Review

Artificial Humic Substances as Biomimetics of Natural Ana-Logues: Production, Characteristics and Preferences in Their Use

Elena Efremenko *, Nikolay Stepanov, Olga Senko, Ilya Lyagin, Olga Maslova, Aysel Aslanli

Posted Date: 14 November 2023

doi: 10.20944/preprints202311.0877.v1

Keywords: waste treatment; composting; anaerobic digestion; pyrolysis; hydrothermal carbonization; biosorbents

Review

Artificial Humic Substances as Biomimetics of Natural Analogues: Production, Characteristics and Preferences in Their Use

Elena Efremenko *, Nikolay Stepanov, Olga Senko, Ilya Lyagin, Olga Maslova and Aysel Aslanli

Faculty of Chemistry, Lomonosov Moscow State University, Lenin Hills 1/3, Moscow 119991, Russia; elena_efremenko@list.ru (E.E.); na.stepanov@gmail.com (N.S.); senkoov@gmail.com (O.S.); lyagin@mail.ru (I.L.); olga.maslova.rabota@gmail.com (O.M.), ayselaslanli@mail.ru (A.A.);

* Correspondence: elena_efremenko@list.ru; Tel.: +7-(495)-939-3170; Fax: +7-(495)-939-5417

Abstract: Humification is a promising strategy to reduce the amount of animal waste generated in agriculture. This makes it possible to accumulate products with artificially obtained humic substances (HS) as analogues of natural HS, usually extracted from fossil sources (coal, peat). The review examines the main characteristics of various biological and physical-chemical methods (composting, anaerobic digestion, pyrolysis, hydrothermal carbonation, acid or alkaline hydrolysis, subcritical water extraction) used to form HS in animal waste humification products. A comparative analysis of the humification rates and yields of HS in these processes, the characteristics of artificial HS in products (humification index, polymerization index, degree of aromaticity, etc.) is carried out in connection with the use of certain methods of humification and types of animal waste. The main factors (additives, process conditions, waste pretreatment, etc.) that can increase the efficiency of humification and the properties of HS resources artificially obtained by various methods are highlighted. A generalizing analysis of the content of chemical elements in artificial HS obtained from various animal husbandry wastes in comparison with natural HS was carried out. Based on the results of the chemical composition analysis, the main trends and preferences regarding the most useful applications of humification products as complex biomimetics are discussed.

Keywords: waste treatment; composting; anaerobic digestion; pyrolysis; hydrothermal carbonization; biosorbents

1. Introduction

Humic substances (HS), their composition and concentrations mostly determine the basic properties of soils, play an important role in regulating growth of plants and soil microorganisms [1,2] accumulation and migration of metal ions, radionuclides and ecotoxicants in soils [3]. It is possible to regulate these processes by changing primarily the concentration of HS in soils due to their introduction [2]. Actively used and damaged soils need constant introduction of HS in significant quantities in order to restore them [4], while the presence of main components of HS (humic acids (HA) and fulvic acids (FA)) and their quantitative ratio predetermine the functions of HS as soil structurators involved in the regulation of soil humidity, air and water permeability. Currently, the raw materials for commercial production and widespread use of HS are mainly peat and coals, from which HS are extracted [5,6]. In nature, the formation of HS occurs as a result of the humification (HF) of bioorganic (mainly plant) residues. However, various methods similar to natural ones are being developed for the "artificial" production of HS from organic wastes accumulated mainly in agriculture (plant wastes and animal excrements). These wastes are generated annually in significant quantities on livestock and poultry farms in various countries of the world (Table 1) [7–19].

 doi:10.20944/preprints202311.0877.v1

Table 1. Annual amounts of animal wastes produced in various countries.

Country / Reference	Animal wastes [Refference]	AP*
USA	Dairy manure [7]	24 000
China	Livestock manure [8]	3 800
	Chicken manure [9]	155.0
Brazil	Cattle manure [10]	1 900
EU]	Farm manure [11]	1 200
France	Farm manure [12]	214.3
Germany	Farm manure [12]	175.7
United Kingdom	Farm manure [12]	112.0
Spain	Farm manure [12]	108.3
Bangladesh	Cow manure [13]	102.6
Poland	Farm manure [12]	91.3
Italy	Farm manure [12]	89.4
India	Poultry manure [14]	38.0
Malaysia	Chicken manure [15]	23.1
Serbia	Farm manure [12]	18.6
Greece	Farm manure [12]	16.9
Belgorod Region, Russia	Total manure [16]	14.2
Turkey	Chicken manure [17]	11.0
Canary Islands	Livestock manure [18]	0.5
Malta	Farm manure [12]	0.3
South Africa	Cattle manure [19]	0.1

Their conversion into HS-resources containing simultaneous sources of carbon (C), nitrogen (N), phosphorus (P) and microelements allows us to simultaneously solve the problem of obtaining HS similar to natural ones and significantly reduce the volumes of wastes. In addition, a number of methods for the HF of these wastes allow, together with the production of HS, the destruction of various micro-pollutants contained in them (pesticides, mycotoxins, microplastics, pharmaceutical pollutants, etc.) [20–23]. However, the initial composition of wastes and the applied HF-methods not only lead to the obtaining of various products (Figure 1), but also HS with different compositions and properties widening the range of fields of their potential use instead of natural HS.

The purpose of this review was to analyze current information on various HF-methods of animal wastes (AW) resulting in HS accumulation, to compare the content of HS depending on the sources and HF-process conditions, to discuss the prospects for the use of HS-resources from AW instead of traditional natural HS from peat and coal.

2. Different methods used for artificial HF of animal wastes (AW)

Various biological (anaerobic digestion (AD**)** and composting) and physical-chemical (hydrothermal carbonization (HTC), pyrolysis, acid or alkaline hydrolysis, subcritical water extraction) methods for the HF of AW are currently investigated (Figure 1, Table 2 [24–70]). To compare the processes and HS-resources obtained by them, the following indicators were taken into account in this review: HF ratio (the ratio of all HS (HA plus FA); to the total carbon content (TOC) in the resulting product; HF index (the ratio of certain acids (HA or FA) to TOC); percentage of HA or FA in the product (the ratio of the HA or FA concentration to the total concentration of HS in the product); HS yield (the weight ratio of the obtained HS to the processed substrate, which can be represented as a percent; polymerization index (ratio HA/FA) [71].

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 November 2023 doi:10.20944/preprints202311.0877.v1

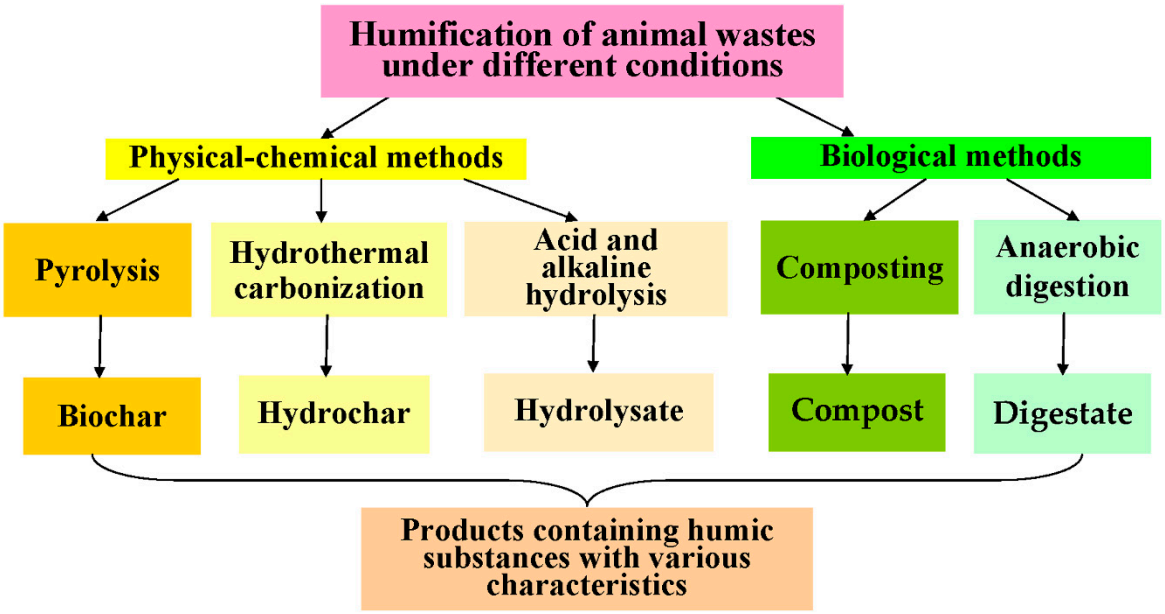

Figure 1. The scheme used in this review for a comparative analysis of the main HF-processes of AW under different conditions, and the HS-resources obtained in them

Table 2. Processing of AW with the production of HS*.

Substrate (Reference)	Conditions/Additives	Products
Composting		
Dairy manure [24]	Thermal pretreatment (90°C, 4 h), 60 days	Compost with 75.0-77.0 g HS/kg
Cow dung and corn straw (ratio 1:2) [25]	Addition of 2.5-5% (d.w.) $FeSO_4$,50 days	Compost with 109.8-129.9 g HS/kg
Maize straw and chicken manure (ratio 6:1) [26]	Addition of benzoic acid (5% d.w.) and soybean residue after oil extraction (15% d.w.), 62 days	Compost with 150.0 g HS/kg
Dairy manure and sugarcane leaves and (ratio 4:1) [27]	Two-step inoculation (0 and 9 days) by *Bacillus licheniformis*, *Aspergillus nidulans* and *A. oryzae* cells (ratio 1:1:1 w/w/w) - 2% d.w., 45 days	Compost with 70.0 g HS/kg
Fresh dairy manure and sawdust (ratio 3.5:1) [28]	Treatment by 0.2 M H_2O_2 (0.5 L) and $CuCl_2$ (0.5 g/kg of compost), 46 days	Compost with 151.9 g HS/kg
Pig manure and sawdust (ratio 2:1) [29]	Addition of Black Tourmaline - 10% d.w., 42 days	Compost with 50.2 g HA/kg and 24.0 g FA/kg
The dairy manure and bagasse pith (ratio 3:1) [30]	Addition of H_2O_2 (2.14 mmol/kg) and ascorbic acid (3.57 mmol/kg of the d.w.), 34 days	Compost with 180.0 g HS/kg
Chicken manure and rice husk (ratio 6.7:1) [31]	Hyper thermophilic pretreatment (≥80°C) for 1-9 days and total process for 44 days	Compost with 65% HS of TS (according to calculations ~260 g HS/kg)
Pig manure and rice straw (C/N = 25) [32]	Hyper thermophilic pretreatment (90°C, 4 h), 60 days	Compost with 87.8 g HS/kg
Chicken manure and corn straw (C/N = 20) [33]	Addition of malonic acid (0.5%), MnO_2 (0.5% d.w.) or their combination, 60 days	Compost with 75.0-87.0 g HS/kg

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 November 2023 doi:10.20944/preprints202311.0877.v1

