Waste Management

Efficient recovery and characterization of humic acids from municipal and manure composts: A comparative study

--Manuscript Draft--

Manuscript Number:	WM-23-1686R2
Article Type:	Full Length Article
Section/Category:	Recycling
Keywords:	Humic acids; Manure compost; Municipal mixed waste compost; Alkaline extraction; contaminants of emerging concern; UHPLC-MS-QTOF
Corresponding Author:	Mónica Coca, PhD University of Valladolid Valladolid, SPAIN
First Author:	Marina Fernández-Delgado
Order of Authors:	Marina Fernández-Delgado
	Juan Carlos López-Linares
	Susana Lucas
	Mª Teresa García-Cubero
	Mónica Coca, PhD
Abstract:	The recovery of humic acids from low-quality compost obtained in municipal solid waste treatment plants provides opportunities for its valorization. This study compares the recovery and properties of the humic acids obtained from municipal mixed waste compost (MMWC) and manure compost. The effects of temperature, time, and KOH concentration on the ratio of humic acids in the extracted liquid and the content of organic carbon of the precipitates were investigated by response surface methodology. Optimal conditions were 30°C and 24 h for both composts, with a KOH concentration of 0.53 M for MMWC and 0.25 M for manure compost. The manure compost provided a liquid extract richer in humic acids than MMWC (76.6% vs. 33.7%), but the precipitates presented similar organic carbon contents (38.1% vs. 42.4%). Regarding composition, both humic acids presented higher organic carbon and nitrogen contents than the composts used as feedstock. The extraction and further precipitation of humic acids reduced the concentration of heavy metals. Humic acids from manure compost have a slightly higher average molecular weight (2650 Da) than those from MMWC (1980 Da), while both present similar C/N ratios and degree of aromaticity. Most contaminants of emerging concern present in the original composts were not detected in the humic acids. Thus, it was demonstrated that MMWC constitutes an attractive source of humic acids with properties similar to those obtained from a high-quality compost and, therefore, with potential economic value.

Highlights

- Recovery of humic acids from manure compost and municipal mixed waste compost.
- Optimization of alkaline extraction conditions by response surface methodology.
- Both humic acids show similar physico-chemical characteristics.
- Concentrations of heavy metals below the regulatory limits.
- Removal of emerging concern contaminants due to the recovery process.

Efficient recovery and characterization of humic acids from municipal and manure composts: A comparative study

Marina Fernández-Delgado[ab], Juan Carlos López-Linares[ab], Susana Lucas[ab], M. Teresa García-Cubero[ab], Mónica Coca[ab,*]

[a]Department of Chemical Engineering and Environmental Technology, University of Valladolid, Dr. Mergelina s/n, 47011 Valladolid, Spain

[b]Institute of Sustainable Processes, Department of Chemical Engineering and Environmental Technology, University of Valladolid, Dr. Mergelina s/n, 47011 Valladolid, Spain

* Corresponding author: Mónica Coca. Tel.: +34 983 18 45 95; E-mail address: monica.coca@uva.es.

Abstract

The recovery of humic acids from low-quality compost obtained in municipal solid waste treatment plants provides opportunities for its valorization. This study compares the recovery and properties of the humic acids obtained from municipal mixed waste compost (MMWC) and manure compost. The effects of temperature, time, and KOH concentration on the ratio of humic acids in the extracted liquid and the content of organic carbon of the precipitates were investigated by response surface methodology. Optimal conditions were 30°C and 24 h for both composts, with a KOH concentration of 0.53 M for MMWC and 0.25 M for manure compost. The manure compost provided a liquid extract richer in humic acids than MMWC (76.6% vs. 33.7%), but the precipitates presented similar organic carbon contents (38.1% vs. 42.4%). Regarding composition, both humic acids presented higher organic carbon and nitrogen contents than the composts used as feedstock. The extraction and further precipitation of humic acids reduced the concentration of heavy metals. Humic acids from manure compost have a slightly higher average molecular weight (2650 Da) than those from MMWC (1980 Da), while both present similar C/N ratios and degree of aromaticity. Most contaminants of emerging concern present in the original composts were not detected in the humic acids. Thus, it was demonstrated that MMWC constitutes an attractive source of humic acids with properties similar to those obtained from a high-quality compost and, therefore, with potential economic value.

Keywords

Humic acids; Manure compost; Municipal mixed waste compost; Alkaline extraction; contaminants of emerging concern; UHPLC-MS-QTOF

1. Introduction

Humic substances (HS) refer to natural organic compounds formed during the decomposition of plant and animal residues (Shao et al., 2022). HS are found in soil, peat, coal, compost, and other organic materials. HS can be classified into three fractions based on their solubility (Genuino et al., 2017): (1) fulvic acids (FA) are soluble in water at any pH; (2) humic acids (HA) are soluble at higher pH but become insoluble in acidic solutions (pH < 2); and (3) humin is insoluble at all pH conditions. HA is the most interesting fraction due to its chemical properties and its interaction with other compounds (Genuino et al., 2017; Katsumi et al., 2016). HA are widely used in multiple applications, including as a feed additive in poultry diets, for soil remediation, as a plant growth stimulator, and the remediation of environmental pollutants (Zhang et al., 2023). The application of HA in soils increases the availability of nutrients, improving the microbial population, water-holding capacity, texture, and structure of the soil (Ore et al., 2023). It has been proved that the oral consumption of HA by domestic animals could reduce the cholesterol, lipids, and glucose content while increasing the red blood cells and hemoglobin (Sutradhar and Fatehi, 2023). Applications of humic acids in medicine, pharmaceuticals and cosmetics as functional agents in the prevention of diseases have also been reported (De Melo et al., 2016). HA contain different functional groups, mainly carboxylic acids, phenolic groups, and also amino, quinone and methoxy groups, which have a significant influence on their properties (Cheng et al., 2019; Li et al., 2023). Commercial HA is commonly obtained from non-renewable carbon sources, such as leonardite and lignite coals (Huculak-Mączka et al., 2018). High-quality organic compost can also be used as a source of HA. Composting produces stable and complex macromolecules and reduces such impurities as heavy metals and other contaminants (Lashermes et al., 2012). In addition, the production of HA is more sustainable if compost is used as a feedstock, since the mining activities needed to obtain lignite or leonardite are highly energy-consuming (Huculak-Mączka et al., 2018). Humic acids have been extracted from different composts produced from fish waste and sugarcane bagasse (Aranganathan et al., 2019), rice husks (Omar et al., 2021), olive residue (Tortosa et al., 2014), or anaerobic sewage sludge (Cristina et al., 2020). HA can be recovered from these materials using various extraction methods, such as conventional extraction with water, alkali or acid solvents (Fernández-Delgado et al., 2020, Kanmaz, 2019), ultrasound-assisted extraction (Moreda-Piñeiro et al., 2004; Raposo et al., 2016), and microwave-assisted extraction (Fernández-Delgado et al., 2022). However, the most common method to extract HA is the conventional process using strong alkaline solvents such as KOH and NaOH (Genuino et al., 2017). The main advantages are that they are simple, well-known devices, are easy to operate, and have a high efficiency (Li et al., 2014; Rashid et al., 2023). Because of its low cost, NaOH has been widely used as an HA extractant. Aranganathan et al. (2019) achieved the maximum HA recovery from fish waste and sugarcane bagasse co-compost using 0.1 M NaOH. Sarlaki et al. (2019) used lignite as a feedstock to recover HA using 0.5 M NaOH and a membrane purification process, achieving HA with a purity of 97%. However, the use of NaOH has some restrictions (Das et al., 2015), because the addition in excess of sodium to the soil has a detrimental influence on fertility, due to its deleterious effects on permeability and nutrient balance (Aranganathan et al., 2019; Rashid et al., 2023). Moreover, NaOH can result in the partial degradation of the chemical structure of HA and thus contribute to the contamination of the final product. Therefore, KOH is a preferred extraction alternative as it can provide HA with a higher purity and K content (Aranganathan et al., 2019; Cheng et al., 2019; Stevenson, 1994).

Low-quality compost, such as municipal mixed waste compost (MMWC), or biostabilized material, has rarely been explored for the recovery of HA. This compost is obtained from the organic fraction of municipal solid waste, recovered from the undifferentiated collection, and can present a higher content of heavy metals and other contaminants, such as Contaminants of Emerging Concern (CECs). CECs include pharmaceutical compounds, plasticizers, personal care products, or flame retardants (Rezaei Adaryani and Keen, 2022). CECs are present in municipal solid waste and remain after composting, with a potential impact on human health and the environment (Langdon et al., 2019). MMWC has restricted applications in agriculture as a fertilizer (European Commission, 2018a). If none is foreseen, the MMWC will be disposed of in landfills (Ribeiro et al., 2017), for which limits will be significantly tightened to reflect the EU's ambitions for the transition to a circular economy. By 2035, the amount of municipal garbage put in landfills should be less than 10% of the entire quantity generated (by weight) (European Commission, 2018b). Thus, developing alternatives for MMWC valorization is a critical social task.

