

Recovery of organic carbon from municipal mixed waste compost for the production of fertilizers

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DETAILED RESPONSE TO REVIEWERS

Ms. Ref. No.: JCLEPRO-D-19-10400R1

Title: Recovery of organic carbon from municipal mixed waste compost for the production of fertilizers

Dear reviewers,

The authors really appreciate the feedback from the reviewers. The authors have assessed the comments and revised carefully the manuscript to clarify all the questions raised. Format and presentation of the paper have been improved according to the suggestions of the reviewer #5. The detailed answers to the comments are summarized below. All changes in the text are highlighted in red in the revised version.

Reviewer #4

1. The paper is correct, but, in my view, the novelty is marginal.

ANSWER:

The paper propose a process for the valorization of MMWC. Organic carbon and nitrogen were extracted to produce an organo-mineral fertilizer in compliance with European Regulations. After extraction, the composition of the spent solid residue shows that it could be further valorized to produce biochar or to satisfy heating needs, in the framework of circular economy. In this way, MMWC can be successfully recycled, minimizing waste, the amount taken to landfill and the dependence of fossil based products. As far as we know, this is the first study that evaluate the valorization of an abundant waste such as MMWC.

ACTION:

See Introduction Lines 125-126. The sentence in the previous version "To the best of our knowledge, there are no previous works related to the production of value-added organic fertilizers from MMWC" was modified as suggested by reviewer #5.

Reviewer #5

1. In the Introduction, you should link your keywords, e.g. organic carbon recovery, organic waste recycling, and circular economy much stronger. Suggest to highlight the contribution of your study and emphasize/link clearer the valorization of the MMWC in approaching circular economy in the Conclusion as well.

ANSWER:

Thank you for the suggestion. In the Introduction, we describe the importance of the recycling of organic wastes for agriculture (L 97-99). Some relevant references about the recovery of organic carbon and humic substances from organic waste are also described (L 101-112).

ACTION:

Introduction. Lines 122-123 have been written to emphasize on the objective of the paper: recover organic matter and nitrogen from MMWC to obtain an organic extract that could be used in agriculture and characterize the spent solid to propose a complete valorization of the MMWC within the framework of circular economy.

Conclusion. Lines 560-562 were added.

Graphical abstract was also modified to highlight the contribution of the study to recycling of organic waste and circular economy.

2. Please provide the full terms for the first time you present the abbreviations and make sure all the abbreviations are used consistently after first defined. This also applies to chemical formula and elements, e.g. KOH, HNO₃, NaOH, K, Cd, Hg, etc. Please check the whole manuscript.

ANSWER:

The authors appreciate the reviewer recommendation. We have carefully checked the full terms and the abbreviations thoroughly to the manuscript to improve consistency.

ACTIONS:

All changes made have been highlighted in red in the text. Some examples are given below:

Line 34: potassium hydroxide (KOH)

Line 35-36: mixed municipal waste compost (MMWC)

Line 54: carbon dioxide (CO₂)

Line 59-60: 13 millions of tons (Mt)

Line 60: European Union (EU)

Line 68: carbon/nitrogen (C/N)

Line 106: sodium hydroxide (NaOH) 1 M and hydrochloric acid (HCl) 6 M

Line 117: solid:liquid (S:L) ratio

Line 118: organic matter (OM)

Line 185: nitric acid (HNO₃)

Line 206: sulfuric acid (H₂SO₄)

Lines 248-249: nitrogen (TN), phosphorus (P) and potassium (K)

Line 288-289: phosphorus pentoxide (P₂O₅)

Line 460: potassium oxide (K₂O)

3. It will be good to further improve the English/presentation. Please check capitalization, as some words should not be capitalized. Inconsistent spacing between a value and unit should also be revised for a more polished paper.

ANSWER:

We have checked capitalization, inconsistent spacing and all suggestions marked by the reviewer throughout the manuscript.

ACTION:

All changes are highlighted in red in the manuscript. Some examples are given below.

Space between a value and the symbol (%) was deleted throughout the manuscript (e.g. L 38: 6.9% w/w, 47.6%).

Reviewer #5 suggested add a separator for the numbers above 1,000 in the manuscript, tables and figures (see L46: 1,600 k€).

Capitalization was checked and corrected (e.g. L51: *Soil organic carbon*. L191-192: *The relative seed germination (RSG) and the relative root growth (RRG)*).

Complete description of the equipments (model name, company, country) is now provide, as suggested by the reviewer 5 in the text (e.g. L137: *Incubator Shaker ES-60, Miulab, China* L138: *Centrifuge Sorvall legend RT+, Thermo Fisher Scientific, Spain*).