Chicken manure, sawdust and urea (C/N = 30) [34]	Addition of 0.1% adenosine triphosphate or 0.5% malonic acid (d.w.), 49 days	Compost with 40.0-50.0 g HS/kg
Digestates and chicken manure [35]	Without additives, 60 days	Compost with 90.0-95.0 g HS/kg
Swine manure and corn stalk (ratio 6:1) [36]	Addition of 1.0% (v/w) *Acinetobacter pittii*, *Bacillus subtilis*, *B. altitudinis* (ratio 1:2:1 v/v), 32 days	Compost with 88.1 g HS/kg
Cattle manure (6.7-30% dry basis), rice straw (21.7-31.7%), biogas residue (30-70%), food waste (8.3%) [8]	Without additives, 30 days	Compost with 75.0-88.5 g HS/kg
Dairy manure and bagasse [37]	Addition of 10% Red mud (d.w.), pH 8.7, 45 days	Compost with 115.0-120.0 g HS/kg
Cow manure and sugar cane straw (ratio 5:1) [38]	Addition of 5% biochar from wood obtained via high temperature gasification (400−550°C), 40 days	Compost with 29.0-31.0 g HS/kg
Chicken manure and rice hulls (C/N = 25) [39]	Addition of lignite (15 % w/w), 55 days	Compost with 80.2 g HS/kg
Chicken manure and rice straw (C/N =25-30) [40]	Addition of 7.5% montmorillonite (w/w) and pretreatment at 550°C, 60 days	Compost with 67.0-71 g HS/kg
Chicken manure and spent mushroom substrate (ratio 1:1.2) [41]	Addition of Garden waste (15% fresh weight), 60 days	Compost with 145.0-155.0 g HS/kg
Horse manure (C/N = 33) [42]	Vermicomposting (10 g earthworms *Eisenia Andrei*/kg), 35°C, 6-9 months	Compost with 26.0-26.6 g HA/kg
Anaerobic digestion		
Chicken manure [43]	37°C, 10.0% of TS, 7.9% of VS, 40 days	Digestate – relative content of HLC (34%) and FLC (6%). HS yield was not controlled
Chicken manure [44]	37°C, 10.0% TS and 7.9%VS, 25 days	Digestate – 7.7 g HA/L
Turkey manure [45]	37°C, 51.2% (w/w wet basis) TS and 71.5% (w/w dry basis) VS, OLR – 0.5 2.5 kg VS/m^3 per day, 77 days	Content HS in liquid fraction of the effluent and entire effluent (with digestate) – 2.36 (2.32 HA, 0.04 FA) and 2.6 (2.04 HA, 0.60 FA) g/L
Sheep bedding and cattle manure [46]	18 ± 4°C, sheep bedding to cattle manure ratios: 0:100, 25:75, 50:50, 75:25, and 100:0, final content of TS –5% ,5 months	Digestate with HA/FA – 1.3-3.0. HS yield was not controlled
Pig manure [47]	Hydrotermal pretreatment (70 – 170 °C, 0.5 h), 37°C, 30 days	Digestate with HLC and FLC – 58.0-65.9 and 35.5-42.0%, respectively. HS yield was not controlled.
Hydrothermal carbonization		
Dried swine manure [48]	180°C, 1 MPa, 15wt.% CaO, 10 h	HCmy – 75.2%
Dried poultry litter [49]	180°C, 1 MPa, 1 h	HCmy – 60.4%
Dried poultry litter [50]	250°C, 4-5 MPa, H_2SO_4 (pH 2.0), 2 h	HCmy – 38.1%
Dry swine and chicken manure [51]	240°C, 3-4MPa, 10 h	HCmy – 54.6%

 doi:10.20944/preprints202311.0877.v1

Dried swine manure with cellulose [52]	210°C, 2 MPa, 5 h	HCmy – 52.0%
Dried swine manure with sawdust [53]	220°C, 2-3 MPa, 10 h	HCmy – 61.8%
Dried pig manure [54]	180°C, 1 MPa, 1–1.5 g KOH per 100 g manure, 1 h	HCmy – 79.0%
Dried swine manure [55]	200°C, 2 MPa, 30 min	HCmy – 58.7%
Chicken litter [56]	220°C, 2-3 MPa, 20 min	HCmy – 68.0%
Air-dried pig manure [57]	200°C, 2 MPa, 2 h	HCmy – 58.8%
Poultry and swine manure, dairy and beef cattle manure, broiler and layer chicken litter [58]	180°C, 1 MPa, 1 h	HCmy – 67.3%
Mixture of chicken manure with sawdust [59]	260°C, 40 min	Biochar yield – 95.1%
Dewatered poultry sludge [60]	268°C, 47 min	Biochar yield – 85.0 %
Pyrolysis		
Dried pig manure [54]	200°C, 1 h	Biochar yield – 40.0%
Poultry litter [61]	Wet torrefaction pretreatment (300°C), 600 or 800°C, supercritical CO_2, 1.5–2 h	Biochar yield – 51.2%
Chicken litter [56]	400°C, 20 min	Biochar yield – 38.0%
Pre-dried broiler manure [62]	350°C, 1 h	Biochar yield – 47%
Dried poultry litter [63]	500°C, Mixed with H_3PO_4 and MgO (biomass:H_3PO_4 ratio = 1:0.5 (w/w), molar P:Mg ratio - 1:1), 2 h	Biochar yield – 60.0%
Air-dried pig manure [57]	300°C, 1 h	Biochar yield – 84%
Dried digested cattle manure [64]	600°C, 30 min	Biochar yield – 44.8%
Poultry and swine manure, dairy and beef cattle manure, broiler and layer chicken litter [58]	400°C, 1 h	Biochar yield – 51.0%
Dried goat manure [65]	300°C, 30 min	Biochar yield – 48.6%
Air-dried poultry manure [66]	200°C, 4 h	Biochar yield – 95.8%
Hydrolysis		
Air dried sheep or cow manures [67]	Acid hydrolysis (0.1-1.0 N HCl or H_2SO_4) at 105°C and extraction (1N KOH), 1 h	HS yield – 45 g/kg (sheep waste) and 56 g/kg (cow waste)
Air dried poultry manure [68]	25°C, 0.1 N NaOH, 24 h	HA – 28.1 g/kg. FA – 13.3 g/kg
Farmyard manure [69]	25°C, 0.1 M NaOH, 450 rpm, 48 h	HA yield – 10%
Fresh chicken manure [70]	Subcritical water extraction (230-250°C, 6 MPa)	Liquid phase with 31.0 g HA/kg and 20 g FA/kg

*VS - volatile solids, TS - total solids, HCmy - hydrochar maximal yield, OLR - organic loading rate, HLC - humic-like compounds, FLC - fulvic-like compounds

2.1. HF by composting of AW

Composting with the formation of compost as main product (Figure 1) containing different concentrations of HS (26-260 g/kg) is widely used among biological methods of HF of AW (Table 2). Composting is an aerobic process during which microbiological degradation of bioorganic substances occurs with the formation of HS-precursors (amino acids, reducing sugars, peptides, etc.) with their subsequent stabilization in self-forming supramolecular ensembles [72]. The composting consists of several stages: heating, cooling and maturation. The temperature in the composted mass begins to rise a few hours after the process beginning as a result of biochemical degradation reactions with an increase in the concentrations of reducing sugars, nucleic and amino acids, phenol residues (in the case of conversion of lignin-containing compounds present in animal excrement), etc. The

 doi:10.20944/preprints202311.0877.v1

subsequent decrease in the concentration of these compounds occurs due to the formation of structurally complex HS at the stage of compost maturation [32].

The formation of HS during composting is influenced by many factors (temperature, pH, C/N ratio, humidity, oxygen concentration, etc.). The maturity of compost is determined precisely by the change in HS concentrations in its content [24,27,29,31,41]. An increase in the composting temperature improves the destruction depth of organic compounds and promotes their interactions with the formation of HS. The dynamics of increasing HS-concentrations in compost also depends on temperature. The concentration of HA remains relatively constant during the first 20 days of the process, and then gradually increases under mesophilic composting conditions [24]. With an increase in the composting temperature (up to 90°C), the HS concentrations decrease by 25% in the first 30 days, and then rises sharply as a result of the HS-formation concurrently with cooling and maturation of compost [34,36,39]. There are general trends in the simultaneous increase in HA content and a decrease in FA concentrations in the HS composition during the mature compost formation [31,39].

FA can be used by microorganisms as substrates and converted into HA by condensation and polymerization reactions, which lead to an increase in the aromaticity of HS and an increase in HF. The HF index is considered higher as a ratio HA/FA increases [26]. The HA/FA ratio can reach 5.4-7.6, as a rule, after 1.5 months of composting in the final compost of AW [39]. The average HS concentration can reach 90-100 g/kg in mature compost with a predominance of high-molecular HA in HS composition, although the overall HS concentrations can vary in the compost due to different initial characteristics of treated AW (Table 2).

The sequence of transformations of various functional groups in HS formation in the compost were analyzed using two-dimensional correlation spectroscopy (2D-COS) [30,31]. At first, the C–O stretching of aromatic acid and aliphatic acid esters was observed. Then, the C–H deformation, vibration, and the C–O stretching of polysaccharides or polysaccharide-like substances was appeared. Further, the C=O stretching of carboxylate, quinone, ketone or amide was revealed. Finally, the C=C stretching of aromatic rings was confirmed [30]. The elemental composition of HS during composting of AW under hyper thermophilic conditions showed an increase in N-content, which is associated with enhanced polymerization and condensation of polysaccharide-like substances with N-containing compounds (proteins, nucleic acids, amino acids) [31].

Composting is a long process: from 1-2 months (Table 2) to six months or longer (with vermicomposting) [42]. Composting is characterized by low process speeds (Figure 2) in spite of high yields of conversion of organic substances into HS. This is the reason for the development of alternative methods of HF of AW, leading to the production of HS, and search for factors capable of HF accelerating.

2.2. HF by anaerobic digestion of AW

Another biological method of converting AW to a product containing HS is AD (Table 2, Figure 1). It allows to simultaneously obtain biogas, consisting mainly of CH_4 and CO_2, used as an alternative energy source, and digestate (Figure 1), containing a consortium of methanogenic cells, products of their metabolism and HS-containing products of anaerobic degradation of AW. Another composition of microorganisms involved in AD [73], in comparison with composting, determines other rates of HS accumulation in the resulting digestate (Table 2, Figure 2). Due to the action of the microbial consortia, some of the substances initially present in AW do not undergo destruction and conversion or occur extremely slowly under AD conditions. This applies to the lignocellulose components of the processed excrements [74] and affects the characteristics of AD and resulting product with HS. The presence of organic N-containing compounds in the treated masses is another problem of HF of AW by AD as compared to composting.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 November 2023 doi:10.20944/preprints202311.0877.v1

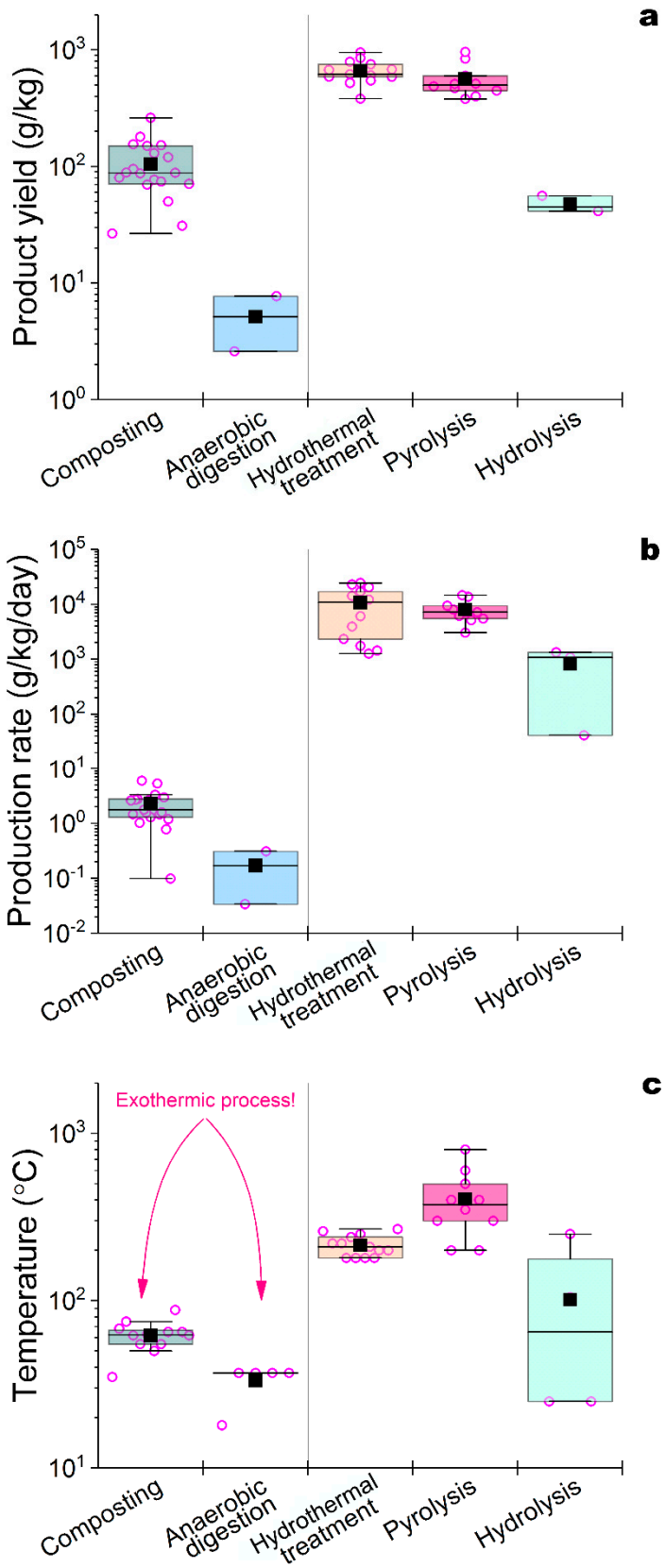

Figure 2. Box-plot visualization of HS yields (**a**), HS production rates (**b**) and temperatures (**c**) in various processes of HF presented in Table 1. Designations: ○ – individual data point; ■ – mean value; the box confines the interquartile range (25–75%) and is sectioned by segment at median value; the whiskers denote the value of 1.5 interquartile range.

 doi:10.20944/preprints202311.0877.v1

To reduce the effect of N-containing compounds (in particular, urea) on AD, its membrane separation from the reaction medium is considered during the process [17]. For successful AW conversion to digestate containing HS, control of a larger number of factors is required in comparison with composting. The initial content of AW loaded to AD reactor, current pH value of the fermentation medium, temperature, concentrations of the products formed, pressure created by accumulated gases in the working AD reactor, etc.) should be controlled [21].