This study aims to valorize a low-quality organic waste, such as MMWC, by extracting humic acids. The properties of the organic substances recovered have been compared with those of HA obtained from cow manure compost, a high-quality compost. Differences in the recovered humic acids, based on (i) the composition of both raw materials, (ii) the optimal extraction conditions, (iii) the physicochemical properties of the humic acids, and (iv) the presence of contaminants of emerging concern, were assessed to investigate the feasibility of using MMWC as a source of humic acids. The extraction process was first optimized using a Central Composite Design to analyze the effects of temperature, time and concentration of KOH on the ratio of humic acids in the extracted liquid and the content of organic carbon of the precipitate. To the best of the authors' knowledge, no references on the presence of CECs in MMWC and manure compost have been published. It is of special interest to determine whether the humic acid extraction process can remove CECs that may have an impact on the environment and human health.

2. Materials and Methods

2.1. Raw Materials

A municipal solid waste treatment plant located in Castilla y León (Spain) kindly donated the MMWC (low-quality compost). The cow manure compost (high-quality compost) was supplied by the Agrarian Technological Institute of Castilla y León (ITACyL). Both samples were stored at -18 ºC until use and dried in an oven at 70 ºC before performing the experimental runs.

2.2. Humic Acid Extraction and Precipitation

The HA extraction process is described as follows: the S:L ratio (10% w/v) was fixed by mixing 10 g of compost and 100 mL of KOH solvent in 250 mL sealed flasks for S:L extraction performed at 200 rpm under the conditions established by the experimental design in an orbital shaker (Incubator Shaker ES-60, Miulab, China). Following extraction, the mixture was centrifuged for 10 minutes at 10000 rpm using a Centrifuge Sorvall legend RT (Thermo Fisher Scientific, Spain). The supernatants were filtered (Filter-lab 1300/80 0.45 mm, Filters AOIA S.A., Spain) before being analyzed. All the experiments were carried out in duplicate.

The supernatant was acidified with 6 M HCl until pH < 1 was reached, and the sample was stored overnight at 4 ºC to ensure complete HA precipitation. After that, the mixture was centrifuged (10 min, 10000 rpm), and the supernatant (fulvic acid fraction) was recovered for further characterization. Then, the HA precipitate was washed and dried in an oven at 105 ºC for 24 h until the sample weight was constant in order to determine the mass recovered. Solids were stored for further analysis.

2.3. Response Surface Methodology for Humic Acid Extraction

In this study, a Response Surface Methodology (RSM) with a Central Composite Design (CCD) was selected to analyze and optimize the effect of temperature (X1: 30 – 60, ºC), time (X2: 4 – 24, h), and KOH concentration (X3: 0.25 – 1, M) on the extraction of HA from MMWC (HA-MMWC) and manure compost (HA-compost). The variable levels were selected based on previous studies (Fernández-Delgado et al., 2021, 2020; Tortosa et al., 2014). The RSM design was performed at an S/L ratio of 10% w/v, based on prior results (Fernández-Delgado et al., 2020).

The optimum operating conditions for the HA extraction were predicted based on two response variables optimized simultaneously. These were based on the determination of the total organic carbon (TOC): (1) the HA ratio in the extracted liquid (% $TOC_{HA}/TOC_{extracted}$), and (2) the TOC content of the precipitate (% TOC_{HA}/precipitate). The HA ratio was calculated as TOC (g) in the precipitated solid per 100 g of TOC in the extracted liquid. Furthermore, the TOC content is referred to as TOC (g) in the precipitated solid per 100 g of the precipitate. The response variables were selected to favor the extraction of humic acids rather than other organic fractions (fulvic acids and non-humic organic matter), and to obtain a HA fraction with a high content in organic carbon. A second-order polynomial model was proposed to obtain a correlation between the independent design variables and the selected responses. Eq. 1 is the general second-order polynomial equation used to analyze the experimental data.

$$Y = b_0 + \sum_{i=1}^{3} b_i X_i + \sum_{i=1}^{3} b_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} b_{ij} X_i X_{ij} \quad \text{Eq. 1}$$

where Y is the response value, b_0 is the offset term, b_i is the linear effect, b_{ii} is the squared effect, b_{ij} is the interaction effect, and X_i and X_j are independent variables.

2.4. Analytical methods

2.4.1. Elemental composition of the samples

Humidity and volatile solids (VS) contents of the solid samples were determined by gravimetry (at 100 ºC and 550 ºC, respectively). The elemental composition (total carbon (TC), TOC, and total nitrogen (TN)) was analyzed by the Dumas Method using an elemental analyzer (EuroVector EA3000, Italy). As for the liquid samples, the elemental composition (TC, TOC, TN) was determined by a TOC-V 5000 analyzer (Shimadzu, Japan). Macro, micronutrient and heavy metal concentrations were determined by ICP analysis for both solid and liquid samples, as described by Fernández-Delgado et al. (2020).

2.4.2. UV-Vis spectroscopy

A UV-Vis spectrophotometer (Shimadzu, Japan) was used to determine the absorption spectra of HA. The dissolution of the precipitated HA was accomplished by adding 0.1 N NaOH until a HA concentration of 1 g/L was reached. This method ensures the preparation of HA solutions suitable for subsequent measurements of UV-Vis parameters (Aranganathan et al., 2019; Kumada, 1987). The absorbance was measured at different wavelengths (of 280 nm, 365 nm, 400 nm, 465 nm, 600 nm, and 665 nm) to determine the HA properties. After that, the photometric ratios E_2/E_3 (A_{280}/A_{365}) and E_4/E_6 (A_{465}/A_{665}) were calculated. The ratio E_2/E_3 is directly related to the degree of aromaticity (DA) through Eq. 2 (Aranganathan et al., 2019).

$$DA = 52.509 - 6.780 E_2/E_3 \quad \text{Eq. 2}$$

The ratio E_4/E_6 is considered as the humification index (Zbytniewski and Buszewski, 2005). The molecular weight (MW) was estimated with the molar absorptivity at 280 nm by Eq. 3 (Chin and Aiken, 1994).

$$MW = 490 + 3.990 \varepsilon_{280} \quad \text{Eq. 3}$$

Finally, to categorize the HA type, the Kumada Index (log(K)) was determined by $\log(A_{400}) - \log(A_{600})$ (Aranganathan et al. 2019; Kumada and Kawamura, 1968).

2.4.3. Fourier transform infrared (FTIR)

FTIR (Bruker Alpha, USA) analyzed the functional-group composition of the precipitated HA. The absorbance spectra were measured between 4000 cm^{-1} and 400 cm^{-1} in the wavelength range.

2.4.4. Identification of CECs using UHPLC-MS-QTOF

The CECs present in the composts and humic acids were identified by ultra-high-performance liquid chromatography (UHPLC) coupled with mass spectrometry at the Laboratory of Instrumental Techniques (University of Valladolid). UHPLC separation was performed on a Phenomenex Kinetex C18 column (50 × 2.1 mm, 1.7µm) held at 40 °C on a SCIEX ExionLC AC System (SCIEX, USA). The mobile phase consisted of water, methanol, and 0.1% formic acid. The flow rate was set at 0.3 mL/min. The injection volume was 5 µL and the total LC runtime was 22 minutes. MS and MS/MS data were on the SCIEX X500R QTOF System (SCIEX, USA) with SCIEX OS Software 1.5, covering a mass range from 100 to 1000 m/z. An electrospray ionization (ESI) in positive mode was carried out. Before analysis, the solids were subjected to a double-step extraction with water:methanol (1:1), under constant stirring for 3 h at room temperature. The organic phase was separated by a vacuum evaporator (Heidolph VV2000, Germany) and stored for subsequent analysis.

2.5. Data analysis

The statistical software R (version 4.2.2. – Innocent and Trusting – 2022) was used to plan the CCD and to analyze the experimental data statistically. ANOVA was used to analyze the experimental design, whereas Tukey's multiple-range test analyzed the central points of CCD to find statistically significant differences at a 95% confidence level ($p < 0.05$).

3. Results and Discussion

3.1. Raw material characterization

The compositions of MMWC and manure compost are shown in Table 1. The contents of TOC and nutrients were similar. Regarding TOC, the concentration was 263.8 g/kg for MMWC and 270.1 g/kg for manure compost, which represents a difference of 2.3%. These values are within the ranges reported by Stehouwer et al. (2022) for MMWC (197 – 354, g/kg) and for manure compost (149 – 471, g/kg). Furthermore, typical TN content ranges from 11 g/kg to 30 g/kg for MMWC and from 8 g/kg to 29 g/kg for manure compost (Stehouwer et al., 2022). The composting processes are managed to ensure optimal conditions for organic matter decomposition, including proper moisture levels, aeration, and temperature control (Chen et al., 2023; Stehouwer et al., 2022). As a result, both composts employed in this study are a potential source of organic carbon that may be valorized through the recovery of HA.

Nevertheless, the concentrations of micronutrients and heavy metals should be considered in the valorization of compost by humic acid extraction, as metals can co-precipitate, thus reducing the quality of the final product (Lee et al., 2023, 2022). As was expected due to its origin, MMWC has a much higher heavy metal and micronutrient content than manure compost, especially copper, lead, nickel, total chromium, and zinc. Heavy metals and micronutrient concentrations in both composts are within the ranges reported by Stehouwer et al. (2022). Compost quality depends on the raw material. Rodrigues et al. (2020) found that plastic in organic waste caused a decrease in nitrogen and phosphorus content and increased levels of heavy metals in the compost. In contrast, compost from biowaste separated at the source presents a higher nutrient content and lower levels of heavy metals. Thus, proper sorting and separation of materials are necessary to ensure the production of high-quality compost.