4. Line 289-290, 325-327, 359-360. The data is not shown in Table? Not clear, please clarify.

ANSWER:

Phosphorus concentration is not shown in the Table 2 because recovery at alkaline pH is low.

ACTION:

In the lines 290, 326, and 360, it has been added the following sentence: "*data not shown*"

5. Line 404, 407, 435. Did you mean TKN? Please revise.

ANSWER:

The authors highly appreciate the reviewer revision. We have corrected abbreviations.

ACTION:

Incorrect abbreviations of TKN have been corrected (TNK, NKT were changed by TKN)

6. Table 4. Suggest to remove the % symbol for the values in the table as the unit is already defined in the first row; i.e. Contribution (%)

ANSWER:

The authors agree with the reviewer. We have removed the % symbol for the values.

ACTION:

See Table 4. Changes are highlighted in red.

7. Figure caption - is it placed above or below the figure? Please check.

ANSWER:

The figure caption is usually placed below the figure. In any case, regarding figure captions and figures, the Authors Information guide points out that:

Figure captions

Ensure that each illustration has a caption. Supply captions separately, not attached to the figure. A caption should comprise a brief title (not on the figure itself) and a description of the illustration. Keep text in the illustrations themselves to a minimum but explain all symbols and abbreviations used.

Submit each illustration as a separate file.

ACTION:

In order to follow the Instructions of the journal, figures and captions were provided in separate files.

8. Please check the overall manuscript format for JCLEPRO (citation, labelling figures/tables, references, etc.).

ANSWER:

The authors have checked the manuscript in order to verify that the format is correct.

ACTION:

Figures and captions were removed and provided in separate files.

Regarding references, the following corrections were made:

Mosca, F., Hidalgo, G.I., Villasante, J., Almajano, M.P., 2018. Continuous or batch solid-liquid extraction of antioxidant compounds from seeds of Sterculia apetala plant and kinetic release study. Molecules 23, 1-12. <https://doi.org/10.3390/molecules23071759>

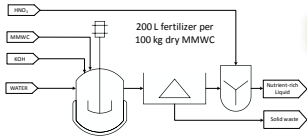
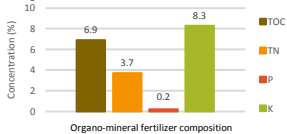
Ozkaynak Kanmaz was replaced by Kanmaz, E.O. in the manuscript and References section.

1 HIGHLIGHTS

- 2 • Recycling of mixed municipal waste compost through the production of
3 fertilizers.
- 4 • Alkaline extraction is suitable for the recovery of organic carbon.
- 5 • Humic acids accounted 47.6% of organic carbon of the extracted liquid.
- 6 • Extracts comply with EU requirements as liquid organo-mineral fertilizers.
- 7 • An economic study proved the viability of the valorization process.

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Graphical Abstract



Block diagram for the industrial plant to produce fertilizer



Germination test of Garden cress (*Lepidium sativum*)



Mixed municipal waste compost (MMWC)

1 **Recovery of organic carbon from municipal mixed waste compost for the**
2 **production of fertilizers**

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Word count: 8119

Abstract

Nowadays, the extensive use of inorganic fertilizers has increased the salinity of soil and decreased optimal assimilation of nutrients by crops. Organic carbon is basic for controlling the nutrient level in soil and nutrient assimilation by plants. The objective of this study was to develop a process for recovering organic carbon using compost from mixed municipal waste as raw material. The use of fertilizers from organic residues could replace mineral fertilizers, contributing to resources preservation and recycling of organic matter. In this way, a Taguchi experimental design was proposed to select the most suitable operating conditions for recovering organic carbon from the organic residue. The variable factors were the solid:liquid ratio, type of solvent, extraction time, and particle size. The optimum extraction conditions were: solid:liquid ratio 1:2.5, 1 M potassium hydroxide (KOH), 72 h, and particle size > 1 mm. Subsequent experiments concluded that separating the mixed municipal waste compost (MMWC) by fractions of different particle sizes before extraction process is not recommended. Under these conditions, the total organic carbon concentration in the extract was 6.9% w/w, of which the content of humic acids was 47.6%. On the other hand, the extract complies with the legal requirements of Regulation (EU) 2019/1009 for fertilizing products regarding composition. Germination tests were carried out to analyze the phytotoxic effects of organic extracts. Finally, a preliminary economic study showed the viability for a production plant with a capacity of 300 kg/h of MMWC. The production of liquid fertilizer was 200 L per 100 kg of dry compost, and the estimated sale price to

obtain economic benefits was 1 €/L of fertilizer for a plant whose total investment cost was 1,600 k€.

