HS content. The difference in HS concentration in the ORF and ORF+I feedstocks may result from the fact that ORF is a fraction of mixed municipal solid waste after autoclaving.
This substrate is highly heterogeneous, with varying contents of lignocellulosic materials (hemicelluloses, celluloses and lignin), which are decomposed to form humic substance precursors.

Studies on humification of organic matter in municipal solid waste that has been autoclaved are scarce despite the fact that this kind of waste is commonly aerobically stabilized. Most studies of the organic fraction of municipal solid waste have focused on effective stabilization of organic matter for obtaining desirable stabilize characteristics. In the studies where HS concentrations have been determined, mostly sewage sludge or agri-food waste have been used. Those studies indicate that the share of lignocellulose substances in the feedstock determines the HS content in the final product after composting/aerobic stabilization. For example, Kulikowska and Sinderewicz [19] investigated humification during sewage sludge composting with different amendments (barley straw, coniferous

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**Fig. 3** Changes in the concentration of L-HA and S-HA in waste during aerobic stabilization of ORF and ORF+I; the table presents the kinetics of HA, L-HA and S-HA formation

| Kinetic parameters | ORF       | ORF+I     |
|--------------------|-----------|-----------|
| L-HA formation     | $k_{L-HA}$ [d$^{-1}$] | 0.058     | 0.063     |
|                    | $r_{L-HA}$ [mg/g OM·d] | 0.99       | 0.64       |
| S-HA formation     | $k_{S-HA}$ [d$^{-1}$] | 0.063     | 0.059     |
|                    | $r_{S-HA}$ [mg/g OM·d] | 1.58       | 0.92       |

**Fig. 4** The percentage of HA ($P_{HA}$) and the degree of polymerization (DP) during aerobic stabilization of ORF and ORF+I
The HS concentration was higher with bark than with straw (178 mg C/g OM vs 84 mg C/g OM). Zhao et al. [38] used four crop straws during composting of sewage sludge. They found that the final contents of HS in the compost piles of sewage sludge amended with rape straw, wheat straw, maize straw and rice straw were 118, 128, 141 and 134 g/kg, respectively.

In Table 1, the contents of HS and HA in composts from various types of waste are shown. The content of HS in the compost depends on the type of composted waste and varies widely from 32 mg C/g OM [39] to 210 mg C/g OM [22]. In this context, it can be seen that the HS concentrations in AS_ORF and AS_ORF+I in the present study, which ranged from 82 to 120 mg C/g OM, are rather high.

Conclusions

High HS concentrations in aerobically stabilized ORF means that their recovery before AS_ORF landfilling can be profitable. This would be consistent with the principles of a circular economy, in which the only wastes that are landfilled are those from which no more valuable products can be obtained.

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References

[1] Tiller, T., Linscott, A.: Evaluation of a steam autoclave for sterilizing medical waste at a University Health Center. Am. J. Inf. Control 32, 9 (2004)
[2] Hossain, M.S., Balakrishnan, V., Rahman, N.N., Sarker, M.Z., Kadir, M.O.: Treatment of clinical solid waste using a steam autoclave as a possible alternative technology to incineration. Int. J. Environ. Res. Public Health 9, 855–867 (2012)
[3] Ökten, H.E., Corum, A., Demir, H.H.: A comparative economic analysis for medical waste treatment options. Environ. Protect. Eng. 41, 137–145 (2015)
[4] Windfeld, E.S., Brooks, M.S.-L.: Medical waste management—a review. J. Environ. Manag. 163, 98–108 (2015)
[5] Papadimitriou, E.K.: Evaluating the Effect of Autoclaving on the Rate of Bioprocessing of Waste-Characteristics of Autoclaving Condensate and Autoclaved Biodegradables from Non-segregated MSW. Report to Defra. University of Leeds, UK Waste Implementation Programme, Leeds (2007)
[6] García, A., Mauatl, C., Torrente, J.M., Sánchez, A., Barrena, R., Font, X.: Biological treatment of the organic fibre from the autoclaving of municipal solid wastes; preliminary results. Bio-syst. Eng. 112, 335–343 (2012)
[7] Senesi, N., Loffredo, E., D’Orazio, E., Brunetti, V., Miano, T.M., Cava, P.: Humic substances and chemical contaminants.

Table 1 Concentrations of HS and HA in composts from different kind of waste and in the stabilized waste from this study

| Feedstock composition form compost production | HS (mg C/g OM) | HA (mg C/g OM) | Literature |
|---------------------------------------------|---------------|----------------|------------|
| Sewage sludge + cotton waste                | 104.7         | 79.0           | Bernal et al. [39] |
| Poultry manure + cotton waste + olive mill wastewater | 55.9         | 29.4           |            |
| Sewage sludge + cotton waste + olive mill wastewater | 32.0         | 13.6           |            |
| Sewage sludge + maize straw                 | 71.2          | 47.3           |            |
| Sewage sludge + maize straw + olive mill wastewater | 103.2        | 6.8            |            |
| Pig slurry + poultry manure + sweet sorghum bagasse | 75.0         | 56.2           |            |
| City refuse + sweet sorghum bagasse          | 33.9          | 21.9           |            |
| Rabbit manure (composting)                  | 104.1         | 66.9           | Campitelli et al. [40] |
| Rabbit manure (vermicomposting)             | 79.4          | 47.8           |            |
| Tanned residues + wheat bran + hair + lime   | 49.3          | 40.6           | Amir et al. [41] |
| Tanned residues + wheat bran + hair + ammonia | 31.5        | 26.8           |            |
| Sewage sludge + wood chips + rape straw     | 210.0         | 112.0          | Kulikowska and Klimiuk [22] |
| Sewage sludge + wood chips + grass          | 147.0         | 91.0           |            |
| Sewage sludge + rape straw                  | 120.2         | 55.6           | Zhao et al. [38] |
| Sewage sludge + wheat straw                 | 139.9         | 72.3           |            |
| Sewage sludge + maize straw                 | 111.1         | 73.3           |            |
| Sewage sludge + rice straw                  | 83.8          | 50.9           |            |
| Sewage sludge + wood chips + leaves         | 178           | 133            | Kulikowska [23] |
| AS_ORF                                      | 82–120        | 52–60          | This study  |