3.2. Humic acid recovery by conventional extraction

3.2.1. Extraction model and statistical analysis

Table 2 shows the CCD experimental set and the responses. In all runs, HA predominated in the organic carbon extracted from manure compost (MMWC: 10% – 30% vs. Manure Compost: 20% – 80%). These data indicate that most organic carbon from manure compost corresponds to humic acids. Generally, most runs reached a HA ratio above 60%, except for runs 9 (t = 0 h) and 11 (KOH = 0 M). The TOC content in humic acids commonly ranges between 30% and 70% of solid. HA from MMWC presented 30% – 65% TOC, whereas HA from manure compost showed 20% – 45% TOC. These differences may be due to the extraction conditions (Aranganathan et al., 2019) and the source of the humic acid (De Melo et al., 2016; Jing et al., 2023). Despite the differences in the values obtained, they are within the expected carbon content.

A multiple regression analysis was conducted to fit the observed data using a quadratic second-order polynomial model, obtaining four equations (Eqs. 4 – 7).

$$Y1 = 28.47 + 0.70X1 + 6.80X2 + 6.28X3 - 2.13X1X2 + 0.90X1X3 - 2.59X2X3 + 1.27X1^2 - 3.82X2^2 - 4.07X3^2 \qquad \text{Eq. 4}$$

$$P1 = 47.66 - 5.98X1 + 5.35X2 - 2.93X3 - 1.35X1X2 + 3.38X1X3 - 6.00X2X3 + 5.68X1^2 - 5.67X2^2 - 1.05X3^2 \qquad \text{Eq. 5}$$

$$Y2 = 70.10 + 3.0X1 + 3.79X2 - 4.41X3 - 2.37X1X2 + 0.32X1X3 + 0.61X2 * X3 + 0.20 * X1^2 - 0.92 * X2^2 - 0.14 * X3^2 \quad \text{Eq. 6}$$

$$P2 = 28.07 + 2.27X1 + 1.99X2 - 7.22X3 - 0.10X1X2 - 0.45X1X3 + 0.42X2X3 + 0.58X1^2 + 0.36X2^2 + 1.54X3^2 \quad \text{Eq. 7}$$

where Y1 and Y2 are the ratio of HA in the extract (% HA) for MMWC and manure compost, respectively; P1 and P2 are the TOC content in HA (% TOC) for MMWC and manure compost, respectively; X1 is the temperature, X2 the time, and X3 the KOH concentration.

Table 3 shows the analysis of variance (ANOVA) of the models for MMWC and manure compost, which are based on CCD to determine the fit of the optimization model. Optimization was carried out considering both the HA ratio in the extract and the TOC content of the precipitate. The statistical models were validated through the lack-of-fit test and the P-value. Both statistical parameters confirm that the model fits the observed data well, indicating its robustness and reliability, as the P-value was below 0.05 and the F-values surpassed the threshold for lack-of-fit. What is more, in the case of manure compost, the lack-of-fit value was negligible, indicating the goodness of fit. The R^2 and the adjusted R^2 values were higher than 0.96, showing the accuracy of the proposed model. In the case of MMWC, the R^2 (0.93) and adjusted R^2 (0.86) values indicate that the model fits reasonably well.

Table 3 shows the optimal operation conditions predicted for the model for both composts. The optimum temperature (30 ºC) and extraction time (24 h) were similar, whereas the KOH concentration differs (0.53 M for MMWC and 0.25 M for manure compost). Under these conditions, the suggested models can predict the HA ratio and the TOC content. The extraction was then performed in triplicate under optimal conditions to validate the model. As can be seen, the observed TOC content and HA ratio were very close to the predicted data, with a deviation below 5%, showing that the proposed models were reliable within the range of operation (Ezzati et al., 2020). The manure compost provides better results under optimal conditions than MMWC for the HA ratio (76.6% vs. 33.7%), but a slightly lower TOC content (38.1% vs. 42.4%), as expected from the experimental results.

3.2.2. Interaction of the extraction parameters

The effect of the operation variables (temperature, time and KOH) was analyzed by a CCD based on RSM. The response surfaces are plotted in Figures 1 (HA-MMWC) and 2 (HA-compost). The 3D graphs facilitate the understanding of the influence of the operating variables on the responses. According to the linear and quadratic model coefficients, the HA ratio was mainly affected by the KOH concentration and operation time. However, all three operation variables influenced the TOC content of the HA.

As shown in Figure 1. C, D, E, F, the KOH concentration significantly influences the HA ratio and TOC content of the HA-MMWC, reaching optimum values (TOC content: 42.4%; HA ratio: 33.7%) at an intermediate KOH concentration (0.53 M). A similar behavior pattern was observed for the HA-compost (Figure 2. C, D, E, F). In this case, both responses reached optimum values of TOC content (38.1%) and HA ratio (76.6%) at a lower KOH concentration (0.25 M), probably due to the differences in the composition of the raw material. Lin et al. (2018) indicated that alkaline conditions promote humic material solubilization due to particle size reduction, making organic particles more accessible for hydrolysis. According to Ma et al. (2019), increasing the pH up to 10 promotes the breakdown of organic matter in the form of proteins, HS, and lignin-like compounds. However, an excessive increase in the alkaline solvent dose does not significantly improve humic acid recovery (Li et al., 2014). De Souza and Bragança (2018) reported that the optimal pH for HA extraction ranges from 10 to 11, which is closely related to the KOH concentration. Genuino et al. (2017) optimized the KOH concentration for HA extraction from municipal solid waste biochar, obtaining a concentration of 0.5 M.

The operation time is another critical variable for HA extraction, reaching maximum values at 24 h for both models (Figures 1 and 2. A, B, E, F), due to the completion of the organic matter solubilization. In addition, an extraction time of longer than 24 h did not lead to significant differences in the response variables and could negatively affect the HA ratio and TOC content of humic acids. HA could be decomposed and degraded over longer times (Rashid et al., 2023). The operation time obtained in this study is consistent with the range commonly used for alkaline extraction (12 – 24, h), using such raw materials as municipal solid waste biochar (Genuino et al., 2017), biowaste and manure compost (Zhang et al., 2022).

As for the temperature, the proposed model for HA-MMWC and the relative plots (Figure 1. A, B, C, D) did not show significant differences within the range studied (30 – 60, ºC). Therefore, the extraction can be performed at 30 ºC, as predicted by the statistical model. On the other hand, regarding the HA-compost model, the response surfaces obtained when maintaining the KOH constant (Figure 2. A-B), showed a different temperature for maximizing TOC content (60 ºC) and HA ratio

(30 ºC). However, since there were no significant differences between the results obtained for both temperatures, the model predicts that the optimal temperature to maximize both responses for the manure compost is 30 ºC. These results agree with other studies that reported HA extraction from different types of compost at 25 ºC – 30 ºC (Cristina et al., 2020; Genuino et al., 2017; Hanc et al., 2019; Wang et al., 2023).

3.3. Characteristics of humic acids

3.3.1. Elementary composition and C/N ratio

Table 1 shows the elementary composition of the humic acids (HA-MMWC and HA-compost) obtained under optimal conditions. The HA-MMWC notably reached a slightly higher concentration of organic compounds than the HA-compost (424 g/kg vs. 381 g/kg). It should be noted that the carbon content was lower than the values reported for humic acids, above 500 g/kg, produced from co-compost of fish waste and sugarcane bagasse (Aranganathan et al., 2019), or the organic fraction of municipal solid waste (Scaglia et al., 2013). However, they are within the typical TOC content range, as explained in section 3.2. On the other hand, analyzing the composition of total nitrogen in the HA, concentrations were similar (45.6 g/kg for MMWC vs. 39.3 g/kg for the manure compost) and within the order reported by other studies, ranging from 20 g/kg (Hanc et al., 2019) to 50 g/kg (Aranganathan et al., 2019).

The C/N ratio of HA was also determined (Table 4) and the results indicated that both samples presented comparable ratios (ranging from 9.3 to 9.7). These values were lower than those reported in previous studies. For example, Hanc et al.

(2019) obtained a ratio between 13 – 18 for HA from horse manure. Aranganathan et al. (2019) found 11.7 for HA from co-composting fish waste and sugarcane bagasse. The low C/N ratios indicate that the nitrogenous substances were incorporated into the HA structure (Hanc et al., 2019). A low C/N ratio is better for agriculture and land applications (Sutradhar and Fatehi, 2023).

Another crucial aspect concerns the differences in micronutrients and heavy metal composition between the compost and the HA. In general, the concentrations of micronutrients and heavy metals were lower in the HA, which may be due to the extraction and precipitation process. It is important to note that this trend does not apply to copper (Cu) or mercury (Hg) due to the sorption capacity of HA (Lee et al., 2022). If both HA are compared, the micronutrients and heavy metal concentrations present significant differences, mainly for Cu, Cr, Ni and Pb (Table 1). Several studies have demonstrated that the presence of improper materials in the composting of biowaste obtained from undifferentiated collection can increase the heavy metal concentration in the final product (Rodrigues et al., 2020). Moreover, HA have a high heavy metal sorption capacity, especially for the above mentioned metals (Lee et al., 2023). According to Lee et al. (2022), municipal solid waste presents a high heavy metal concentration on its surface. During the alkaline extraction, the HA can interact with the heavy metals in the compost forming complexes and chelates (Molaey et al., 2021). Regulation (EU) 2019/1009 establishes limit values for concentrations of Cd: 3 mg/kg; Hg: 1 mg/kg, Ni: 50 mg/kg, Pb: 120 mg/kg, As: 40 mg/kg, Cu: 600 mg/kg, and Zn: 1500 mg/kg. It should be noted that the heavy metal contents in both HA are below the regulatory limits.