As well as in composting, with increasing duration of the process, the concentration of humic-like compounds (HLC) gradually increases, while the concentration of fulvic-like compounds (FLC) decreases on the contrary [43]. These are common trends in changes in the composition of HS in products obtained in two different biological processes of HF of AW (composting and AD). The use of 2D-COS [44], as in the case of composting, made it possible to study the structural changes in the active functional groups of HSs obtained as a result of AD of chicken manure. It was found that the active functional groups of HS changed in the following sequence: aliphatic-like substances (C–H), amides (H–N) or carbohydrates (O–H), carboxylic acids (C=O), polysaccharides (C=O), aromatic compounds and ketones (C=C). If we compare these results with those mentioned earlier for the HF of AW by composting (Section 2.1.), then we can note a clear general similarity in the identified sequences of changes in organic matter its HF under aerobic and anaerobic conditions.

During the HF of lignocellulose raw materials, much more HLC are formed during AD than in the similar AD of AW. The lignocellulose gives an increased number of precursors for the formation of HS, although the HF of plant raw materials under AD conditions is much slower [43].

It has been established that HS formed with a more complex and stable structure [45,46] from lignocellulose, characterized by a high degree of aromaticity and have a notable inhibitory effect on AD. For the subsequent biodegradation of such HS, their oxidation is necessary, and under AD conditions such type of conversion is less possible than in composting. In this regard, AW are more attractive substrates for the formation of HS by AD in comparison with lignocellulose raw materials. The accumulation of HS during AD reduces the velocity and efficiency of the process due to inhibition of hydrolytic activity of cells participating in functioning of methanogenic consortia [73,75]. A decrease in the HS concentrations in the digestate can also be observed with an increase in the temperature of the process due to the predominant formation of gas products (CH_4 and CO_2), and not HS. In this regard, the HF of AW by AD proceeds at lower speeds than by composting (Figure 2), but since AD is accompanied by the production of biogas, which can be used as biofuel, this process of HS obtaining retains interest.

2.3. Hydrothermal carbonation and wet torrefaction of AW

Hydrothermal carbonation (HTC), carried out in an aqueous environment at 170-280°C and high pressure for several minutes or hours, can be used for HF of AW at higher speeds than in composting and AD (Table 2). Initially, a mass of AW is prepared, which is dried, crushed, and then mixed with water in different proportions [48,51–53,55]. HTC begins with the hydrolysis of high-molecular compounds to monomers, and then the dehydration of monomers occurs, and the final product (hydrochar) with HS (Figure 1) is formed due to polymerization and aromatization processes [54]. Liquid (organic (acetic, propionic, butanoic) acids [51], ketones, aromatic compounds, aldehydes, alcohols) and gaseous (mainly CO_2, CO, CH_4) products can accumulate in HTC. Depending on the conditions of the process and the AW used, it is possible to obtain final products with different yields, chemical compositions and characteristics of the product with HS [49]. Interestingly, the yield of hydrochar in the HTC of chicken manure (44.6%) was almost close to the result obtained with swine manure (43.4%) [52], while it exceeded by 4-5% the same characteristic of HTC of lignocellulose raw materials. Among the HS detected in the composition of hydrochar, 20% were compounds corresponding to HS isolated from the soil, 30-40% were FLCs with a large molecular size, 10-25% of the compounds were characterized as "reduced quinones" with high aromaticity and 12-23% were protein-like substances contained structures similar to aromatic amino acids (tyrosine and tryptophan) [54].

 doi:10.20944/preprints202311.0877.v1

The wet torrefaction is process similar to HTC [59,60] and can be conducted in an aqueous or steam-water media at temperatures slightly lower as compared to HTC (150-260°C) with a processing time of up to 40 minutes (Table 2). The torrefaction temperature has a significant effect on the residual humidity, ash content and yield of the resulting biochar from AW [59]. The yield of hydrochar with HS decreases with increasing process temperature [60]. The characteristics of the hydrochar should be carefully controlled. Despite the need for significant energy costs, as well as the use of special equipment that ensures the maintenance of the necessary temperature conditions of the process, HTC currently attracts a lot of attention due to high speeds of HF. The HS yields during the HF of various AW by HTC (Table 2, Figure 2) are similar to known for natural HF of organic matter.

2.4. HF of AW by pyrolysis

Among the physical-chemical methods used for HF of AW pyrolysis is one of the most actively studied and consists in the heat treatment of dry raw materials in the absence of oxygen. Pyrolysis results in the formation of biochar with HS, bio-oil with benzenes, alcohols, alkanes, alkenes, ketones, phenols and poly aromatic hydrocarbons and non-condensable gases (CO_2, CO, CH_4, H_2, NH_3, H_2S, hydrocarbons). The yield of biochar with HS is determined by the conditions of the process and the composition of the AW (Table 2). In the pyrolysis of AW with an increase in temperature (from 400 to 700°C) and the duration of the process (from 20 to 40 minutes), an increase in the proportion of the gas fraction among the products obtained (up to 40-60 wt.%) is observed. The yield of biochar decreases with increasing temperature (from 38 to 28 wt.%), the degree of aromaticity of the HS present in it increases [56]. Usually, up to 50% of the initial content of C, N and S in the AW is lost in the form of volatile compounds, whereas the relative content of ash and metals increases by 2-2.4 times in comparison with the AW [57,62]. The composition of HS in biochar is similar to the composition of HS in chernozem and peat, which are characterized by a large number of surface -COOH groups, providing them with a large capacity of cation exchange. The sum of all O-containing functional groups (C–O, C=O and COOH) in the composition of biochar HS is lower than that of HS from various types of soils, which means higher hydrophobicity of biochar surface (Jin et al., 2018). In general, the HS of biochar obtained as a product of pyrolysis of AW are similar in their production rates and yields to the same parameters known for HTC (Figure 2), however, higher temperatures are required for pyrolysis. In this regard, pyrolysis as a method of HF of AW refers to processes with high energy consumption, but with HS, which in their elemental composition and characteristics are as close as possible to natural analogues.

2.5. Acid and alkaline hydrolysis as HF method of AW

As an alternative to high-temperature methods of HF of AW, acid and alkaline hydrolytic processes are actively investigated today (Figure 1, Table 2). The efficiency of conversion of AW to HS using hydrolytic treatment depends on the type of processed mass [67]. The use of HCl or H_2SO_4 for acid hydrolysis of AW is most successful for processing mass with a high content of polysaccharides [67], however, other components of AW remain without effective hydrolytic action. The efficiency of alkaline hydrolysis of AW depends on the alkaline agent used, as which KOH, NaOH, NH_4OH, CaO, $Ca(OH)_2$, $CaCO_3$ are applied in different concentrations (0.1-2 M) [20,68]. The temperature of the process (24-100°C) and its duration (1-48 h) affect the depth of HF of AW. These hydrolytic processes are interesting because they combine hydrolytic reactions, HF, and accumulation of HS in the liquid phase, which is usually carried out by extraction of HS from natural sources (coal and peat). According to the speed and the applied temperature conditions, hydrolytic processes occupy an intermediate position between biological (composting and AD) and physical-chemical high-temperature methods of HF of AW (HTC and pyrolysis) (Figure 2). They ensure the immediate production of HS dissolved in the reaction medium, without significant energy and large time costs for the process. Innovative studies using subcritical water extraction, in which H_2O and CO_2 act like organic solvents such as methanol and chloroform, respectively, should be noted in this review [70]. A high yield of HS from chicken manure (51 g/kg) was achieved during subcritical water extraction at 250°C and a pressure of 50-60 atm. An increase in the temperature of the process (to

 doi:10.20944/preprints202311.0877.v1

270°C) led to a decrease in the content of HS, just as it was noted earlier in other processes of HF. However, so far, such studies are rare, since the process is energy-intensive, demands in subcritical extractants and expensive equipment that provides high temperatures and pressure. Thus, alkaline hydrolysis is under active investigation now, because it enables quite easy obtaining of HS from AW in a relatively short time and at compromise temperatures. At the same time, the productivity of this process is lower than that of HTC and pyrolysis, and the issue of alkaline solid-phase waste disposal or application after separation of the liquid fraction with HS remains unresolved.

3. Approaches to intensification of artificial HF of AW

When using different methods of artificial HF of AW, especially biological methods, many researchers are searching for approaches to improving the indicators of HF (speed and depth of the process) (Table 2). The use of various additives to reaction media (lignocellulose containing wastes, mineral particles, biochar, hydrochar, lignite, metal salts and nanoparticles, oxidizing agents, acidic or alkaline agents, conductive and dielectric materials, precursors of HS, suspended or immobilized microbial cells, artificial consortia, etc) are mostly studied to improve characteristics of the HF processes. Several procedures of AW pretreatments also discussed as efficient solutions for HF improving. Some of these approaches are common for different methods of HF, but, in some cases, their preferences remain.

3.1. Composting

Cell immobilization [76], construction of artificial consortia and the introduction of precursors of HS or compounds, capable of accelerating the hydrolysis and oxidation of substrates, into the medium are widely used for improvement of results of biological methods of HF (Table 2). Addition of cellulose-containing wastes (straw, sawdust, corn stalk and rice hulls, spent mushroom substrate, bagasse and bagasse pith sugarcane leaves, spent coffee grounds) (Table 2), which sorb substances inhibiting the HF by composting (heavy metals, organic acids, etc.) and change the C/N ratio in HS [77], is effective for introduction into the compostable mass. To increase the HF of various AW by composting, the application of mineral sorbents (black tourmaline [29], red sludge [37], montmorillonite and illite [40] has been shown. The use of various oxidizing agents (H_2O_2, MnO_2, $CuCl_2$) during composting is possible to accelerate the decomposition of organic substances, especially lignocellulose in the content of AW, and their conversion to HS [30,33]. A 20% increase in HS in compost can be achieved in this case.

The introduction of exogenous precursors of HS in the form of amino acids [78] and benzoic acid [26] or inhibitors of the tricarboxylic acid cycle (adenosine triphosphate and molonic acid), reducing the formation of CO_2 [33,34] during AW composting leads to an increase in the concentration of HS, especially HA (by 66.9%), in the compost. To accelerate composting, the AW are heated to a temperature above 80°C for several hours [24,31,32]. To reduce carbon losses (up to 77% due to CO_2 emissions), biochar is introduced into the composted AW [38]. Biochar retains water, maintains desired pH, and can be used by microorganisms as a carrier for immobilization, which improves stability of cell metabolism and conversion of organic substances into HS [38].

The porous structure of various minerals, large surface area, ion exchange and adsorption-desorption capacity promote the use of such additive in composting of AW, improving the metabolic activity of microorganisms, reducing NH_3 and N_2O emissions and increasing the HF of AW [37,40]. The introduction of cells of various microorganisms [27,36] induces biotransformation of organic matter in compost and formation of HS (Table 2). This approach is most often used in practice, and there are many biologics on the market that improve and accelerate the compost maturation. However, obtaining compost with a modified microbial composition and its subsequent use requires monitoring of the compost for toxicity before use.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 November 2023 doi:10.20944/preprints202311.0877.v1

3.2. Anaerobic digestion

For effective HF of AW by AD, as well as by composting, the hydrothermal pretreatment of excrements at 70-170°C has been confirmed [47]. It increases the biodegradability of manure components, increasing the level of FLC formation in the digestate. For HF of lignocellulose as a part of undigested feed residues, pretreatment of AW is carried out before AD. Physical-chemical and biological methods of pretreatment of AW, including acid or alkaline hydrolysis, alkaline hydrogen peroxide pretreatment, hydrothermal or enzymatic treatment, hydrodynamic cavitation [74,79], are investigated to improve the AD efficiency of AW. The use of urea as an additive is known for AD [80]. It allows maintaining the pH balance of the medium, neutralizing organic acids accumulated in the digestate and providing favorable conditions for HF. The combined addition of urea and KOH to the AD medium increases the biodegradability of AW and promotes HF [81]. Zeolites, $FeSO_4$, $MgCl_2$, $MgSO_4$ or $MgCl_2$ are added to media with AW, since high concentrations of N-containing compounds in media for AD are not desirable due to their conversion to NH_3 [82]. This leads to 20% increase in the concentration of HS formed.