*a Stabilized, not compost

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In: Proceedings of a Workshop and Symposium Cosponsored by the International Humic substances Society, the Soil Science of America, and the American Society of Agronomy, Anaheim, USA, 26–27 October, pp. 129–153 (1997)

8. Gardea-Torresdey, J.L., Tang, L., Salvador, J.M.: Copper adsorption by esterified and unesterified fractions of Sphagnum peat moss and its different humic substances. J. Hazard. Mater. 48, 191–206 (1996)

9. van Herwijnen, R., Laverie, T., Poole, J., Hodson, M.E., Hutchings, T.R.: The effect of organic materials on the mobility and toxicity of metals in contaminated soils. Appl. Geochem. 22, 2242–2434 (2007)

10. Chen, H.S., Huang, Q.Y., Liu, L.N., Cai, P., Liang, W., Li, M.: Poultry manure compost alleviates the phytotoxicity of soil cadmium: influence on growth of pakchoi (Brassica chinensis). Pedosphere 20, 63–70 (2010)

11. Farrell, M., Perkins, W.T., Hobbs, P.J., Griffith, G.W., Jones, D.I.: Migration of heavy metals in soil as influenced by compost amendments. Environ. Pollut. 158, 55–64 (2010)

12. He, X., Logan, T., Traina, S.: Physical and chemical characteristics of selected U.S. municipal solid waste composts. J. Environ. Qual. 24, 543–552 (1995)

13. Garcia-Gil, J.C., Ceppi, S., Valesca, M., Polo, A., Sensei, N.: Long-term effects of amendment with municipal solid waste compost on the elemental and functional group composition and pH-buffer capacity of soil humic acid. Geoderma 121, 135–142 (2004)

14. Spark, K.M., Wells, J.D., Johnson, B.B.: The interaction of a humic acid with heavy metals. Aust. J. Soil Res. 35, 89–101 (1997)

15. Kulikowska, D., Gusiatin, Z.M., Bulkowski, K., Klik, B.: Feasibility of using humic substances from compost to remove heavy metals (Cd, Cu, Ni, Pb, Zn) from contaminated soil aged for different periods of time. J. Hazard. Mater. 300, 882–891 (2015)

16. Kulikowska, D., Gusiatin, Z.M., Bulkowski, K., Kierklo, K.: Humic substances from sewage sludge compost as washing agent effectively remove Cu and Cd from soil. Chemosphere 136, 42–49 (2015)

17. Gusiatin, Z.M., Kulikowska, D., Klik, B.: Suitability of humic substances recovered from sewage sludge to remedy soils from a former As mining area—a novel approach. J. Hazard. Mater. 38, 160–166 (2017)

18. Meng, F., Yuan, G., Wei, J., Bi, D., Ok, Y.S., Wang, H.: Humic substances as a washing agent for Cd-contaminated soils. Chemosphere 181, 461–467 (2017)

19. Kulikowska, D., Sindreweicz, S.: Effect of barley straw and coniferous bark on humification process during sewage sludge composting. Waste Manag. 79, 2007–2013 (2018)

20. Zhou, Y., Selvam, A., Wong, J.W.: Evaluation of humic substances during co-composting of food waste, sawdust and Chinese medicinal herbal residues. Bioresour. Technol. 168, 229–234 (2014)

21. Wojnowska-Baryla, I., Kulikowska, D., Bernat, K., Kasifiski, S., Zaborowska, M., Kielak, T.: Stabilization of municipal solid waste after autoclaving in a passively aerated bioreactor. Waste Manag. Res. 37, 542–550 (2019)

22. Kulikowska, D., Klimiuk, E.: Organic matter transformations and kinetics during sewage sludge composting in a two-stage system. Bioresour. Technol. 102, 10951–10958 (2011)

23. Kulikowska, D.: Kinetics of organic matter removal and humification progress during sewage sludge composting. Waste Manag. 49, 196–203 (2016)

24. Bustamante, M.A., Paredes, C., Marruenda-Egea, F.C., Pérez-Espinoza, A., Bernal, M.P., Moral, R.: Co-composting of distillery with animal manures: carbon and nitrogen transformations in the evaluation of compost stability. Chemosphere 72, 551–557 (2008)
Affiliations

Dorota Kulikowska¹ · Katarzyna Bernat¹ · Irena Wojnowska-Baryła¹ · Barbara Klik¹ · Sylwia Michałowska¹ · Sławomir Kasiński¹

¹ Department of Environmental Biotechnology, University of Warmia and Mazury in Olsztyn, Słoneczna 45G, 10-709 Olsztyn, Poland