3.3.2. Precipitation ratio

Regarding the precipitation ratio (Table 4), the value obtained for HA-compost was almost 3 times higher than that for HA-MMWC (56 vs. 144, $g_{HA}/kg_{initial\ solid}$). Lu et al. (2023) obtained 55 g/kg of HA from cow manure compost. Genuino et al. (2017) reached up to 188 g/kg using municipal solid waste biochar as the raw material. Doskočil et al. (2018) reported values from 30 g/kg to 114 g/kg for HA recovery from lignite. Scaglia et al. (2013) reported a ratio of 87.5 g/kg using municipal solid waste as the raw material. The precipitation ratio of HA is strongly related to the extraction procedure, the affinity of raw materials for alkaline extractants (Aranganathan et al., 2019), and the method selected for purifying the HA (Doskočil et al., 2018). The differences in the precipitation ratio may be related to the HA ratio obtained under optimal conditions (Table 3), which was higher for manure compost.

3.3.3. Spectroscopic characterization

3.3.3.1. Degree of Aromaticity and Humidification Index

Table 4 presents the results of the characterization of HA. Similar results were obtained when comparing the absorption ratios E2/E3 (2.1 – 2.2). This ratio commonly assesses the degree of aromaticity of the HA, presenting similar values (about 38%, Table 4). Results were comparable to those obtained by Aranganathan et al. (2019), who reported a degree of aromaticity of 38% for HA recovered from sugarcane bagasse compost. The ratio E4/E6 is related to the degree of aromaticity and the molecular weight of HA. The E4/E6 ratio depends mainly on the molecular weight of the sample and is correlated with the concentration of free radicals and contents of O, C, CO_2H, among other factors

(Chen et al., 1977). Low E4/E6 ratios are related to high molecular structures and more condensed aromatic groups (Boguta and Sokołowska, 2014). The ratio in the HA samples was 9.4 – 10.3 (Table 4). Similar values were obtained by Hanc et al. (2019) for HA from horse manure compost (E4/E6 ratio of 8.5). In both cases, the E2/E3 ratio is low (~ 2), and the E4/E6 ratio is high (~ 10), which indicates that the number of aliphatic groups is greater than that of the aromatic groups (Boguta and Sokolowska, 2014; de Melo et al., 2016; Li et al., 2013). This agrees with the degree of aromaticity (38%). He et al. (2008) concluded similar results for HA extracted from river sediments, obtaining a degree of aromaticity of around 30% – 40% and a degree of aliphaticity of around 60% – 70%.

3.3.3.2. Molecular weight

The molar specific absorption (ε_{280}) indicates the presence of aromatic compounds. Table 4 shows that the humic acids from manure compost have higher molar absorption than those from MMWC (542 vs. 373, L $(cm \cdot mol_{CO})^{-1}$). Absorption is directly related to the apparent molecular weight (Eq. 3). So, HA-compost has an average molecular weight of 2650 Da, whereas HA-MMWC has an average molecular weight of 1980 Da. If the MMWC and the manure compost contain impurities and aliphatic groups, as pointed out in the previous section, the molecular weight decreases. The values obtained (Table 4) are within the range of HA molecular weight distribution reported by Mackie et al. (2022), which varied from 1136 to 7180 Da for HA in rivers and municipal wastewater.

3.3.3.3. Kumada Index

The Kumada Index (ΔlogK) was calculated to identify the HA type. Both samples presented a ΔlogK > 0.8, confirming that the precipitated HA belongs to "type Rp"

(Kumada, 1987). Rp-type HA is assumed to be generated during the rotting of plant wastes and farmyard manures during the initial stage of humification in composting (Suzuki & Kumada, 1972). This would also explain the low molecular weight obtained and the low degree of aromaticity (38%) in both HA. Usually, Rp-type HA has a relatively low molecular weight compared to other types of humic acid, with a range typically between 1000 Da and 10000 Da (Kumada, 1987).

3.3.4. FTIR analysis

The Fourier transform infrared (FTIR) spectroscopy technique is commonly used to study the functional groups in humic acids (Tahiri et al., 2016). Figure 3 shows the FTIR spectra of HA recovered from MMWC and manure compost. The use of FTIR spectroscopy to identify the functional groups and structural characteristics of HA at various vibrations is widespread. From the 4000 cm^{-1} to 500 cm^{-1} range, aromatic substitutions, aliphatic structure, hydrogen bond areas, and O-containing groups may be confirmed by this analysis (Rashid et al., 2023, Wang et al., 2017). The peaks between 2800 cm^{-1} and 3000 cm^{-1} represent the vibration of methoxy groups relative to saturated aliphatic chains (C-H). The methyl group ($-CH_3$) stretching vibration linked to the oxygen atom may cause this peak. The carboxyl groups are commonly found in the FTIR spectrum as a broad band at 1700-1600 cm^{-1}. This band is caused by the carbonyl group's stretching vibration (C=O) and the carboxylate group's asymmetric stretching vibration (-COO-). The presence of carboxyl groups in humic acid is also verified by a strong peak at 1393 cm^{-1} caused by the carboxylate group's symmetric stretching vibration. Upon analysis of the peaks at 1710, 2850, and 2920 cm^{-1} (Figure 3), it can be observed that HA-MMWC contains a higher concentration of aliphatic and carboxylic functional groups than

HA-compost, as indicated by the more pronounced peaks. The low-intensity peaks at the 1700–1500 cm^{-1} region represent vibrations in aromatic structures and double bonds, with significant peaks relating to C=O linkages attached to the aromatic ring (C_6H_4) (~1600 cm^{-1}), N-H bending of amides and other nitro groups (~1550 cm^{-1}), and aromatic C=C bonds (1510 cm^{-1}). In addition, the peaks between 1180 and 1250 cm^{-1} indicate the deformation of carboxylic groups (C==O). The peaks at 1025 at 811 cm^{-1} indicate the C-O stretching due to the presence of polysaccharides and amines ($R-H_2$) of a different order (Aranganathan et al., 2019; Genuino et al., 2017; Rashid et al., 2023). Finally, the peaks below 700 cm^{-1} (e.g., 465 cm^{-1}) indicate that inorganic and mineral impurities are present in the solid (Hanc et al., 2019). HA-MMWC has more pronounced peaks in this region (Figure 3), so it contains more impurities than the HA-compost.

3.4. Tentative identification of organic contaminants by UHPLC-QTOF analysis

UHPLC-MS-QTOF analysis of both composts and HA allowed the tentative identification of 47 CECs (Table 5), which were determined based on the accurate mass data, an area over $1x10^5$, and the retention time (RT) (when the standard was available). These compounds were classified according to their primary use. When comparing the composts, it becomes evident that MMWC exhibits a higher concentration of CECs than manure compost, especially pesticides and drugs. This difference may stem from various factors, including the origin of the organic matter (municipal organic waste or cow manure, respectively) and the lack of testing for pesticides in commercial composts (O'Connor et al., 2022). However, manure compost presents a higher number of industrial chemicals, which are associated with medicines for animals, food moisturizers and plasticizers. Finally, both composts contain surfactants such as PEGs, which are usually additives in cosmetic products, personal hygiene and cleaning products. As far as the authors know, this is the first tentative identification and comparison of CECs in high and low-quality compost and in the HAs recovered from them. In this case, it becomes apparent that, except for surfactants, the presence of CECs in the HA diminishes drastically due to the recovery process. This implies that the recovery of HA higher-quality products than the original raw materials.

4. Conclusions

This study compared two types of compost, MMWC and cow manure compost, as raw materials to recover humic acids. The optimization of the process conditions resulted in 24 h and 30 ºC for both composts and a KOH concentration of 0.25 M for manure compost and 0.53 M for MMWC. Regarding the elementary composition, HA-MMWC and HA-compost presented similar concentrations of organic compounds and nutrients. HA-MMWC presented higher heavy metal impurities due to the chelating properties of humic acids, but the composition is within the legal requirements of the EU. Spectroscopic and FTIR analyses also effectively identified the differences between the recovered humic acids. The UHPLC-QTOF analysis identified 47 CECs in the composts and the HAs. MMWC exhibited a higher number of CECs (especially drugs and pesticides), but the HA recovery process can remove them, emphasizing the potential for producing high-quality organic products. In conclusion, this study confirms that humic acids can be successfully extracted from a low-quality compost, such as MMWC, with properties comparable to those extracted from a high-quality compost like cow manure compost. The findings demonstrate the potential of reusing low-quality composts to produce high-quality products such as humic acids. Future research could explore ways to increase process yield and to reduce the concentration of heavy metals and other impurities in humic acids to improve their quality for broader applications.