Keywords

Organic carbon recovery; mixed municipal waste compost; liquid fertilizer; organic waste recycling; circular economy

1. Introduction

Soil organic carbon (SOC) is an essential compound for agriculture. SOC improves physical soil conditions, nutrient retention, bacterial diversity, and fertility. Moreover, SOC has a primal relevance for the mitigation of global warming. Small losses in SOC significant impacts on carbon dioxide (CO₂) concentration in the atmosphere (Matschullat et al., 2018). A typical organic carbon source is the application of humic substances, which can be used in agricultural lands to enhance plant growth and water holding capacity as well as for their bactericidal and fungicidal properties (Kanmaz, 2019).

Agriculture is currently monopolized by chemical fertilizers. Around 13 millions of tons (Mt) of inorganic fertilizers were consumed in the European Union (EU) in 2017 (Eurostat, 2019a). Adverse effects of excessive or inappropriate chemical fertilization are the rapid nutrition of plants, contamination of surface and groundwater resources (Liang et al., 2013) and emissions of greenhouse gases (Zhu et al., 2019). Intensive agriculture can increase soil salinity, especially in arid and semiarid areas. Salinization is responsible for higher erosion rates, reduced microbial and enzymatic activities, and the consequent soil degradation. These circumstances aggravate SOC depletion

(Daliakopoulos et al., 2016). Changes in the carbon/nitrogen (C/N) ratio could modify remarkably soil microbial diversity (Sepehri and Sarrafzadeh, 2019).

The use of organic and organo-mineral fertilizers, mainly through the recycling of crop residues, manure, or other biomasses, is emerging to overcome the drawbacks of inorganic fertilizers. The development of organic fertilizers that do not depend on the availability of mineral resources or energy-intensive processes and based on the use of renewable materials is a significant advance towards circular economy that reincorporates waste materials into the production cycle (Paungfoo-Lonhienne et al., 2019).

The EU produced nearly 250 Mt of municipal solid waste per year, 486 kg per capita (Eurostat, 2019b). Mechanical biological treatment (MBT) is the most widespread alternative for processing mixed municipal waste. In 2017, there were about 570 MBT plants throughout Europe, with a treatment capacity of 55 Mt (Ecoprog, 2017). The organic fraction of municipal waste recovered in MBT is usually stabilized through composting. The resulting stabilized residue is of low quality, and the application of the European regulations will restrict its use in agriculture as an end-product fertilizer (European Commission, 2018a). So, if no agricultural use is envisaged, such bad quality compost will be disposed of in landfills (Ribeiro et al., 2017). Landfill restrictions will be significantly strengthened to reflect the EU's ambition to shift to a circular economy. By 2035 the amount of municipal waste landfilled should be lower than 10% of the total quantity (by weight) generated (European Commission, 2018b). Thus, the development of alternatives for valorization of MMWC from MBT plants is an essential societal challenge.

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92 Although MMWC can be used as cover material for landfills and embankments,
93 the excess is finally dumped. The average composition of total carbon (TC) in
94 MMWC, ranging from 280 to 380 g/kg dry matter (DM) (Lin et al., 2018a),
95 makes it suitable to be valorized through the production of added-value
96 products, such as adsorbents for the removal of metals (Lima et al., 2018) or
97 soil fertilizers and amendments. The recycling of organic wastes for agricultural
98 uses is essential to sustain soil productivity in areas where SOC is low (Tortosa
99 et al., 2014).

100 To date, no references have been found in the literature regarding valorization
101 alternatives of MMWC for agricultural uses. There are previous works that
102 corroborate the viability of processes based on extraction using alkali solvents,
103 ultrasound, or subcritical water for the recovery of organic carbon and humic
104 substances from organic wastes. Raposo et al. (2016) proposed the recovery of
105 humic substances by ultrasound extraction from estuarine sediments. Using
106 sodium hydroxide (NaOH) 1 M and hydrochloric acid (HCl) 6 M, the humic and
107 fulvic acids recoveries were 100% and 60%, respectively. On the other hand,
108 Tortosa et al. (2014) obtained a liquid extract from olive residues compost with
109 a composition of 6.3% of total organic carbon (TOC) after extraction with 1 M
110 KOH at 70 °C. Finally, Kanmaz (2019) recovered about 68.2% of humic acids
111 from food by-products by subcritical water extraction at 200 °C and 1500 psi for
112 15 min.