An increase in the HS concentration in the digestate inhibits the metabolic activity of cells that catalyze AD. The use of immobilized form of natural and artificial anaerobic methanogenic consortia instead of suspended analogues reduces the inhibition of cells by HS [83]. The immobilization of anaerobic cells in high concentration makes it possible to obtain efficiently functioning biocatalysts in a state of quorum sensing [20]. The use of artificially created anaerobic consortia for the HF of AW makes it possible to increase the rate of AD even in the presence of micropollutants [21,84].

The efficiency of AD can be improved by introducing biochar (Table 2) or conductive and dielectric materials (stainless-steel mesh and carbon or polyester felt) to reaction media [85]. Such materials can improve the direct interspecies electron transfer and act as a carrier for the formation of stable microbial biofilms inside the AD reactor. Studies of new composite additives for HF of AW by AD look attractive and can compose a novel trend in the development of science. The addition of various salts ($CaCl_2$, $MgCl_2$, $FeCl_3$) to the AW for HF by pyrolysis increases the aromaticity and stability of HS in the resulting biochar [86]. The addition of H_3PO_4 and MgO during pyrolysis of AW in a mixture with coffee husks increases the yield of biochar up to 65% [63].

3.3. Hydrothermal carbonation and pyrolysis

Interestingly, the addition of acids (CH_3COOH or H_2SO_4) to AW before HTC increases the yield of hydrochar and concentration of HS in it [50]. However, presence of alkaline additives (CaO or NaOH) in pyrolysis of AW more positively affects the characteristics of biochar by increasing its pH, aromaticity of HS, electrical conductivity and ash content (Table 2). A similar addition of an alkaline agent (KOH or CaO) to HTC media similarly increases the yield and porosity of hydrochar from AW and the content of HLC in it [48,54]. In fact, the combination of pyrolysis or HTC with alkaline hydrolysis of AW gives improved results in HF and the quality of the resulting products.

4. Comparison of characteristics of natural and artificial HS obtained in various processes of HF of AW

It is extremely interesting to compare the content of main chemical elements of HS obtained by different methods in HF of AW and of HS from different natural sources (Table 3) [31,42,44,48–52,56–58,60,63,64,68,69,87–89]. Results of such comparison should help to assess the possible and most appropriate ways to use the artificial HS.

Table 3. Combination of AFPs with different antifungal agents.

Sample of waste [Reference]	Chemical elements (%)					Ratios		
	C	H	N	O	S	H/C	C/N	O/C
Composting								
Chicken manure and rice husk [31]	41.10	3.40[a]	5.70[a]	n/d	n/d	0.08	7.14	n/d

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 November 2023 doi:10.20944/preprints202311.0877.v1

Horse manure [42]	38.42[a]	42.36[a]	2.29[a]	17.19[a]	n/d	1.10[b]	16.76[b]	0.47[b]
Anaerobic digestion								
Chiken manure [44]	n/d	n/d	n/d	n/d	n/d	1.78[b]	5.01[b]	n/d
Hydrothermal carbonization								
Dried swine manure [48]	35.09	4.64	1.97	26.65	n/d	0.13	17.8	0.76
Dried poultry liter [49]	33.61	3.91	1.95	20.84	0.31	0.12	17.2	0.62
Dried poultry liter [50]	56.40	4.99	5.13	7.78	1.22	0.09	11.0	0.14
Dried swine manure [51]	40.61	4.15	2.11	11.72	0.18	0.10	19.2	0.29
Dried poultry manure [51]	28.44	2.84	2.05	5.65	0.25	0.10	13.9	0.20
Dried swine manure [52]	40.42	3.71	1.94	18.10	0.18	1.10[b]	20.8	0.33[b]
Dried swine manure with sawdust [48]	40.85	6.30	3.73	31.30	0.42	1.55[b]	11.0	0.57[b]
Poultry liter [56]	37.5	n/d	8.01	n/d	n/d	n/d	4.7	n/d
Dewatered poultry sludge [60]	53.43	8.17	3.67	11.24	0.52	1.86[b]	14.6	0.16[b]
Air-dried pig manure [57]	33.77	4.22	2.49	14.96	0.55	1.50[b]	13.6	0.33[b]
Swine manure Zhou [58]	35.96	4.36	2.02	22.30	0.54	0.12	17.8	0.62
Daily cattle manure [58]	43.63	5.27	2.17	26.92	0.58	0.12	20.1	0.62
Beef cattle manure [58]	38.79	4.33	1.78	24.10	0.48	0.11	21.8	0.62
Broiler liter [58]	38.19	4.53	3.45	23.57	0.65	0.12	11.1	0.62
Layer chicken liter [58]	39.58	5.02	2.09	22.04	0.62	0.13	18.9	0.56
Pyrolysis								
Dried poultry manure [63]	43.30	2.15	n/d	n/d	n/d	0.05[b]	n/d	n/d
Air-dried pig manure [57]	29.04	1.41	1.36	0.29	4.82	0.58[b]	21.6	0.12[b]
Air-dried poultry manure [57]	39.70	5.62	3.53	42.3	n/d	0.14	11.2	1.07
Dried digested dairy cattle manure [64]	39.60	0.85	1.84	n/d	0.94	0.02	21.5	n/d
Swine manure [58]	34.89	1.96	2.44	10.16	0.51	0.06	14.3	0.29
Daily cattle manure [58]	42.27	2.41	2.46	11.39	0.57	0.06	17.2	0.27
Beef cattle manure [58]	40.55	2.09	2.04	11.39	0.45	0.05	19.9	0.28
Broiler liter [58]	37.59	2.18	4.57	6.13	1.06	0.06	8.23	0.16
Layer chicken liter [58]	35.39	1.98	2.52	7.76	0.88	0.06	14.0	0.22
Alkaline hydrolysis								
Air dried poultry manure [68]	45.06	4.08	6.01	44.85	n/d	0.09[b]	7.49	0.99[b]
Farmyard manure [69]	53.10	5.45	3.24	37.63	0.58	0.10[b]	16.39[b]	0.71[b]
Natural HS extracted from different environmental sources (for comparison)								
HA from peat [87]	40.1	4.2	2.5	n/d	2.2	0.10	16.0	n/d
HA from peat [88]	52.25	4.51	2.59	n/d	0.77	1.03[b]	20.2	0.57[b]
HA from peat [88]	56.34	5.71	2.34	n/d	0.88	1.20[b]	24.1	0.45[b]
HA from raw lignite coal [89]	72.20	4.44	1.97	18.07	3.31	0.06[b]	36.6	0.25[b]
HA from native bituminous coal [89]	56.20	10.99	3.07	18.59	11.15	0.19[b]	18.3	0.18[b]

[a] Concentration of HA; [b] Data from publications. Ratios without this index were calculated for this review based on the data presented in the cited references; [c] Characteristics of the obtained chars are given; n/d - no data

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 November 2023 doi:10.20944/preprints202311.0877.v1

The H/C ratio is an important indicator determining the aromaticity of HS. The higher atomic H/C ratios correspond to lower aromaticity [90]. The high aromaticity of HS ensures their stability under environmental conditions. The H/C ratio ranges for HS obtained by HF of AW (0.05-1.86) and for HS from traditional sources (0.06-1.23) are comparable (Table 3). For products obtained by HF of AW this indicator depends on the source of wastes and the process used. Thus, HF by AD gives more aliphatic HS than by composting, which makes them more easily biodegradable when applied to soils. In this regard, digestate looks like a more attractive object for use as agrochemicals and is comparable in this with HS from peat. Most samples of HS in products obtained in the processes of HTC and pyrolysis are characterized by increased aromaticity and are close in their characteristics to the HS from natural coal.

High C/N ratios of HS correspond to a high condensation degree and HF degree of the organic matter. This ratio is the key for ensuring favorable conditions for the functioning of microorganisms in soils when using HS as agrochemicals. The optimal value of this parameter is 20-40 [91]. For HS obtained from traditional sources (peat and coal), the C/N ratio is within the optimal range (Table 3). Among all the methods of HF, pyrolysis and HTC of AW give the maximum C/N ratios in HS of obtained products. For HS samples produced from poultry manure, the C/N ratio is on average lower than those values revealed for HS from the wastes of other animals, regardless of the method of HF used, since chicken wastes contain a lot of N (Table 3). Biological methods of HF (composting, AD) and alkaline hydrolysis of AW lead to the formation of HS with a high N-content and, accordingly, with a low C/N ratio (Table 3). Such HS are not promising as agrochemicals, because balancing of the C/N ratio is required. However, a C/N ratio of less than 10 leads to the activity inhibition of microorganisms, including pathogenic ones [91]. This can be taken into account and used for inhibition of negative microbial processes by such HS.

The O/C ratio in HS reflects the content of oxygen-containing functional (carboxyl, hydroxyl, carbonyl) groups in combination with aromatic structures and testifies to the ability of HS to enter into exchange and donor-acceptor interactions, form hydrogen bonds, and actively participate in sorption processes. The O/C ratio (Table 3) for the majority of HS obtained by various methods from AW is comparable to the similar characteristic of HS extracted from traditional sources (0.18-0.55). However, pyrolysis and alkaline hydrolysis of air-dried poultry manure produced HS with a maximum O/C ratio (0.99 and 1.07), which determines the area of effective use of these products for sorption processes and remediation of soils.

The ratio N/S is important for the plants, and the optimal range is 5-15 [93]. The sulfur content in artificial HS is significantly lower in most cases than in traditional samples of HS (Table 3), and the high level of N in artificial HS provide the necessary N/S ratio (4.8-11.7). The natural HS have ratio N/S lower the optimum (0.3-3.4). This is evident when comparing HS in natural coals and HS in chars obtained by physical-chemical methods of artificial HF from AW. So, this information is useful for considering the possible replacement of natural coals with artificial chars (biomimetics) in their applications (Figure 3).

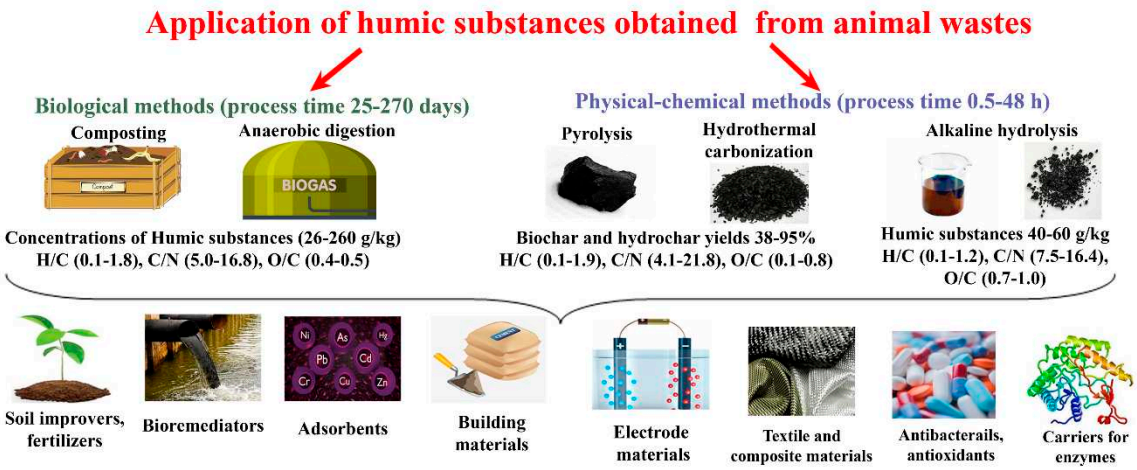

Figure 3. Properties of biomimetic HS obtained by various methods and their practical potential.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 14 November 2023 doi:10.20944/preprints202311.0877.v1

5. Prospects and preferences for the use of HS-containing products, obtained by HF of AW

Samples of HS from AW can be used as a part of various products (compost, bio- and hydrocarbons, anaerobic digestate, hydrolysates of AW, etc (Figure 3, Table 2). The palette of applications can be very wide, which has already been confirmed in current studies (Table 4) [93–111]. Analysis of characteristics of artificial HS from AW (Table 3) showed that it is possible to expect their similar or more effective use in comparison with HS from coal and peat.