Acknowledgments

The authors acknowledge the financial support from the Programme of Cooperation INTERREG V-A Spain-Portugal (POCTEP) 2014-2020, European Regional Development Fund (EU-FEDER) (Project 0765_VALUECOMP_2_P). The support of Junta de Castilla y Leon is also acknowledged (UIC 320, CL-EI-2021-07). M. Fernández-Delgado also thanks Junta de Castilla y León for providing her postdoctoral grant (E-47-2019-0114592). The authors thank ITACyL for providing the manure compost. The authors also acknowledge Nora Carrera and Begoña Ribón, researchers at the Laboratory of Instrumental Techniques (University of Valladolid), for their assistance on UHPLC-MS-QTOF and ICP analysis.

References

Aranganathan, L., Rajasree, S.R.R., Suman, T.Y., Remya, R.R., Gayathri, S., Jayaseelan, C., Karthih, M.G., Gobalakrishnan, M., 2019. Comparison of molecular characteristics of Type A humic acids derived from fish waste and sugarcane bagasse co-compost influenced by various alkaline extraction protocols. Microchemical Journal 149. https://doi.org/10.1016/j.microc.2019.104038

Boguta, P., Sokołowska, Z., 2014. Statistical relationship between selected physicochemical properties of peaty-muck soils and their fraction of humic acids. Int Agrophys 28, 269–278. https://doi.org/10.2478/intag-2014-0017

Chen, L., Chen, Yaoning, Li, Y., Liu, Y., Jiang, H., Li, H., Yuan, Y., Chen, Yanrong, Zou, B., 2023. Improving the humification by additives during composting: A review. Waste Management 158, 93–106. https://doi.org/10.1016/j.wasman.2022.12.040

Chen, Y., Senesi, N., Schnitzer, M., 1977. Information Provided on Humic Substances by E4/E6 Ratios. Soil Science Society of America Journal 41, 352–358. https://doi.org/10.2136/sssaj1977.03615995004100020037x

Cheng, G., Niu, Z., Zhang, C., Zhang, X., Li, X., 2019. Extraction of humic acid from lignite by KOH-hydrothermal method. Applied Sciences (Switzerland) 9. https://doi.org/10.3390/app9071356

Chin, Y.-Pi., Aiken, G., 1994. Molecular Weight, Polydispersity, and Spectroscopic Properties of Aquatic Humic Substances. Environ, Sci. Technol 28, 1853–1858. https://doi.org/10.1021/es00060a015

Cristina, G., Camelin, E., Ottone, C., Fraterrigo Garofalo, S., Jorquera, L., Castro, M., Fino, D., Schiappacasse, M.C., Tommasi, T., 2020. Recovery of humic acids from anaerobic sewage sludge: Extraction, characterization and encapsulation in alginate beads. Int J Biol Macromol 164, 277–285. https://doi.org/10.1016/j.ijbiomac.2020.07.097

Das, T., Saikia, B.K., Baruah, B.P., Das, D., 2015. Characterizations of humic acid isolated from coals of two Nagaland Coalfields of India in relation to their origin.

Journal of the Geological Society of India 86, 468–474. https://doi.org/10.1007/S12594-015-0334-0/metrics

De Melo, B.A.G., Motta, F.L., Santana, M.H.A., 2016. Humic acids: Structural properties and multiple functionalities for novel technological developments. Materials Science and Engineering C 62, 967–974. https://doi.org/10.1016/j.msec.2015.12.001

De Souza, F., Bragança, S.R., 2018. Extraction and characterization of humic acid from coal for the application as dispersant of ceramic powders. Journal of Materials Research and Technology 7, 254–260. https://doi.org/10.1016/j.jmrt.2017.08.008

Doskočil, L., Burdíková-Szewieczková, J., Enev, V., Kalina, L., Wasserbauer, J., 2018. Spectral characterization and comparison of humic acids isolated from some European lignites. Fuel 213, 123–132. https://doi.org/10.1016/j.fuel.2017.10.114

European Commission, 2018a. Directive (EU) 2018/851 of the European Parliament and of the Council of 30 May 2018 amending Directive 2008/98/EC on waste [WWW Document].

European Commission, 2018b. Directive (EU) 2018/850 of the European Parliament and of the Council of 30 May 2018 amending Directive 1999/31/EC on the landfill of waste [WWW Document].

Ezzati, S., Ayaseh, A., Ghanbarzadeh, B., Heshmati, M.K., 2020. Pectin from sunflower by-product: Optimization of ultrasound-assisted extraction, characterization, and functional analysis. Int J Biol Macromol 165, 776–786. https://doi.org/10.1016/j.ijbiomac.2020.09.205

Fernández-Delgado, M., Amo-Mateos, E. del, Lucas, S., García-Cubero, M.T., Coca, M., 2020. Recovery of organic carbon from municipal mixed waste compost for the production of fertilizers. J Clean Prod 265, 121805. https://doi.org/10.1016/j.jclepro.2020.121805

Fernández-Delgado, M., Amo-Mateos, E., García-Cubero, M.T., Lucas, S., 2021. Phosphorus recovery from organic waste for its agronomic valorization : technical and economic evaluation. https://doi.org/10.1002/jctb.6926

Fernández-Delgado, M., del Amo-Mateos, E., Lucas, S., García-Cubero, M.T., Coca, M., 2022. Liquid fertilizer production from organic waste by conventional and microwave-assisted extraction technologies: Techno-economic and environmental assessment. Science of The Total Environment 806, 150904. https://doi.org/10.1016/j.scitotenv.2021.150904

Genuino, D.A.D., Bataller, B.G., Capareda, S.C., De Luna, M.D.G., 2017. Application of artificial neural network in the modeling and optimization of humic acid extraction from municipal solid waste biochar. J Environ Chem Eng 5, 4101–4107. https://doi.org/10.1016/j.jece.2017.07.071

Hanc, A., Enev, V., Hrebeckova, T., Klucakova, M., Pekar, M., 2019. Characterization of humic acids in a continuous-feeding vermicomposting system with horse manure. Waste Management 99, 1–11. https://doi.org/10.1016/j.wasman.2019.08.032

He, M., Shi, Y., Lin, C., 2008. Characterization of humic acids extracted from the sediments of the various rivers and lakes in China. Journal of Environmental Sciences 20, 1294–1299. https://doi.org/10.1016/S1001-0742(08)62224-X

Huculak-Mączka, M., Hoffmann, J., Hoffmann, K., 2018. Evaluation of the possibilities of using humic acids obtained from lignite in the production of commercial fertilizers. J Soils Sediments 18, 2868–2880. https://doi.org/10.1007/S11368-017-1907-x

Jing, T. fang, Zhang, D. xia, Jin, Y., Si, G. dong, Li, B. xing, Mu, W., Liu, F., 2023. Humic acid nature and compound structure together determine the capacity of soil to sorb Avermectin B1a and its derivatives. Chemical Engineering Journal 453. https://doi.org/10.1016/j.cej.2022.139914

Kanmaz, E.Ö., 2019. Humic acid formation during subcritical water extraction of food by-products using accelerated solvent extractor. Food and Bioproducts Processing 115, 118–125. https://doi.org/10.1016/j.fbp.2019.03.008

Katsumi, N., Yonebayashi, K., Okazaki, M., 2016. Effects of heating on composition, degree of darkness, and stacking nanostructure of soil humic acids. Science of The Total Environment 541, 23–32. https://doi.org/10.1016/j.scitotenv.2015.09.012

Kumada, K., 1987. Chemistry of Soil Organic Matter, 1st ed, Developments in Soil Science. Elsevier, Tokyo.

Kumada, K., Kawamura, Y., 1968. Viscosimetric characteristics of humic acid. Soil Sci Plant Nutr 14, 190–197. https://doi.org/10.1080/00380768.1968.10432764

Langdon, K.A., Chandra, A., Bowles, K., Symons, A., Pablo, F., Osborne, K., 2019. A preliminary ecological and human health risk assessment for organic contaminants in composted municipal solid waste generated in New South Wales, Australia. Waste Management 100, 199–207. https://doi.org/10.1016/j.wasman.2019.09.001

Lashermes, G., Barriuso, E., Houot, S., 2012. Dissipation pathways of organic pollutants during the composting of organic wastes. Chemosphere 87, 137–143. https://doi.org/10.1016/j.chemosphere.2011.12.004

Lee, H., Coulon, F., Beriro, D.J., Wagland, S.T., 2023. Increasing recovery opportunities of metal(loid)s from municipal solid waste via landfill leachate recirculation. Waste Management 158, 116–124. https://doi.org/10.1016/j.wasman.2023.01.011

Lee, H., Coulon, F., Wagland, S.T., 2022. Influence of pH, depth and humic acid on metal and metalloids recovery from municipal solid waste landfills. Science of the Total Environment 806, 150332. https://doi.org/10.1016/j.scitotenv.2021.150332

Li, H., Ding, S., Yuan, J., 2023. Extraction of Humic Acids from Lignite and Its Use as a Biochar Activator. ACS Omega 8, 12206–12216. https://doi.org/10.1021/acsomega.2c08192

Li, H., Li, Y., Zou, S., Li, C., 2014. Extracting humic acids from digested sludge by alkaline treatment and ultrafiltration. J Mater Cycles Waste Manag 16, 93–100. https://doi.org/10.1007/s10163-013-0153-6

Li, M. tang, Zhao, L. po, Zhang, J. jing, 2013. Effect of Temperature, pH and Salt on Fluorescent Quality of Water Extractable Organic Matter in Black Soil. J Integr Agric 12, 1251–1257. https://doi.org/10.1016/S2095-3119(13)60436-0