113 This work aims to recover organic carbon, humic substances and other
114 nutrients from MMWC to obtain liquids rich in organic carbon in order to be used
115 for agricultural purposes while complying with legal requirements. The main

objectives were (1) to select the more suitable extraction conditions, such as solid:liquid (S:L) ratio, solvent, particle size and time, for the recovery of organic matter (OM) and nutrients from MMWC using Taguchi experimental design; (2) to analyze completely the optimum nutrient-rich extract in order to check its compliance with EU requirements for fertilizing products; (3) to perform germination tests to check the quality of the final product; (4) to characterize the spent solid originating from the extraction process for recycling MMWC within the framework of circular economy and (5) to carry out a preliminary study to analyze the economic viability of the extraction process to produce organic fertilizers on an industrial scale. This study evaluate for the first time the production of value-added organic fertilizers from MMWC.

2. Materials and Methods

2.1. Raw material

The MMWC was kindly donated by Resíduos do Nordeste (Mirandela, Portugal), stored at -18 °C until use and dried in an oven at 70 °C before performing the experimental runs.

2.2. Extraction

The general procedure for organic carbon extraction was as follows: S:L extraction was conducted using 250 mL sealed flasks in which the appropriate amount of MMWC and solvent (125 mL) were blended to achieve the required S:L mass ratio. The extraction was carried out in an orbital shaker (Incubator Shaker ES-60, Miulab, China) under the experimental conditions established. After extraction, the mixture was centrifuged (Centrifuge Sorvall legend RT+, Thermo Fisher Scientific, Spain) for 15 min at 12500 g. The corresponding

supernatants were carefully recovery through filtration (Filter-lab 1300/80 0.45 μm , Filters AOIA S.A., Spain) and stored at 4°C until being analyzed.

Experiments were performed in duplicate.

2.3. Optimization based on Taguchi experimental design

In order to establish the conditions for extracting nutrients, a literature revision about the recovery of OM and nitrogen from such organic residues as MMWC (Fernández-Delgado et al., 2018), olive residues compost (Tortosa et al., 2014) and cow manure compost (Islam et al., 2016) was made. From this revision, six critical factors and their operation ranges were identified: S:L ratio (1:2.5-1:40), type of solvent (water and KOH), extraction time (2-144 h), particle size (< 1 mm and > 1 mm), extraction temperature (30-70 °C), and agitation (100-300 rpm).

A series of preliminary experiments were carried out to simplify the optimization of nutrient extraction conditions through a Taguchi experimental design. The influence of the type of solvent (water or 0.5 M KOH), agitation (100, 200 and 300 rpm) and temperature (30, 45 and 60 °C) was studied. All other parameters remained constant: S:L ratio 1:2.5, 24 h extraction time and mixture particle size (MMWC not separated by particle sizes). From the preliminary experimental results, the most critical factors regarding nutrient extraction were identified and used to build a Taguchi experimental design.

A Taguchi design is a set of experiments that allows choosing a product or process that works with greater consistency in the operating environment.

Taguchi designs recognize that not all the factors that cause variability can be controlled, as raw material composition. This work aims to maximize the response variables that are the organic carbon and other nutrient

concentrations in the extracts. Four factors, with three different levels, were selected in the experimental design. The factor and levels were: A = S:L ratio (1:2.5, 1:10, 1:20; dimensionless), B = solvent (distilled water, 0.5 M KOH, 1 M KOH), C = time (24, 48, 72 h) and D = particle size (< 1 mm, mixture, > 1 mm). The experiments were carried out in duplicate, leading to a total of 18 runs. Finally, in order to verify the results obtained in the experimental design, a confirmatory run was carried out under the optimal conditions obtained in the Taguchi design, varying only the particle size of the raw material (<1 mm, mixture, > 1 mm).

2.4. Phytotoxicity study

The germination test determinates the phytotoxic effects of organic extracts from MMWC for agriculture use. Zucconi et al. (1981) developed a method of phytotoxicity analysis through seed germination and plant growth, being evaluated through the germination index (GI). If the GI ranges between 80 and 100%, it means that germination is not affected by phytotoxic substances. In the interval of 50 to 80%, phytotoxic substances affect germination moderately. Finally, values lower than 50% means that there is a considerably amount of these substances.