Table 4. Application of artificial and natural HS-resources.

Product with HS	Application	Characteristics
HS from animal wastes		
Chicken manure biochar [93]	Adsorbent for the removal of phenol and 2,4-dinitrophenol from wastewater	Maximum adsorption capacity: 106.2 mg/g phenol, 148.6 mg/g 2,4-dinitrophenol
Chicken manure biochar [94]	Remediation of metals from water and soil	Removal efficiency: 98% of Pb^{2+}; 42% of Zn^{2+}
Swine manure biochar [95]	Adsorption of U(VI)	Maximum adsorption capacity: 221.4 mg/g
Swine manure hydrochar modified with manganese ferrite ($MnFe_2O_4$) nanoparticles [96]	Removal of chlortetracycline and Cd (II) from water	Maximum adsorption capacity: 753.0 mg/g (chlortetracycline), 62.2 mg/g (Cd (II)),
Cattle manure hydrochar [97]	Soil conditioner	Hydrochar improves: total soil phosphorus (by 6.8–18.9%), soil organic carbon (by 8.2%), dissolved organic carbon (by 18.7%), rice yield (by 36.9%)
Swine manure hydrochar [98]	Removal of metal from aqueous solutions	Maximum adsorption capacity (mg/g): 81.1 (Cd II), 13.1 (Sb III)
Hydrochar made from digestate of manure [99]	Soil amendment	Increase of soil pH (from 7.0 to 7.4), cation exchange capacity (from 11.5 to 12.6 meq/100 g soil), soil organic matter (from 2.4 to 2.8%), P, K, Ca, Mg content. Twice increase in dry weights of roots, leaves, and plant *Lactuca sativa*
Compost made from farm yard manure with addition of biochar [100]	Soil amendment	Increase of growth, yield and chlorophyll content and decrease of Cd content in wheat tissues
HS extracted from compost containing cow manure [101]	Biosurfactant	Percent of metal removal: Cu - 17%, Pb - 35%, Zn 8%, Cd -38% and Cr - 0.6%
Hydrochar from digestate of cow manure and corn straw [102]	Additive to AD	Enhancing of CH_4 yield - 34%
Chicken manure biochar [103]	Additive to composting mass	Decrease in emission of N_2O, CH_4 and NH_3 on 27.4 %, 55.9 % and 56.9%, respectively
HS from other types of wastes		
HA from compost [104]	Treatment of diesel-contaminated soil	Diesel removal - 89.4%
HA from vermicompost [105]	Adsorption of aflatoxin B_1 (AFB_1) from maize-soybean meal for broiler chickens (100 μg AFB_1/kg)	Improved adsorption - 99.7%

 doi:10.20944/preprints202311.0877.v1

Mixture of bamboo biochar and pig manure [106]	Soil remediation	Soil treatment with biochar–pig manure increased concentration of arbuscular mycorrhizal fungi
Biochar obtained in pyrolysis of bamboo and rice husk [107]	Additive to composting mass	Improving of organic matter decomposition, enhanced HA concentration (>80 g/kg), reduced volatilization of NH_3 and N_2O (40%)
Wheat straw biochar [108]	Additive to composting mass	Notable prolongation of thermophilic period of pig manure composting with stabilization of bacteria richness.
Hydrochar from olive mill waste and cellulose [109]	Enzyme immobilization	Absorption immobilization of enzyme - 20-30%
Corn straw hydrochar [110]	Electrode material	The mass-specific capacitance - 98 F/g. Power density - 9500 W/kg. Energy density - 77 W h/kg at 20 A/g
HS extracted from composted artichoke residues [111]	Antibacterial agent and antioxidant	Minimal inhibitory concentrations (mg/L) against bacterial cells in concentration of 5×10^5 CFU/mL: against *Staphylococcus aureus* - 1.2, *Pseudomonas aeruginosa* – 1.8, *Enterococcus faecalis* – 2.0, *Escherichia coli* – 1.7, *Klebsiella pneumoniae* – 2.3. Antioxidant activity (expressed as gallic acid equivalents) – 150 mol/g.

The use of hydrochar obtained from AW during HTC leads to an increase in the HS content in the soil, which contributes to an increase in rice yield by 36% [97]. Hydrochar made from digest of manure is effective as a soil improver for lettuce growth [99]. Biochar obtained by pyrolysis, when added to the soil with cattle manure, causes changes in the content of microbial community, increasing the number of fungi-plant symbionts [106]. Sources of nitrogen (N) are often added to natural HS or the GWS themselves are specially modified for the subsequent slow release of nitrogen compounds into the soil for plant growth [112]. However, in the case of HS obtained from chicken manure, the N-content in them has already been increased (Table 3) and allows the use of artificial HS as organic fertilizer without additional modification and N- enrichment.

One of the main properties of chars from AW for agricultural use is their electrical conductivity (EC) (the higher the EC, the higher the concentration of soluble salts). It was shown that EC of the biochar HS decreased with an increase in the pyrolysis temperature of dairy cattle manure. Low EC values of biochar, used as an agrochemical, reduces soil salinity. In addition, the water holding capacity of biochars obtained at temperatures from 300 to 550°C was 380-485%. Thus, such biochar can improve the water-holding capacity of soils, and by varying the temperature of biochar pyrolysis, this characteristic can be changed and controlled [113].

HS are used as ameliorants for bioremediation of soils contaminated with oil [114], heavy metals [108], and salts [115]. Similarly, hydrochar and biochar obtained by HF of AW were used not only as agrochemicals, but also as adsorbents for the removal of various substances polluting soil and water [53,55,64,116,117]. Biochar obtained by pyrolysis of pig manure was used for sorption of uranium, and its treatment with NaOH significantly increased sorption capacity [98]. HS isolated from composted cow manure was used to remove metals (Cu, Pb, Zn, Cd, Cr) from the soil in comparison with HS obtained from coal (leonardite) [101]. HS from compost had a greater complexing ability than HS from coal due to the high content of carboxyl and phenolic groups. HS extracted from vermicompost adsorbed up to 99.7% aflatoxin B1 from broiler feed [105]. Biochar from pyrolyzed chicken manure was used as an adsorbent to remove phenol and 2,4-dinitrophenol from wastewater [93]. The loss of the adsorption capacity of such a biochar was less than 20% after 5 repeated uses. A hydrochar obtained from pig manure by HTC and modified with $MnFe_2O_4$ nanoparticles was repeatedly used to remove chlortetracycline and Cd from water [96].

The addition of HS from AW in the form of hydro- or biochar to reaction media for AD [102] or composting of different wastes [103,107,108] leads to an improvement in their HF indicators. It has been established that for artificial HS obtained not from AW in processes similar to those discussed above (Tables 2, Table4), the possibility of use has already been demonstrated in a number of areas where HS from AW has not yet been studied. For example, it has been shown that HA (10 g/L) from HS of compost in combination with KH_2PO_4 and H_2O_2 can remove up to 90% of diesel pollution from the soil [104]. Hydrochar from olive mill waste and cellulose can be used for enzymes immobilization [109] and production of electrode materials [110]. The antioxidant and antimicrobial activity of HS extracted from compost is interesting for their use in the treatment of contaminated objects and media [111]. Hydrochars can also be used as catalysts in various processes and for energy production [118], for the capture of free radicals, cholesterol, glucose, and viral particles [119]. The use of HS as feed additives [120], as a part of building materials (fresh mortars and aggregates in cementitious composites) [121], various composite materials (wood polypropylene composites, plastics, etc.) [122] and textiles [123] with improved functional properties has been demonstrated.

Thus, HS obtained from various AW by different methods of HF can be effectively used in a variety of fields along with natural HS from coal and peat. It is obvious that some of those fields of potential application that are already known for natural HS are still unexplored for artificial HS from AW. However, the areas and volumes of their possible use constitute a serious commercial and environmental potential.

6. Conclusions

The artificial HF of AW enables solution of several tasks at once: to reduce the volume of biowaste with N-containing compounds, to obtain HS-biomimetics, capable of using to overcome various environmental problems in the same ways (bioremediation, decontamination, fertilization, etc.) as natural HS from peat and coal are used. Due to characteristics of artificially obtained HS from AW, their use for agriculture or nature-like technologies in some cases can be more attractive as compared to natural HS. The complete list of possible applications of artificial HS has not yet been investigated, and it composes notable potential for further development of science in this area.

Author Contributions: Conceptualization, E.E.; Visualization, N.S., I.L.; Investigation, N.S., I.L., O.S., O.M., A.A., E.E.; Writing – original draft, N.S., I.L., O.S., O.M., A.A., E.E.; Writing – review & editing, N.S., O.S., O.M., E.E.; Supervision, E.E.

Funding: The research was supported by State Task of Lomonosov Moscow State University (122040600057-3).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Filho, J.F.D.C.L.; Thomason, W.E.; Evanylo, G.K.; Zhang, X.; Strickland, M.S.; Chim, B.K.; Diatta, A.A. The synergistic effects of humic substances and biofertilizers on plant development and microbial activity: a review. *Int. J. Plant. Soil Sci.* **2020**, *32*, 56-75. doi:10.9734/ijpss/2020/v32i730306
2. Kulikova, N.A.; Perminova, I.V. Interactions between humic substances and microorganisms and their implications for nature-like bioremediation technologies. *Molecules* **2021**, *26*, 2706. doi:10.3390/molecules26092706
3. Yang, F.; Tang, C.; Antonietti, M. Natural and artificial humic substances to manage minerals, ions, water, and soil microorganisms. *Chem. Soc. Rev.* **2021**, *50*, 6221-6239. doi:/10.1039/D0CS01363C
4. Huezo, L.; Shah, A. Effect of hydrochar from anaerobically digested sewage sludge and manure as a soil amendment on soil properties and plant responses. *Bioenerg. Res.* **2023**, *16*, 1195–1204. doi:10.1007/s12155-022-10479-1
5. Marcinčák, S.; Semjon, B.; Marcinčáková, D.; Reitznerová, A.; Mudroňová, D.; Vašková, J.; Nagy, J. Humic substances as a feed supplement and the benefits of produced chicken meat. *Life* **2023**, *13*, 927. doi:10.3390/life13040927