Lin, L., Li, R. hong, Li, X. yan, 2018. Recovery of organic resources from sewage sludge of Al-enhanced primary sedimentation by alkali pretreatment and acidogenic fermentation. J Clean Prod 172, 3334–3341. https://doi.org/10.1016/j.jclepro.2017.11.199

Lu, Q., Jiang, Z., Feng, W., Yu, C., Jiang, F., Huang, J., Cui, J., 2023. Exploration of bacterial community-induced polycyclic aromatic hydrocarbons degradation and humus formation during co-composting of cow manure waste combined with contaminated soil. J Environ Manage 326, 116852. https://doi.org/10.1016/j.jenvman.2022.116852

Ma, S., Hu, H., Wang, J., Liao, K., Ma, H., Ren, H., 2019. The characterization of dissolved organic matter in alkaline fermentation of sewage sludge with different pH for volatile fatty acids production. Water Res 164. https://doi.org/10.1016/j.watres.2019.114924

Mackie, A.L., Park, Y., Gagnon, G.A., 2022. Calibration of high performance size exclusion chromatography (HPSEC) for molecular weight estimation of aquatic humic substances. J Environ Chem Eng 10, 108913. https://doi.org/10.1016/j.jece.2022.108913

Molaey, R., Yesil, H., Calli, B., Tugtas, A.E., 2021. Influence of volatile fatty acids in anaerobic bioleaching of potentially toxic metals. J Environ Manage 285, 112118. https://doi.org/10.1016/j.jenvman.2021.112118

Moreda-Piñeiro, A., Bermejo-Barrera, A., Bermejo-Barrera, P., 2004. New trends involving the use of ultrasound energy for the extraction of humic substances from marine sediments. Anal Chim Acta 524, 97–107. https://doi.org/10.1016/j.aca.2004.03.096

Novák, J., Kozler, J., Janoš, P., Čežíková, J., Tokarová, V., Madronová, L., 2001. Humic acids from coals of the North-Bohemian coal field - I. Preparation and characterization. React Funct Polym 47, 101–109. https://doi.org/10.1016/S1381-5148(00)00076-6

O'Connor, J., Mickan, B.S., Siddique, K.H.M., Rinklebe, J., Kirkham, M.B., Bolan, N.S., 2022. Physical, chemical, and microbial contaminants in food waste management for soil application: A review. Environmental Pollution 300. https://doi.org/10.1016/j.envpol.2022.118860

Omar, L., Ahmed, O.H., Jalloh, M.B., Muhamad, N., Majid, A., Byrne, K., 2021. Rice Husk Compost Production and Use in Mitigating Ammonia Volatilization from Urea. Sustainability 13, 1832. https://doi.org/10.3390/su13041832

Ore, O.T., Adeola, A.O., Fapohunda, O., Adedipe, D.T., Bayode, A.A., Adebiyi, F.M., 2023. Humic substances derived from unconventional resources: extraction, properties, environmental impacts, and prospects. Environmental Science and Pollution Research 30, 59106–59127. https://doi.org/10.1007/s11356-023-26809-5

Raposo, J.C., Villanueva, U., Olivares, M., Madariaga, J.M., 2016. Determination of humic substances in sediments by focused ultrasound extraction and ultraviolet visible spectroscopy. Microchemical Journal 128, 26–33. https://doi.org/10.1016/j.microc.2016.04.004

Rashid, T., Sher, F., Jusoh, M., Joya, T.A., Zhang, S., Rasheed, T., Lima, E.C., 2023. Parametric optimization and structural feature analysis of humic acid extraction from lignite. Environ Res 220, 115160. https://doi.org/10.1016/j.envres.2022.115160

Rezaei Adaryani, A., Keen, O., 2022. Occurrence of pharmaceuticals and plasticizers in leachate from municipal landfills of different age. Waste Management 141, 1–7. https://doi.org/10.1016/j.wasman.2022.01.023

Ribeiro, R.S., Rodrigues, R.O., Silva, A.M.T., Tavares, P.B., Carvalho, A.M.C., Figueiredo, J.L., Faria, J.L., Gomes, H.T., 2017. Hybrid magnetic graphitic nanocomposites towards catalytic wet peroxide oxidation of the liquid effluent from a mechanical biological treatment plant for municipal solid waste. Appl Catal B 219, 645–657. https://doi.org/10.1016/j.apcatb.2017.08.013

Rodrigues, L.C., Puig-Ventosa, I., López, M., Martínez, F.X., Ruiz, A.G., Bertrán, T.G., 2020. The impact of improper materials in biowaste on the quality of compost. J Clean Prod 251, 119601. https://doi.org/10.1016/j.jclepro.2019.119601

Sarlaki, E., Sharif Paghaleh, A., Kianmehr, M.H., Asefpour Vakilian, K., 2019. Extraction and purification of humic acids from lignite wastes using alkaline treatment and membrane ultrafiltration. J Clean Prod 235, 712–723. https://doi.org/10.1016/j.jclepro.2019.07.028

Scaglia, B., Tambone, F., Adani, F., 2013. Cr(VI) reduction capability of humic acid extracted from the organic component of municipal solid waste. Journal of Environmental Sciences 25, 487–494. https://doi.org/10.1016/S1001-0742(12)60078-3

Shao, Y., Bao, M., Huo, W., Ye, R., Liu, Y., Lu, W., 2022. Production of artificial humic acid from biomass residues by a non-catalytic hydrothermal process. J Clean Prod 335, 130302. https://doi.org/10.1016/j.jclepro.2021.130302

Stehouwer, R., Cooperband, L., Rynk, R., Biala, J., Bonhotal, J., Antler, S., Lewandowski, T., Nichols, H., 2022. Compost characteristics and quality. The Composting Handbook 737–775. https://doi.org/10.1016/B978-0-323-85602-7.00012-1

Stevenson, F.J., 1994. Humus Chemistry: Genesis, Composition, Reactions, 2nd ed. Wiley & Sons, Inc, Canada.

Sutradhar, S., Fatehi, P., 2023. Latest development in the fabrication and use of lignin-derived humic acid. Biotechnology for Biofuels and Bioproducts 16, 38. https://doi.org/10.1186/s13068-023-02278-3

Suzuki, M., Kumada, K., 1972. Several properties of rp type humic acid. Soil Sci Plant Nutr 18, 53–64. https://doi.org/10.1080/00380768.1972.10433275

Tahiri, A., Richel, A., Destain, J., Druart, P., Thonart, P., Ongena, M., 2016. Comprehensive comparison of the chemical and structural characterization of landfill leachate and leonardite humic fractions. Anal Bioanal Chem 408, 1917–1928. https://doi.org/10.1007/S00216-016-9305-6

Tortosa, G., Alburquerque, J.A., Bedmar, E.J., Ait-Baddi, G., Cegarra, J., 2014. Strategies to produce commercial liquid organic fertilisers from “alperujo” composts. J Clean Prod 82, 37–44. https://doi.org/10.1016/j.jclepro.2014.06.083

Wang, C.F., Fan, X., Zhang, F., Wang, S.Z., Zhao, Y.P., Zhao, X.Y., Zhao, W., Zhu, T.G., Lu, J.L., Wei, X.Y., 2017. Characterization of humic acids extracted from a lignite and interpretation for the mass spectra. RSC Adv 7, 20677–20684. https://doi.org/10.1039/C7RA01497J

Wang, R., Li, D., Zheng, G., Cao, Z., Deng, F., 2023. Co-production of water-soluble humic acid fertilizer and crude cellulose from rice straw via urea assisted artificial humification under room temperature. Chemical Engineering Journal 455, 140916. https://doi.org/10.1016/j.cej.2022.140916

Zbytniewski, R., Buszewski, B., 2005. Characterization of natural organic matter (NOM) derived from sewage sludge compost. Part 1: chemical and spectroscopic properties. Bioresour Technol 96, 471–478. https://doi.org/10.1016/j.biortech.2004.05.018

Zhang, J., Li, X., Xu, H., Zhang, W., Feng, X., Yao, Y., Ma, Y., Su, L., Ren, S., Li, S., 2023. Removal of Cd2+, Pb2+ and Ni2+ from water by adsorption onto magnetic composites prepared using humic acid from waste biomass. J Clean Prod 411, 137237. https://doi.org/10.1016/j.jclepro.2023.137237

Zhang, W., Zhao, Y., Lu, Q., Feng, W., Wang, L., Wei, Z., 2022. Evaluating differences in humic substances formation based on the shikimic acid pathway during different materials composting. Bioresour Technol 364, 128060. https://doi.org/10.1016/j.biortech.2022.128060

Table 1. Composition of MMWC, manure compost and the recovered humic acids.

Parameters[a]	**Units**	**MMWC**	**Manure compost**	**HA-MMWC**	**HA-Compost**
Organic compounds					
TC	g/kg	285.1	279.1	427.6	384.1
TOC	g/kg	263.8	270.1	424.3	380.9
Principal and secondary nutrients					
TN	g/kg	21.7	31.3	45.6	39.3
P	g/kg	4.4	4.5	0.3	1.1
K	g/kg	8.0	18.1	81.7	109
Ca	g/kg	56.0	46.5	1.5	5.7
Mg	g/kg	7.6	11.4	0.6	1.0
Na	g/kg	4.7	1.2	2.0	1.6
Micronutrients and heavy metals					
Fe	g/kg	9.9	3.5	2.0	0.5
As	mg/kg	2.5	1.5	0.8	0.9
Cu	mg/kg	101	15	418	43
Mn	mg/kg	169	155	13	16
Zn	mg/kg	279	78	47	19
Pb	mg/kg	54.4	2.5	8.0	0.9
Total Cr	mg/kg	106	13.4	9.2	1.3
Ni	mg/kg	46.1	5.8	7.0	2.8
Hg	mg/kg	0.16	0.05	0.5	0.2
Cd	mg/kg	0.8	0.05	0.1	0.03

Note: Data are shown as the mean value with less than 5% of relative error.