In this case, the seeds chosen were *Lepidium sativum*. Germination tests were conducted by evenly spacing ten seeds in a Petri dish containing a filter paper (Filter-lab 1300/80 0.45 µm, Filters AOIA S.A., Spain) as support. Firstly, the organic extract without dilution was adjusted to pH 6.5 with nitric acid (HNO₃) 69% (3 mL per 100 mL of extract). Subsequently, 25 mL of distilled water (control) or the organic extract without dilution or water diluted to 1/10, 1/100,

1/1000, and 1/10000 were added to the Petri dish. Each test was carried out in triplicate. The Petri dishes were then incubated under dark conditions at 27 °C for 120 h. After that, germinated seeds were counted, and the root and shoot lengths were measured. The relative seed germination (RSG) and the relative root growth (RRG) indexes were calculated. The values of RSG and RRG allow the GI to be determined by the following equations (Eq. 1-3), according to Tiquia et al. (1996).

$$RSG (\%) = (\text{number of seeds germinated in liter extract}) / (\text{number of seeds germinated in control}) * 100 \quad (1)$$

$$RRG (\%) = (\text{mean root length in liter extract}) / (\text{mean root length in control}) * 100 \quad (2)$$

$$GI (\%) = (RSG) * (RRG) / 100 \quad (3)$$

2.5. Analytical methods

2.5.1. Solid samples

The dried samples of MMWC were sieved to determinate the particle size distribution (sieves CISA ISO-3310.1 and .2). The humidity and volatile solids (VS) were determined by gravimetry (at 100 °C and 550 °C, respectively). Elementary composition (carbon and nitrogen contents) was analyzed by a LECO CHN-2000 analyzer (LECO Instruments, Spain). Phosphorus was characterized by wet digestion with sulfuric acid (H₂SO₄) and HNO₃ followed by phosphorus measurement in extracts by spectrophotometry (HITACHI UV 2000 spectrophotometer, Hitachi Healthcare Americas, United States) according to the molybdenum blue method (APHA, 2012). Macro, micronutrients and heavy metals were analyzed by ICP Optical Emission Spectrometry (ICP-MS with Agilent HP 7500c Octopolar Reaction System, Agilent, United States) and ICP

Mass Spectrometry (Atomic emission spectrophotometer ICP-OES Radial Simultaneous Agilent 725-ES, Agilent, United States) after microwave digestion (Milestone Ultrawave, Milestone, Italy) for 10 min at 250 °C with 2 mL HNO₃.

2.5.2. Liquid samples

TOC was determined by a TOC-V 5000 analyzer (Shimadzu, Japan). Total Kjeldahl nitrogen (TKN) was analyzed by acid digestion with H₂SO₄ and distillation (KjelFlex K-360 distillatory, BUCHI, Mexico) and ammonium ion (NH₄⁺) was characterized by distillation without previous digestion (APHA, 2012). Nitrate ion concentrations (NO₃⁻) were obtained by liquid chromatography with an ICPak™ Anion HC column (Waters, United States) coupled with a conductivity detector (Waters 432) feeding 2.0 mL/min of a borate/gluconate/acetonitrile solution as eluent at 30 °C. Samples were filtered through a 0.22 µm membrane before injection. Organic nitrogen (ON) was obtained by the difference between TKN, NO₃⁻ and NH₄⁺. Phosphorus, macro and micronutrients, and heavy metals were analyzed as previously described in section 2.5.1.

2.6. Data analysis

ANOVA test and the Taguchi experimental design were carried out with the Statgraphics Centurion XVIII version. ANOVA test was used to conclude the statistical differences at a confidence level of 95% (p < 0.05). Tukey's multiple range tests have allowed identifying means that are significantly different from each other. Taguchi design is an orthogonal array that maximize the response variables selected.

3. Results and discussion

3.1. Characterization of the raw material

The physicochemical characteristics of the MMWC were firstly analyzed.

Regarding the particle size, the 0.04% of MMWC had a particle size greater than 20 mm; the 0.76% was between 10 mm and 20 mm, the 4.18% was between 5 mm and 10 mm, the 46.13% was between 1 mm and 5 mm, and the rest was under 1 mm.

The composition of MMWC was compared with previously published data on the characteristics of compost obtained from municipal waste in Italy (Cesaro et al., 2019) and the data published by Lin et al. (2018a). Comparing the characteristics (Table 1), it can be seen that the OM content of the MMWC (543.2 g/kg) compares well with the values reported by Lin et al. (2018a) for municipal compost. TOC content (287.2 g/kg) is also within the typical range reported. Analyzing the primary and secondary nutrients, total nitrogen (TN), phosphorus (P) and potassium (K) contents (21 g TN/kg, 6.5 g P/kg and 15.5 g K/kg) are within the range of the values reported for MMWC. Calcium concentration (69.2 g/kg) was above the maximum expected value (50 g/kg), whereas magnesium and sodium exhibited concentrations within the expected intervals. Therefore, due to its composition, the MMWC used in this study is a potential source of organic carbon and other nutrients, which can be recovered to obtain liquid fertilizers.