6. Vašková, J.; Stupák, M.; Vidová Ugurbaş, M.; Žatko, D.; Vaško, L. Therapeutic efficiency of humic acids in intoxications. *Life* **2023**, *13*, 971. doi:10.3390/life13040971
7. Font-Palma, C. Methods for the treatment of cattle manure - A review. *C* **2019**, *5*, 27. doi:/10.3390/c5020027
8. Bai, L.; Deng, Y.; Li, J.; Ji, M.; Ruan, W. Role of the proportion of cattle manure and biogas residue on the degradation of lignocellulose and humification during composting. *Bioresour. Technol.* **2020**, *307*, 122941. doi:10.1016/j.biortech.2020.122941
9. J Jurgutis, L.; Slepetiene, A.; Volungevicius, J.; Amaleviciute-Volunge, K. Biogas production from chicken manure at different organic loading rates in a mesophilic full scale anaerobic digestion plant. *Biomass Bioenerg.* **2020**, *141*, 105693. doi:10.1016/j.biombioe.2020.105693
10. Santana, K.V.; Apolônio, F.C.; Wisniewski, A. Valorization of cattle manure by thermoconversion process in a rotary kiln reactor to produce environmentally friendly products. *Bioenergy Res.* **2020**, *13*, 605-617. doi;10.1007/s12155-019-10047-0
11. Achinas, S.; Euverink, G.J.W. Rambling facets of manure-based biogas production in Europe: A briefing. *Renew. Sust. Energ. Rev.* **2020,** *119*, 109566. doi:10.1016/j.rser.2019.109566
12. Scarlat, N.; Fahl, F.; Dallemand, J.F.; Monforti, F.; Motola, V. A spatial analysis of biogas potential from manure in Europe. *Renew. Sust. Energ. Rev.* **2018**, *94*, 915-930. doi:10.1016/j.rser.2018.06.035
13. Ali, M.Y.; Hassan, M.; Rahman, M.A.; Kafy, A.A.; Ara, I.; Javed, A.; Rahman, M.R. Life cycle energy and cost analysis of small scale biogas plant and solar PV system in rural areas of Bangladesh. *Energy Procedia* **2019**, *160*, 277-284. doi:10.1016/j.egypro.2019.02.147
14. Prabakaran, R.; Valavan, S.E. Wealth from poultry waste: an overview. *Worlds Poult. Sci J.* **2021**, *77*, 389-401. doi: 10.1080/00439339.2021.1901557
15. Manogaran, M.D.; Shamsuddin, R.; Yusoff, M.H.M.; Lay, M.; Siyal, A.A. A review on treatment processes of chicken manure. *Cleaner Circ. Bioecon.* **2022**, *2*, 100013. doi:10.1016/j.clcb.2022.100013
16. Miroshnichenko, I.; Lomazov, V.; Petrosov, D.; Oskina, A. Bioenergetics' potential of the poultry and swine wastes in Belgorod region of Russia. *IOP Conf. Se.r Earth Environ. Sci.* **2021**, *845*, 012147. doi:10.1088/1755-1315/845/1/012147
17. Bayrakdar, A.; Sürmeli, R.Ö.; Çalli, B. Anaerobic digestion of chicken manure by a leach-bed process coupled with side-stream membrane ammonia separation. *Bioresour. Technol.* **2018**, *258*, 41-47. doi:10.1016/j.biortech.2018.02.117
18. Ramos-Suárez, J.L.; Ritter, A.; González, J.M.; Pérez, A.C. Biogas from animal manure: A sustainable energy opportunity in the Canary Islands. *Renew Sust. Energ. Rev.* **2019**, *104*, 137-150. doi:10.1016/j.rser.2019.01.025
19. Sawyerr, N.; Trois, C.; Workneh, T. Identification and characterization of potential feedstock for biogas production in South Africa. *J. Ecol. Eng.* **2019**, *20*, 103-116. doi:10.12911/22998993/108652.
20. Efremenko, E.; Senko, O.; Stepanov, N.; Aslanli, A.; Maslova, O.; Lyagin, I. Quorum sensing as a trigger that improves characteristics of microbial biocatalysts. *Microorganisms* **2023**, *11*, 1395.. doi:10.3390/toxins15030205
21. Maslova, O.; Senko, O.; Stepanov, N.; Gladchenko, M.; Gaydamaka, S.; Akopyan, A.; Eseva, E.; Anisimov, A.; Efremenko, E. Sulfur containing mixed wastes in anaerobic processing by new immobilized synthetic consortia. *Bioresour. Technol.* **2022**, *362*, 127794. doi:10.1016/j.biortech.2022.127794
22. Sheriff, I.; Yusoff, M.S.; Abd Manan, T.S.B.; Koroma, M. Microplastics in manure: sources, analytical methods, toxicodynamic, and toxicokinetic endpoints in livestock and poultry. *Environ. Adv.* **2023**, *12*, 100372. doi:10.1016/j.envadv.2023.100372
23. Tawfk, A.; Eraky, M.; Osman, A.; Ai, P.; Zhou, Z.; Meng, F.; Rooney, D. Bioenergy production from chicken manure: a review. *Environ. Chem. Lett.* **2023**, *21*, 2707–2727. doi:10.1007/s10311-023-01618-x
24. Zhu, N.; Gao, J.; Liang, D.; Zhu, Y.; Li, B.; Jin, H. Thermal pretreatment enhances the degradation and humification of lignocellulose by stimulating thermophilic bacteria during dairy manure composting. *Bioresour. Technol.* **2021**, *319*, 124149. doi:10.1016/j.biortech.2020.124149
25. Mei, J.; Ji, K.; Su, L.; Wu, M.; Zhou, X.; Duan, E. Effects of $FeSO_4$ dosage on nitrogen loss and humification during the composting of cow dung and corn straw. *Bioresour. Technol.* **2021**, *341*, 125867. doi;10.1016/j.biortech.2021.125867
26. Zhang, Z; Zhao, Y; Wang, R; Lu, Q; Wu, J; Zhang, D. Nie, Z; Wei, Z. Effect of the addition of exogenous precursors on humic substance formation during composting. *Waste Manage*. **2018**, *79*, 462-471. doi:10.1016/j.wasman.2018.08.025
27. Xu, J.; Jiang, Z.; Li, M.; Li, Q. A compost-derived thermophilic microbial consortium enhances the humification process and alters the microbial diversity during composting. *J. Environ. Manage.* **2019**, *243*, 240-249. doi:10.1016/j.jenvman.2019.05.008
28. Niu, Q.; Meng, Q.; Yang, H.; Wang, Y.; Li, X.; Li, G.; Li, Q. Humification process and mechanisms investigated by Fenton-like reaction and laccase functional expression during composting. *Bioresour. Technol.* **2021**, *341*, 125906. doi:10.1016/j.biortech.2021.125906

29. Ren, X.; Wang, Q.; Zhang, Y.; Awasthi, M.K.; He, Y.; Li, R.; Zhang, Z. Improvement of humification and mechanism of nitrogen transformation during pig manure composting with Black Tourmaline. *Bioresour. Technol.* **2020**, *307*, 123236. doi:10.1016/j.biortech.2020.123236
30. Niu Q, Yan H, Meng Q, Wang S, Li G, Zhu Q, Li X, Li Q (2021) Hydrogen peroxide plus ascorbic acid enhanced organic matter deconstructions and composting performances via changing microbial communities. J Environ Manage 295:113126. https://doi.org/10.1016/j.jenvman.2021.113126
31. Cui, P.; Liao, H.; Bai, Y.; Li, X, Zhao, Q.; Chen, Z.; Yu, Z.; Yi, Z.; Zhou, S. Hyperthermophilic composting reduces nitrogen loss via inhibiting ammonifiers and enhancing nitrogenous humic substance formation. *Sci. Total. Environ.* **2019**, *692*, 98-106. doi:10.1016/j.scitotenv.2019.07.239
32. Cao, Y.; Wang, J.; Huang. H.; Sun, E.; Butterly, C.; Xu, Y.; He, H.; Zhang, J.; Chang, Z. Spectroscopic evidence for hyperthermophilic pretreatment intensifying humification during pig manure and rice straw composting. *Bioresour. Technol.* **2019**, *294*, 22131. doi:10.1016/j.biortech.2019.122131
33. Zhang, S.; Wei, Z.; Zhao, M.; Chen, X.; Wu, J.; Kang, K.; Wu, Y. Influence of malonic acid and manganese dioxide on humic substance formation and inhibition of CO_2 release during composting. *Bioresour. Technol.* **2020**, *318*, 124075. doi:10.1016/j.biortech.2020.124075
34. Wang, L.; Zhao, Y.; Ge, J.; Zhu, L.; Wei, Z.; Wu, J.; Zhang, Z.; Pan, C. Effect of tricarboxylic acid cycle regulators on the formation of humic substance during composting: The performance in labile and refractory materials. *Bioresour. Technol.* **2019,** *292*, 121949. doi:10.1016/j.biortech.2019.121949
35. Wu, J.; Zhao, Y.; Yu, H.; Wei, D.; Yang, T.; Wei, Z.; Lu, Q.; Zhang, X. Effects of aeration rates on the structural changes in humic substance during co-composting of digestates and chicken manure. *Sci. Total. Environ.* **2019**, *658*, 510-520. doi:10.1016/j.scitotenv.2018.12.198
36. Li, C.; Li, H.; Yao, T.; Su, M.; Ran, F.; Li, J.; He, L.; Chen, X.; Zhang, C.; Qiu, H. Effects of swine manure composting by microbial inoculation: heavy metal fractions, humic substances, and bacterial community metabolism. *J. Hazard. Mater.* **2021**, *415*, 125559. doi:10.1016/j.jhazmat.2021.125559
37. Jiang, Z.; Li, X.; Li, M.; Zhu, Q.; Li, G.; Ma, C.; Li, Q.; Meng, J.; Liu, Y.; Li, Q. Impacts of red mud on lignin depolymerization and humic substance formation mediated by laccase-producing bacterial community during composting. *J. Hazard. Mater.* **2021**, *410*, 124557. doi:10.1016/j.jhazmat.2020.124557
38. Yan, H.; Niu, Q.; Zhu, Q.; Wang, S.; Meng, Q.; Li, G.; Li, X.; Ma, C.; Li, Q. Biochar reinforced the populations of cbbL-containing autotrophic microbes and humic substance formation via sequestrating CO_2 in composting process. *J. Biotechnol.* **2021**, *333*, 39-48. doi:10.1016/j.jbiotec.2021.04.011
39. Wang, Y.; Zhang, C.; Zhao, Y.; Wei, Z.; Li, J.; Song, C.; Chen, X.; Zhao, M. Lignite drove phenol precursors to participate in the formation of humic acid during chicken manure composting. *Sci. Total. Environ.* **2023**, *874*, 162609. doi:10.1016/j.scitotenv.2023.162609
40. Pan, C.; Zhao, Y.; Zhao, L.; Wu, J.; Zhang, X.; Xie, X.; Kang, K.; Jia, L. Modified montmorillonite and illite adjusted the preference of biotic and abiotic pathways of humus formation during chicken manure composting. *Bioresour. Technol.* **2021**, *319*, 124121. doi:10.1016/j.biortech.2020.124121
41. Jia, P.; Huang, Y.; Chen, M.; Qi, X.; Hou, H. Comprehensive evaluation of spent mushroom substrate-chicken manure co-composting by garden waste improvement: physicochemical properties, humification process, and the spectral characteristics of dissolved organic matter. *Environ. Sci. Pollut. Res.* **2023**, *30*, 8987–8997. doi:10.1007/s11356-022-20879-7
42. Hanc, A.; Enev, V.; Hrebeckova, T.; Klucakova, M.; Pekar, M. Characterization of humic acids in a continuous-feeding vermicomposting system with horse manure. *Waste Manage.* **2019**, *99*, 1-11. doi:10.1016/j.wasman.2019.08.032
43. Wang, X.; Lyu, T.; Dong, R.; Liu, H.; Wu, S. Dynamic evolution of humic acids during anaerobic digestion: Exploring an effective auxiliary agent for heavy metal remediation. *Bioresour. Technol.* **2021**, *320*, 124331. doi:10.1016/j.biortech.2020.124331
44. Wang, X.; Muhmood, A.; Lyu, T.; Dong, R.; Liu, H.; Wu, S. Mechanisms of genuine humic acid evolution and its dynamic interaction with methane production in anaerobic digestion processes. *Chem. Eng. J.* **2021**, *408*, 127322. doi:10.1016/j.cej.2020.127322
45. Rolando, C.; Elba, V.; Carlos, R. Anaerobic mono-digestion of Turkey manure: Efficient revaluation to obtain methane and soil conditioner. *J. Water. Resource Prot.* **2011**, *3*, 6987. doi:10.4236/jwarp.2011.38067
46. Cestonaro, T.; de Mendonça Costa, M.S.S.; de Mendonça Costa, L.A.; Rozatti, M.A.T.; Pereira, D.C.; Lorin, H.E.F.; Carneiro, L.J. The anaerobic co-digestion of sheep bedding and 50% cattle manure increases biogas production and improves biofertilizer quality. *Waste Manage.* **2015**, *46*, 612-618. doi:10.1016/j.wasman.2015.08.040
47. Renjiie, D.; Zijia, Z.; Sheng, L.; Yanfang, M.; Shan, L. Effects of hydrothermal pretreatments on the anaerobic digestion of pig manure and ecological safety of biogas slurry. *TCSAE* **2022**, *38*, 193-203. doi:10.11975/j.issn.1002-6819.2022.06.022
48. Lang, Q.; Zhang, B.; Liu, Z.; Jiao, W.; Xia, Y.; Chen, Z.; Li, D.; Ma, J.; Gai, C. Properties of hydrochars derived from swine manure by CaO assisted hydrothermal carbonization. *J. Environ. Manage.* **2019**, *233*, 440-446. doi:10.1016/j.jenvman.2018.12.072