Table 2. Central Composite Design (CCD): HA ratio and TOC content obtained under different extraction conditions from MMWC and manure compost.

Run	X_1: Temperature (ºC)	X_2: Time (h)	X_3: KOH (M)	Y1: HA ratio (% HA in extract)		Y2: TOC content (% TOC in HA)	
				MMWC	Manure Compost	MMWC	Manure Compost
1	30	4	0.25	9.5	67.9	48.3	30.6
2	60	4	0.25	10.5	75.3	32.3	40.2
3	30	24	0.25	23.8	77.1	63.5	37.7
4	60	24	0.25	22.0	77.8	52.3	44.4
5	30	4	1	19.1	54.4	47.7	19.9
6	60	4	1	29.4	67.2	45.2	22.5
7	30	24	1	32.2	69.2	49.1	23.8
8	60	24	1	28.3	70.0	41.2	28.9
9	45	0	0.5	0.0	0.0	0.0	0.0
10	45	36	0.5	27.4	75.0	37.5	36.5
11	45	12	0	2.2	21.5	22.0	30.0
12	45	12	1.25	29.1	61.4	46.4	19.8
13	45	12	0.5	24.7	70.1	45.8	29.2
14	45	12	0.5	26.0	70.5	45.5	29.7
15	45	12	0.5	27.2	71.9	47.2	30.8
16	45	12	0.5	25.3	70.8	49.8	29.3
17	45	12	0.5	25.0	69.2	44.1	28.5
18	45	12	0.5	22.4	69.5	50.3	29.5
19	45	12	0.5	26.4	71.1	48.9	31.9
20	45	12	0.5	22.8	72.1	45.4	32.3
21	45	12	0.5	22.9	72.0	46.5	31.4

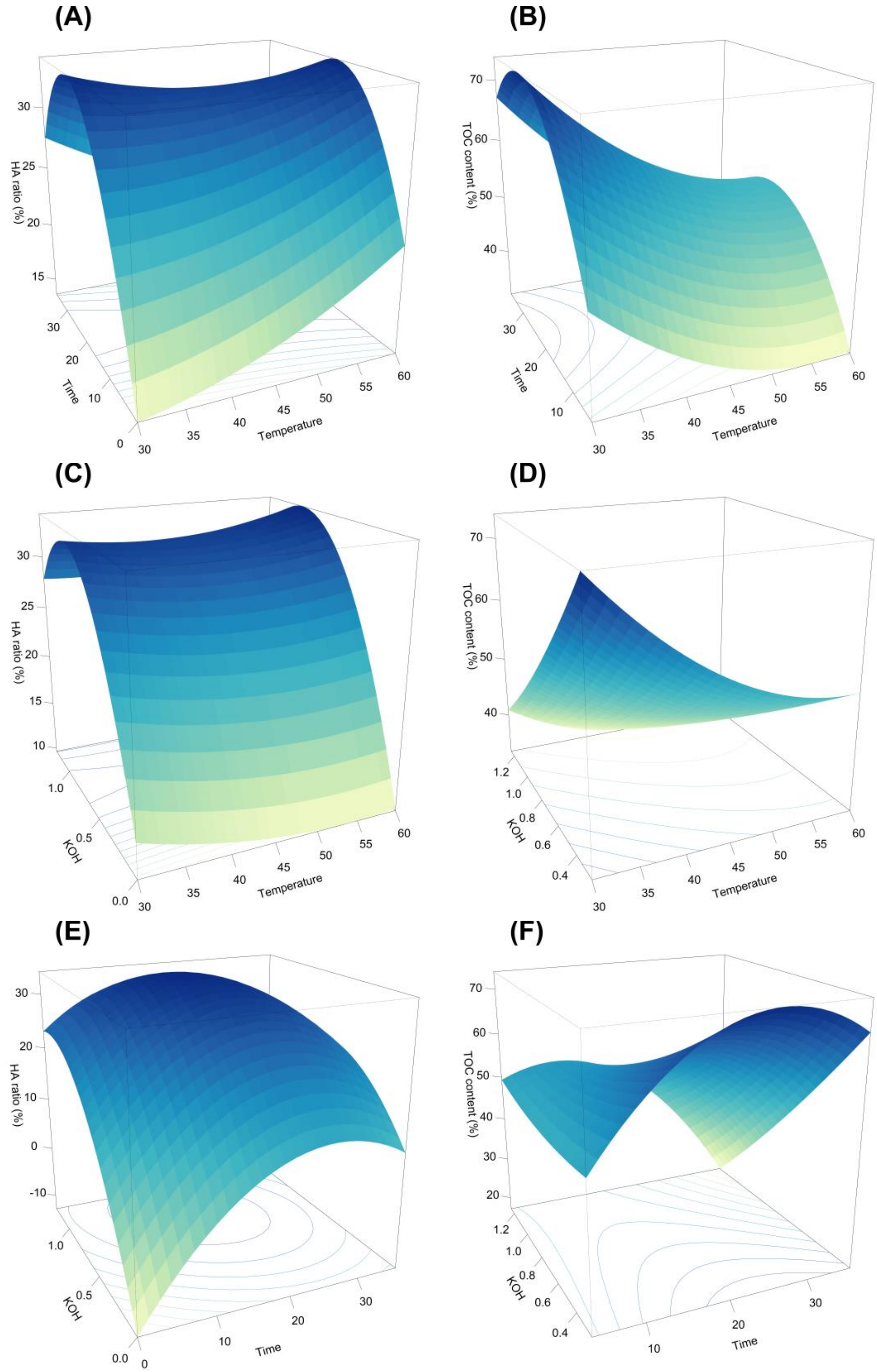
Note: Data are shown as the mean value with less than 5% of relative error.

MMWC: Municipal Mixed Waste Compost: Low-Quality Compost

Manure compost: Cow manure Compost: High-Quality Compost

Table 3. Analysis of variance, optimal operation conditions, predicted and observed results.

	MMWC	**Manure compost**
Analysis of Variance		
R^2	0.9261	0.9787
Adjusted R^2	0.8595	0.9674
Lack of Fit (F-Value)	12.76	0.93
F-Value	13.93	86.69
P-Value	< 0.001	< 0.001
Optimal Operation Conditions		
X1: Temperature (ºC)	30	30
X2: time (h)	24	24
X3: KOH (M)	0.53	0.25
Predicted Results		
TOC content	45.5	42.0
HA ratio	32.6	77.2
Observed Results		
TOC content	42.4	38.1
HA ratio	33.7	76.6



(A)
HA ratio (%)
Time
Temperature
(B)
TOC content (%)
Time
Temperature
(C)
HA ratio (%)
KOH
Temperature
(D)
TOC content (%)
KOH
Temperature
(E)
HA ratio (%)
KOH
Time
(F)
TOC content (%)
KOH
Time

Figure 1. Response surface plots showing the effect of operating variables on the HA ratio (%) and TOC content (%) for the MMWC. (A) and (B): the KOH was constant at 0.53 M. (C) and (D): the time was constant at 24 h. (E) and (F): the temperature was constant at 30 ºC.

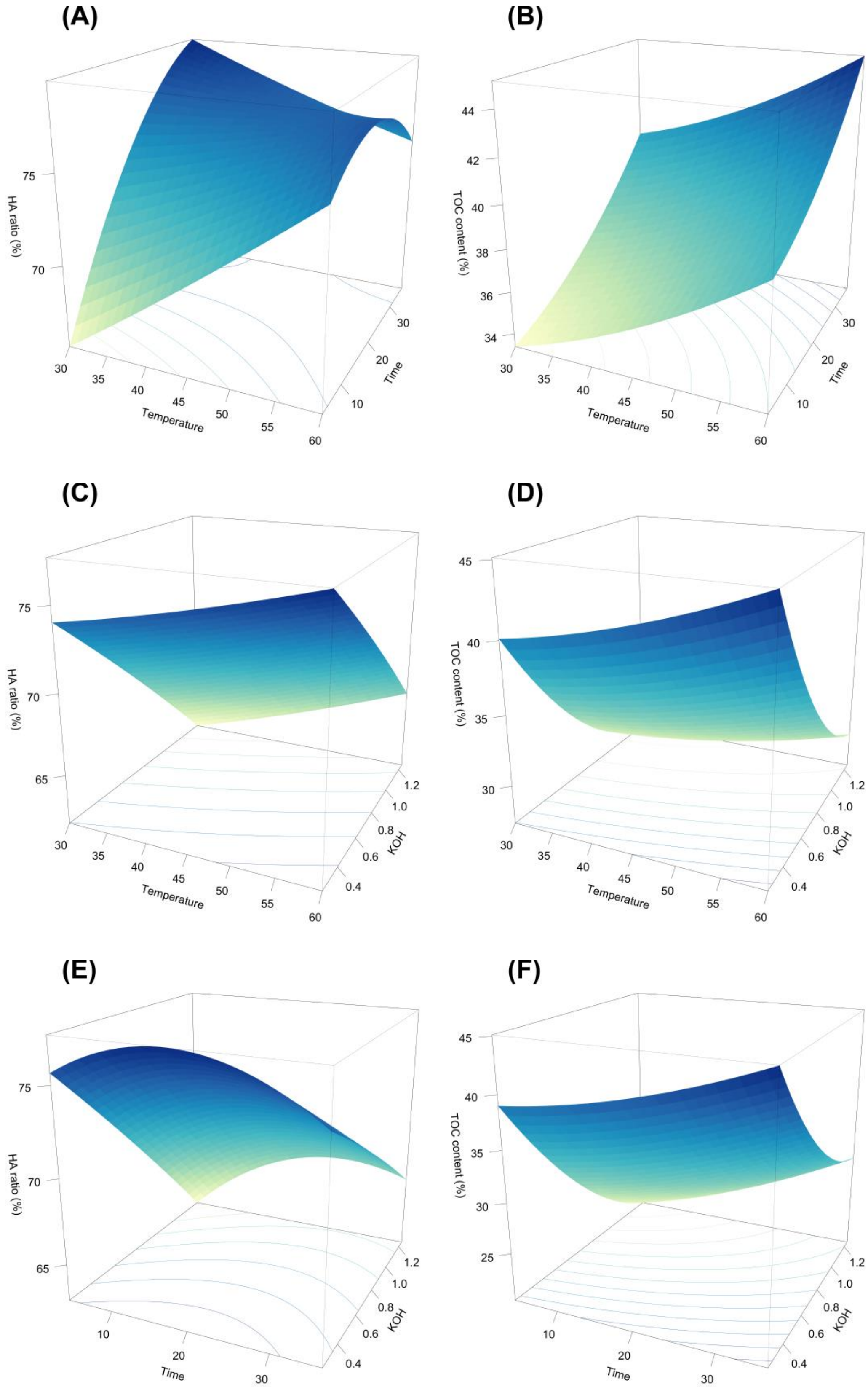

(A)
HA ratio (%)
70
75
30 35 40 45 50 55 60
Temperature
10 20 30
Time
(B)
TOC content (%)
34 36 38 40 42 44
30 35 40 45 50 55 60
Temperature
10 20 30
Time
(C)
HA ratio (%)
65 70 75
30 35 40 45 50 55 60
Temperature
0.4 0.6 0.8 1.0 1.2
KOH
(D)
TOC content (%)
30 35 40 45
30 35 40 45 50 55 60
Temperature
0.4 0.6 0.8 1.0 1.2
KOH
(E)
HA ratio (%)
65 70 75
10 20 30
Time
0.4 0.6 0.8 1.0 1.2
KOH
(F)
TOC content (%)
25 30 35 40 45
10 20 30
Time
0.4 0.6 0.8 1.0 1.2
KOH

Figure 2. Response surface plots showing the effect of operating variables on the HA ratio (%) and TOC content (%) for the manure compost. (A) and (B): the KOH was constant at 0.25 M. (C) and (D): the time was constant at 24 h. (E) and (F): the temperature was constant at 30 ºC.

Table 4. Physical properties measured for the HA obtained from both composts.

Properties	**Units**	**HA-MMWC**	**HA-Compost**
Precipitation ratio	$g_{HA}/kg_{initial\ solid}$	56	144
C/N		9.3	9.7
Molecular weight	Da	1980	2650
Degree of Aromaticity	%	38.4	37.8
ΔlogK		0.97	1.1
ε_{280}	$L\ (cm \cdot mol_{CO})^{-1}$	373	542
E2/E3		2.1	2.2
E4/E6		9.4	10.3

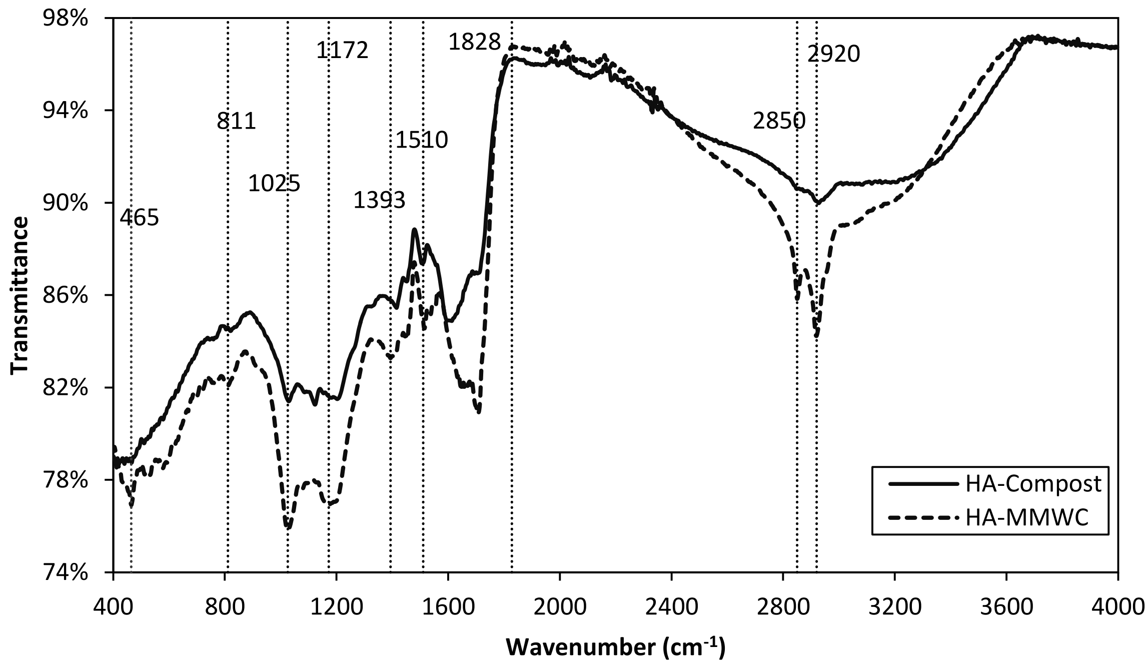


Figure 3. FTIR spectra of HA obtained from MMWC and cow manure compost.

Table 5. Compounds identified in the composts and the precipitated humic acids.

Compound	RT (min)	MMWC	HA-MMWC	Manure Compost	HA-Compost
Drugs and Pharmaceuticals					
Adenosine	0.72	-	-	+	-
2-Piperidinone	1.16	-	-	+	-
8-Hydroxyquinoline	5.92	+	-	-	-
Acetaminophen	1.47	+	-	-	-
Acetophenone	0.69	-	-	+	-
Amphetamine	3.09	+	-	-	-
Benzoylecgonine	7.47	+	-	-	-
Caffeine	6.53	+	-	-	-
Diethyl Tartrate	2.96	+	-	-	-
Ibuprofen lysine	3.95	-	-	+	-
Indoleacrylic acid	1.95	+	-	+	-
Meprylcaine	9.79	+	-	-	-
Metformin	8.92	+	-	-	-
Molsidomine	5.89	+	-	-	-
Morphine-d6	9.79	+	-	-	-
Naproxen	10.72	+	-	+	-
Nicotine	0.64	+	-	-	-
Pivagabine	7.89	+	-	-	-
Salmeterol	12.02	-	-	+	-
Stachydrine hydrochloride	0.57	+	-	-	-
Ursodeoxycholic acid	12.56	+	-	-	-
Industrial Chemicals					
3-Chloro-2,2',4-trifluorobiphenyl	0.41	-	-	+	-
4-(Trifluoromethyl)benzyl cyanide	11.75	-	-	+	-
4-Chlorotetrafluorophenol	0.41	-	-	+	-
Decylurea	6.58	+	-	-	-
Dioctyl phthalate (DNOP)	14.07	-	-	+	-
N-Isopropylsalicylamide	3.95	+	-	-	-
Pesticides, Fungicides and Herbicides					
Benalaxyl	11.71	+	-	-	-
Boscalid	10.92	-	-	+	-
Butylate	8.86	+	-	-	-
Carbendazim	3.48	+	-	-	-
Diphenylamine	5.62	+	-	+	-
Dodine	12.83	+	-	-	-
Fenpropimorph	13.48	+	-	-	-
Formetanate	8.59	+	-	-	-

Inabenfide	12.96	+	-	-	-
Metrafenone	11.92	-	-	+	-
Terbutryn	7.04	+	-	-	-
Surfactants					
Acetyl tributyl citrate	12.61	+	-	-	-
Dioctyl phthalate	14.07	+	-	-	-
Lauramide	12.16	+	-	+	-
PEG-10mer Ammonium adduct	8.47	+	+	+	+
PEG-11mer Ammonium adduct	8.65	+	+	+	+
PEG-12mer Ammonium adduct	8.82	+	+	+	+
PEG-7mer Ammonium adduct	7.62	+	+	+	+
PEG-8mer Ammonium adduct	7.99	+	+	+	+
PEG-9mer Ammonium adduct	8.25	+	+	+	+

Note: Positive "+" means that the chemical was detected in the solid.

Negative "-"means not detected in the solid.

Graphical Abstract