49. Mau, V.; Arye, G.; Gross, A. Poultry litter hydrochar as an amendment for sandy soils. *J. Environ. Manage.* **2020**, *271*, 110959. doi:10.1016/j.jenvman.2020.110959
50. Ghanim, B.M.; Kwapinski, W.; Leahy, J.J. Hydrothermal carbonisation of poultry litter: Effects of initial pH on yields and chemical properties of hydrochars. *Bioresour. Technol.* **2017**, *238*, 78-85. doi:10.1016/j.biortech.2017.04.025
51. Li, Q.; Zhang, S.; Gholizadeh, M.; Hu, X.; Yuan, X.; Sarkar, B.; Ok, Y.S. Co-hydrothermal carbonization of swine and chicken manure: Influence of cross-interaction on hydrochar and liquid characteristics. *Sci. Total. Environ.* **2021**, *786*, 147381. doi:10.1016/j.scitotenv.2021.147381
52. Li, Q.; Lin, H.; Zhang, S.; Yuan, X.; Gholizadeh, M.; Wang, Y.; Xiang, J.; Hu, S.; Hu, X. Co-hydrothermal carbonization of swine manure and cellulose: Influence of mutual interaction of intermediates on properties of the products. *Sci. Total. Environ.* **2021**, *791*, 148134.. doi:10.1016/j.scitotenv.2021.148134
53. Lang, Q.; Guo, Y.; Zheng, Q.; Liu, Z.; Gai, C. Co-hydrothermal carbonization of lignocellulosic biomass and swine manure: Hydrochar properties and heavy metal transformation behavior. *Bioresour. Technol.* **2018**, *266*, 242-248. doi:10.1016/j.biortech.2018.06.084
54. Song, C.; Shan, S.; Yang, C.; Zhang, C.; Zhou, X.; Ma, Q.; Yrjälä, K.; Zheng, H.; Cao, Y. The comparison of dissolved organic matter in hydrochars and biochars from pig manure. *Sci. Total. Environ.* **2020**, *720*, 137423. doi:10.1016/j.scitotenv.2020.137423
55. Xiong, J.B.; Pan, Z.Q.; Xiao, X.F.; Huang, H.J.; Lai, F.Y.; Wang, J.X.; Chen, S.W. Study on the hydrothermal carbonization of swine manure: The effect of process parameters on the yield/properties of hydrochar and process water. *J. Anal. Appl. Pyrolysis* **2019**, *144*, 104692. doi:10.1016/j.jaap.2019.104692
56. Gómez, E.M.P.; Domínguez, R.E.; López, D.A.; Téllez, J.F.; Marino, M.D.; Almada, N..; Gange, J.M.; Moyano, E.L. Chicken litter: A waste or a source of chemicals? Fast pyrolysis and hydrothermal conversion as alternatives in the valorisation of poultry waste. *J. Anal. Appl. Pyrolysis* **2023**, *169*, 105796. doi:10.1016/j.jaap.2022.105796
57. Gascó, G.; Paz-Ferreiro, J.; Álvarez, M.L.; Saa, A.; Méndez, A. Biochars and hydrochars prepared by pyrolysis and hydrothermal carbonisation of pig manure. *Waste Manage.* **2018**, 79, 395-403. doi:10.1016/j.wasman.2018.08.015
58. Zhou, S.;Liang, H.; Han, L.; Huang, G.; Yang, Z. The influence of manure feedstock, slow pyrolysis, and hydrothermal temperature on manure thermochemical and combustion properties. *Waste Manage.* **2019**, *88*, 85-95. doi:10.1016/j.wasman.2019.03.025
59. Isemin, R.; Mikhalev, A.; Milovanov, O.; Nebyvaev, A. Some results of poultry litter processing into a fertilizer by the wet torrefaction method in a fluidized bed. *Energies* **2022**, *5*, 2414. doi:10.3390/en15072414
60. Diker, İ.; Ozkan, G.M. An investigation on implementing wet torrefaction to dewatered poultry sludge. *Biomass Conv. Bioref.* **2022**, *2022*, 1-14. doi:10.1007/s13399-022-02874-7
61. Arauzo, P.J.; Maziarka, P.A.; Olszewski, M.P.; Isemin, R.L.; Muratova, N.S.; Ronsse, F.; Kruse, A. Valorization of the poultry litter through wet torrefaction and different activation treatments. *Sci. Total. Environ.* **2020**, *732*, 139288. doi:10.1016/j.scitotenv.2020.139288
62. Keskinen, R.; Hyväluoma, J.; Sohlo, L.; Help, H.; Rasa, K. Fertilizer and soil conditioner value of broiler manure biochars. *Biochar* **2019**, *1*, 259–270. doi:10.1007/s42773-019-00020-7
63. Carneiro, J.S.D.S.; Lustosa Filho, J.F.; Nardis, B.O.; Ribeiro-Soares, J.; Zinn, Y.L.; Melo, L.C.A. Carbon stability of engineered biochar-based phosphate fertilizers. *ACS Sustainable Chem. Eng.* **2018**, *6*, 14203-14212. doi:10.1021/acssuschemeng.8b02841
64. Atienza-Martínez, M.; Ábrego, J.; Gea, G.; Marías, F. Pyrolysis of dairy cattle manure: evolution of char characteristics. *J. Anal. Appl. Pyrolysis* **2020**, *145*, 104724. doi:10.1016/j.jaap.2019.104724
65. Erdogdu, A.E.; Polat, R.; Ozbay, G. Pyrolysis of goat manure to produce bio-oil. *Eng. Sci. Technol. Int. J.* **2019**, *22*, 452-457. doi:/10.1016/j.jestch.2018.11.002
66. Zolfi Bavariani, M.; Ronaghi, A.; Ghasemi, R. Influence of pyrolysis temperatures on FTIR analysis, nutrient bioavailability, and agricultural use of poultry manure biochars. *Commun. Soil Sci. Plant Anal.* **2019**, *50*, 402-411. doi:10.1080/00103624.2018.1563101
67. Bellera, C.; Abaalkheel, I.; Rovira, P.; Alrefai, A. Obtaining commercial humic products from uncomposted manures: previous acid hydrolysis to enhance yields. *Int. J. Recycl. Org. Waste Agricult.* **2015**, *4*, 219–231. doi:10.1007/s40093-015-0102-6
68. Gayathri, B.; Srinivasamurthy, C.; Vasanthi, B.; Naveen, D.; Prakash, N.; Bhaskar, S. Extraction and charactrisation of humic acid from different organic wastes and its physico-chemical properties. *Int. J. Chem. Stud.* **2020**, *8*, 769-775. doi:10.22271/chemi.2020.v8.i1k.8359
69. Mosa, A.; Taha, A.A.; Elsaeid, M. In-situ and ex-situ remediation of potentially toxic elements by humic acid extracted from different feedstocks: Experimental observations on a contaminated soil subjected to long-term irrigation with sewage effluents. *Environ. Technol. Innov.* **2021**, *23*, 101599. doi:10.1016/j.eti.2021.101599

70. Sushkova, S.; Minkina, T.; Chaplygin, V.; Nevidomskaya, D.; Rajput, V.; Bauer, T.; Mazarji, M.; Bren, A.B.; Popov, I.; Mazanko, M. Subcritical water extraction of organic acids from chicken manure. *J. Sci. Food Agric.* **2021**, *101*, 1523-1529. doi:10.1002/jsfa.10768
71. Bernal, M.P.; Alburquerque, J.A.; Moral, R. Composting of animal manures and chemical criteria for compost maturity assessment. A review. *Bioresour. Technol.* **2009**, *100*, 5444–5453. doi:10.1016/j.biortech.2008.11.027
72. Angelico, R.; Colombo, C.; Di Iorio, E.; Brtnický, M.; Fojt, J.; Conte, P. Humic substances: from supramolecular aggregation to fractal conformation—Is there time for a new paradigm? *Appl. Sci.* **2023**, *13*, 2236. doi:10.3390/app13042236
73. Efremenko, E.; Stepanov, N.; Senko, O.; Maslova, O.; Volikov, A.; Zhirkova, A.; Perminova, I.; Strategies for variable regulation of methanogenesis efficiency and velocity. *Appl. Microbiol. Biotechnol.* **2022**, *106*, 6833–6845. doi:10.1007/s00253-022-12148-x
74. Orlando, M.Q.; Borja, V.M. Pretreatment of animal manure biomass to improve biogas production: A Review. *Energies* **2020**, *13*, 3573. doi:10.3390/en13143573
75. Wang Z, Li X, Siddiqui MA, Liu H, Zhou T, Zheng L, Huang S, Gao L, Lin CSK, Wang Q (2023b) Effect of humic substances on the anaerobic digestion of secondary sludge in wastewater treatment plants: a review. Environ Chem Lett 21:3023–3040. doi:.1007/s10311-023-01632-z 170-172
76. Yu, H.; Zhao, Y.; Zhang, C.; Wei, D.; Wu, J.; Zhao, X.; Hao, J.; Wei, Z. Driving effects of minerals on humic acid formation during chicken manure composting: Emphasis on the carrier role of bacterial community. *Bioresour. Technol.* **2019**, *294*, 122239. doi:10.1016/j.biortech.2019.122239
77. Chen, L.; Chen, Y.; Li, Y.; Liu, Y.; Jiang, H.; Li, H.; Yuan, Y.; Zou, B. Improving the humification by additives during composting: A review. *Waste Manage.* **2023**, *158*, 93-106. doi:10.1016/j.wasman.2022.12.040
78. Zheng, G.; Liu, C.; Deng, Z.; Wei, Z.; Zhao, Y.; Qi, H.; Xie, X.; Wu, D.; Zhang, Z.; Yang, H. Identifying the role of exogenous amino acids in catalyzing lignocellulosic biomass into humus during straw composting. *Bioresour. Technol*. **2021**, *340*, 125639. doi:10.1016/j.biortech.2021.125639.
79. Kim, J.R.; Karthikeyan, K.G. Effects of severe pretreatment conditions and lignocellulose-derived furan byproducts on anaerobic digestion of dairy manure. *Bioresour. Technol.* **2021**, *340*, 125632. doi.org/10.1016/j.biortech.2021.125632
80. Yu, Q.; Sun, C.; Liu, R.; Yellezuome, D.; Zhu, X.; Bai, R.; Liu, M.; Sun, M. Anaerobic co-digestion of corn stover and chicken manure using continuous stirred tank reactor: The effect of biochar addition and urea pretreatment. *Bioresour. Technol.* **2021**, *319*, 124197. doi:10.1016/j.biortech.2020.124197
81. Shao, Z.; Gnanasekar, P.; Tratnik, N.; Tanguy, N.R.; Guo, X.; Zhu, M.; Qui, L.; Yan, N.; Chen, H. Low-temperature torrefaction assisted with solid-state KOH/urea pretreatment for accelerated methane production in wheat straw anaerobic digestion. *Bioresour. Technol.* **2023**, *377*, 128940. doi:10.1016/j.biortech.2023.128940
82. Romero-Güiza, M.S.; Vila, J.; Mata-Alvarez, J.; Chimenos, J.M.; Astals, S. The role of additives on anaerobic digestion: a review. *Renew. Sust. Energ. Rev.* **2016**, *58*, 1486-1499. doi:10.1016/j.rser.2015.12.094
83. Senko, O.; Gladchenko, M.; Maslova, O.; Efremenko, E. Long-term storage and use of artificially immobilized anaerobic sludge as a powerful biocatalyst for conversion of various wastes including those containing xenobiotics to biogas. *Catalysts* **2019**, *9*, 26. doi:10.3390/catal9040326
84. Efremenko, E.; Senko, O.; Maslova, O.; Lyagin, I.; Aslanli, A.; Stepanov, N. Destruction of mycotoxins in poultry waste under anaerobic conditions within methanogenesis catalyzed by artificial microbial consortia. *Toxins* **2023** *15*, 205. doi;10.3390/toxins15030205
85. Zhuravleva, E.A.; Shekhurdina, S.V.; Kotova, I.B.; Loiko, N.G.; Popova, N.M.; Kryukov, E.; Kovalev, A.A.; Kovalev, D.A.; Litti, Y.V. Effects of various materials used to promote the direct interspecies electron transfer on anaerobic digestion of low-concentration swine manure. *Sci. Total. Environ.* **2022**, *839*, 156073. doi:10.1016/j.scitotenv.2022.156073
86. Xiao, R.; Wang, J.J.; Gaston, L.A.; Zhou, B.; Park, J.H.; Li, R.; Dodla, S.K.; Zhang, Z. Biochar produced from mineral salt-impregnated chicken manure: fertility properties and potential for carbon sequestration. *Waste Manage.* **2018**, *78*, 802-810. doi;10.1016/j.wasman.2018.06.047
87. Nieweś, D.; Biegun, M.; Huculak-Mączka, M.; Marecka, K.; Kaniewski, M.; Zieliński, J.; Hoffmann, J. Extraction of humic acid from peat and lignite and the thermal behavior of their mixtures with ammonium nitrate. *J. Therm. Anal. Calorim.* **2023**, *2023*. doi:10.1007/s10973-023-12326-7
88. Klavins, M.; Purmalis, O. Characterization of humic acids from raised bog peat. *Latv. J. Chem.* **2014**, *52*, 83-97. doi:10.2478/ljc-2013-0010
89. Fatima, N.; Jamal, A.; Huang, Z.; Liaquat, R.; Ahmad, B.; Haider, R.; Ali, M.I; Shoukat, T.; Alothman, Z.A.; Ouladsmane. M.; Ali, T. Extraction and chemical characterization of humic acid from nitric acid treated lignite and bituminous coal samples. *Sustainability* **2021**, *13*, 8969. doi:10.3390/su13168969
90. Polyakov, V.; Zazovskaya, E.; Abakumov, E. Molecular composition of humic substances isolated from selected soils and cryconite of the Grønfjorden area, Spitsbergen. *Pol. Polar. Res.* **2019**, *40*, 105-120. doi:10.24425/ppr.2019.128369

91. Khudzari, J.M.; Tartakovsky, B.; Raghavan, G.V. Effect of C/N ratio and salinity on power generation in compost microbial fuel cells. *Waste Manage.* **2016**, *48*, 135-142. doi:10.1016/j.wasman.2015.11.022
92. Tipping, E.; Somerville, C.J.; Luster, J. The C:N:P:S stoichiometry of soil organic matter. *Biogeochemistry* **2016**, *130*, 117–131. doi:10.1007/s10533-016-0247-z
93. Thang, P.Q.; Jitae, K.; Giang, B.L.; Viet, N.M.; Huong, P.T. Potential application of chicken manure biochar towards toxic phenol and 2, 4-dinitrophenol in wastewaters. *J. Environ. Manage.* **2019**, *251*, 109556. doi:10.1016/j.jenvman.2019.109556
94. Zhao, M.; Dai, Y.; Zhang, M.; Feng, C.; Qin, B.; Zhang, W.; Zhao, N.; Li, Y.; Ni, Z.; Xu, Z.; Tsang, D.C.W.; Qiu, R. Mechanisms of Pb and/or Zn adsorption by different biochars: Biochar characteristics, stability, and binding energies. *Sci. Total Environ.* **2020**, *717*, 136894. doi:10.1016/j.scitotenv.2020.136894
95. Han, L.; Zhang, E.; Yang, Y.; Sun, K.; Fang, L. Highly efficient U (VI) removal by chemically modified hydrochar and pyrochar derived from animal manure. *J. Clean. Prod.* **2020**, *264*, 121542. doi;10.1016/j.jclepro.2020.121542
96. Minale, M.; Guadie, A.; Liu, Y.; Meng, Y.; Wang, X.; Zhao, J. Insight into adsorption behavior of chlortetracycline and cadmium in aqueous solution using a novel manganese ferrite loaded swine manure hydrochar. *J. Environ. Chem. Eng.* **2021**, *9*, 106785. doi:10.1016/j.jece.2021.106785
97. Ding, S.; Wang, B.; Feng, Y.; Fu, H.; Feng, Y.; Xie, H.; Xue, L. Livestock manure-derived hydrochar improved rice paddy soil nutrients as a cleaner soil conditioner in contrast to raw material. *J. Clean. Prod.* **2022**, *372*, 133798. doi:10.1016/j.jclepro.2022.133798
98. Han, L.; Sun, H.; Ro, K.S.; Sun, K.; Libra, J.A.; Xing, B. Removal of antimony (III) and cadmium (II) from aqueous solution using animal manure-derived hydrochars and pyrochars. *Bioresour. Technol.* **2017**, *234*, 77-85. doi:10.1016/j.biortech.2017.02.130
99. Huezo, L.; Shah, A. Effect of hydrochar from anaerobically digested sewage sludge and manure as a soil amendment on soil properties and plant responses. *Bioenerg. Res.* **2023**, *16*, 1195–1204. doi:10.1007/s12155-022-10479-1
100. Bashir, A.; Rizwan, M.; ur Rehman, M.Z.; Zubair, M.; Riaz, M.; Qayyum, M.F.; Alharby, H.S.; Bamagoos, A.A.; Ali, S. Application of co-composted farm manure and biochar increased the wheat growth and decreased cadmium accumulation in plants under different water regimes. *Chemosphere* **2020** *246*, 125809. doi:10.1016/j.chemosphere.2019.125809
101. Piccolo, A.; Spaccini, R.; De Martino, A.; Scognamiglio, F.; di Meo, V. Soil washing with solutions of humic substances from manure compost removes heavy metal contaminants as a function of humic molecular composition. *Chemosphere* **2019**, *225*, 150-156. doi:10.1016/j.chemosphere.2019.03.019
102. Yang, Y.; Wang, M.; Yan, S.; Yong, X.; Zhang, X.; Awasthi, M.K.; Xi, Y.; Zhou, J. Effects of hydrochar and biogas slurry reflux on methane production by mixed anaerobic digestion of cow manure and corn straw. *Chemosphere* **2023**, *310*, 136876. doi:10.1016/j.chemosphere.2022.136876
103. Chen, H.; Awasthi, S.K.; Liu, T.; Duan, Y.; Ren, X.; Zhang, Z.; Pandey, A.; Awasthi, M.K. Effects of microbial culture and chicken manure biochar on compost maturity and greenhouse gas emissions during chicken manure composting. *J. Hazard. Mater.* **2020**, *389*, 121908. doi:10.1016/j.jhazmat.2019.121908.
104. Zingaretti, D.; Lominchar, M.A.; Verginelli, I.; Santos, A.; Baciocchi, R. Humic acids extracted from compost as amendments for Fenton treatment of diesel-contaminated soil. *Environ. Sci. Pollut. Res.* **2020**, *27*, 22225–22234 doi:10.1007/s11356-020-08221-5.
105. Maguey-González, J.A.; Nava-Ramírez, M.dJ.; Gómez-Rosales, S.; Ángeles, Md.L.; Solís-Cruz, B.; Hernández-Patlán, D.; Merino-Guzmán, R.; Hernández-Velasco, X.; Figueroa-Cárdenas, J.dD.; Vázquez-Durán, A.; Hargis, B.M.; Tellez-Isaisas, J.dD. Humic acids preparation, characterization, and their potential adsorption capacity for aflatoxin B1 in an *in vitro* poultry digestive model. *Toxins* **2023**, *15*, 83. doi:10.3390/toxins15020083
106. Wang, Y.; Pan, F.; Wang, Q.; Luo, J.; Zhang, Q.; Pan, Y.; Wu, C.; Liu, W. The effect of different remediation treatments on soil fungal communities in rare earth tailings soil. *Forests* **2022**, *13*, 1987. doi:10.3390/f13121987
107. Gong, X.; Zou, L.; Wang, L.; Zhang, B.; Awasthi, M.K.; Xi, Y.; Jiang, J. Biochar improves compost humification, maturity and mitigates nitrogen loss during the vermicomposting of cattle manure-maize straw. *J. Environ. Manage.* **2023**, *325*, 116432. doi:10.1016/j.jenvman.2022.116432
108. Awasthi, M.K.; Duan, Y.; Awasthi, S.K.; Liu, T.; Chen, H.; Pandey, A.; Taherzadeh, M.J. Emerging applications of biochar: Improving pig manure composting and attenuation of heavy metal mobility in mature compost. *J. Hazard. Mater.* **2020**, *389*, 122116. doi:10.1016/j.jhazmat.2020.122116
109. Primozic, M.; Podrepsek, G.H.; Pavlovic, I.; Skerget, M.; Knez, Z.; Leitgeb, M. Enzyme immobilization onto biochar produced by the hydrothermal carbonization of biomass. *Acta Chim. Slov.* **2019**, *66*, 732–739. doi:10.17344/acsi.2019.5013
110. Liu, D.; Wang, Y.; Jia, B.; Wei, J.; Liu, C.; Zhu, J.; Tang, S.; Wu, Z.; Chen, G. Microwave-assisted hydrothermal preparation of corn straw hydrochar as supercapacitor electrode materials. *ACS omega* **2020**, *5*, 26084-26093. doi:/10.1021/acsomega.0c03605

111. Verrillo, M.; Salzano, M.; Savy, D.; Di Meo, V.; Valentini, M.; Cozzolino, V.; Piccolo, A. Antibacterial and antioxidant properties of humic substances from composted agricultural biomasses. *Chem. Biol. Technol. Agric.* **2022**, 9, 28. doi:10.1186/s40538-022-00291-6
112. Kulikova, N.A.; Filippova, O.I.; Volikov, A.B.; Perminova, I.V. Slow nitrogen release from humic substances modified with aminoorganosilanes. *J. Soils Sediments* **2018**, *18*, 1400-1408. doi: 10.1007/s11368-016-1507-1
113. Wystalska, K.; Malińska, K.; Barczak, M. Poultry manure derived biochars – the impact of pyrolysis temperature on selected properties and potentials for further modifications. *J. Sustainable Dev. Energy Water Environ. Syst.* **2021**, *9*, 246295. doi:10.13044/j.sdewes.d8.0337
114. Linkevich, E.V.; Yudina, N.V.; Savel'eva, A.V. Role of humic acids in the detoxification of petroleum hydrocarbons in soil. *Solid Fuel Chem.* **2021**, *55*, 332-337. doi:10.3103/S0361521921050049
115. Guo, Y.; Liu, H.; Gong, P.; Li, P.; Tian, R.; Zhang, Y.; Xu, Y.; Xue, B. Preliminary studies on how to reduce the effects of salinity. *Agronomy* **2022**, *12*, 3006. doi:10.3390/agronomy12123006
116. Luo, D.; Wang, L.; Nan, H.; Cao, Y.; Wang, H.; Kumar, T.V.; Wang, C. Phosphorus adsorption by functionalized biochar: a review. *Environ. Chem. Lett.* **2023**, *21*, 497-524. doi:10.1007/s10311-022-01519-5
117. Osman, A.I.; Fawzy, S.; Farghali, M.; El-Azazy, M.; Elgarahy, A.M.; Fahim, R.A.; Maksoud, M.A.; Ajlan, A.A.; Yousry, M.; Saleem, Y.; Rooney, D.W. Biochar for agronomy, animal farming, anaerobic digestion, composting, water treatment, soil remediation, construction, energy storage, and carbon sequestration: a review. *Environ. Chem. Lett.* **2022**, *20*, 2385-2485. doi:10.1007/s10311-022-01424-x 436-441
118. Masoumi, S.; Borugadda, V.B.; Nanda, S.; Dalai, A.K. Hydrochar: a review on its production technologies and applications. *Catalysts* **2021**, *11*, 939. https://doi.org/10.3390/catal11080939
119. Hafez, M.; Popov, A.I.; Zelenkov, V.N.; Teplyakova, T.V.; Rashad, M. Humic substances as an environmental-friendly organic wastes potentially help as natural anti-virus to inhibit COVID-19. *Sci. Arch.* **2020**, *1*, 53–60. doi:10.47587/SA.2020.1202
120. Marcinčák, S.; Semjon, B.; Marcinčáková, D.; Reitznerová, A.; Mudroňová, D.; Vašková, J.; Nagy, J. Humic substances as a feed supplement and the benefits of produced chicken meat. *Life* **2023**, *13*, 927. doi:10.3390/life13040927
121. Legan, M.; Gotvajn, A.Ž.; Zupan, K. Potential of biochar use in building materials. *J. Environ. Manage.* **2022**, *309*, 114704. doi:10.1016/j.jenvman.2022.114704
122. Liang, Q.; Pan, D.; Zhang, X. Construction and application of biochar-based composite phase change materials. *Chem. Eng. J.* **2023**, *453*, 139441. doi;10.1016/j.cej.2022.139441
123. Çay, A.; Yanık, J.; Akduman, Ç.; Duman, G.; Ertaş, H. Application of textile waste derived biochars onto cotton fabric for improved performance and functional properties. *J. Clean. Prod.* **2020**, *251*, 119664. doi;10.1016/j.jclepro.2019.119664