Table 1. Comparison of the composition of different MMWCs.

Parameters	Units	MMWC (this work)	Cesaro et al. (2019)	Lin et al. (2018a)
------------	-------	---------------------	----------------------	--------------------

pH		7.1	7.07	7.1-8.5
Moisture ^(a)	%	23.5	18.8	--
Ash content ^(a)	%	35.0	--	--
Organic compounds ^(b)				
OM	g/kg	543.2	--	330-720
TOC	g/kg	287.2	245	280-380 ^(c)
Acid Lignin	g/kg	344.8	--	--
Cellulose	g/kg	137.7	--	--
Hemicellulose	g/kg	22.8	--	--
Principal and secondary nutrients ^(b)				
TN	g/kg	21.0	19.3	17-34
P	g/kg	6.5	--	6-19
K	g/kg	15.5	--	6-21
Calcium (Ca)	g/kg	69.2	--	33-50
Magnesium (Mg)	g/kg	7.1	--	3-10
Sodium (Na)	g/kg	5.8	--	2-6
Micronutrients and heavy metals ^(b)				
Iron (Fe)	g/kg	17.9	--	--
Arsenic (As)	mg/kg	10.1	--	4-59
Copper (Cu)	mg/kg	202	39.2	183-862
Manganese (Mn)	mg/kg	337	--	354-1227
Zinc (Zn)	mg/kg	463	114.7	793-1338
Lead (Pb)	mg/kg	108.5	34.9	1.0-3.3
Total Chromium (Cr)	mg/kg	264	--	11-14
Nickel (Ni)	mg/kg	64.1	9.84	2-89
Mercury (Hg)	mg/kg	0.4	< 0.01	< 0.1
Cadmium (Cd)	mg/kg	1.9	< 0.01	0.4-1.4

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

^(a) Total weight basis.

^(b) Dry weight basis.

^(c) Referred to **TC**.

On the other hand, the concentrations of micronutrients and heavy metals (Table 1) have to be taken into account for the valorization of MMWC. In this case, the concentrations of metals in MMWC were higher than the values reported for **MMWC**, especially **Pb, Cr, Hg and Cd**. These discrepancies could be probably due to the origin of the raw material. MMWC comes from the composting of non-separated municipal organic matter, which has been recovered in a **MBT** plant from materials such as plastics (e. g. bottles or bags),

glass (e.g. colored glass or broken glassware), metals (e.g. foil or railings) and others types of materials (e. g. textiles or e-waste) (Meena et al., 2019).

3.2. Preliminary experiments

Preliminary experiments were carried out to analyze the effect of extraction parameters such as type of solvent used (water or 0.5 M KOH), agitation (100, 200 and 300 rpm) and temperature (30, 45 and 60 °C) on the extraction of organic carbon and nitrogen from MMWC. The S:L ratio was set at 1:2.5 to check if maximum TOC and TKN concentrations reached in the extract could comply with EU requirements for liquid organo-mineral fertilizers. Results from the preliminary experiments are shown in Table 2.

Table 2. Preliminary experiments. TKN and TOC extraction from MMWC. (A) Effect of type of solvent; (B) effect of agitation, and (C) effect of temperature. The experimental conditions were: mixture (MMWC not separated by particle sizes before extraction), 24 h extraction time, and S:L ratio: 1:2.5.

			Concentrations (g/L)		Extraction yield (%)	
Type of solvent	T (°C)	ω (rpm)	TKN	TOC	TKN	TOC
(A)						
Water	60	300	2.4 ± 0.3	17.2 ± 0.7	28.3 ± 3.1	17.8 ± 0.5
0.5 M KOH			5.2 ± 0.2	56.5 ± 2.5	62.0 ± 2.1	49.2 ± 0.9
(B)						
0.5 M KOH	60	100	4.5 ± 0.1	45.5 ± 1.5	53.2 ± 1.4	39.6 ± 0.5
		200	4.6 ± 0.1	52.9 ± 2.3	54.9 ± 1.0	46.4 ± 2.3
		300	5.2 ± 0.2	56.5 ± 2.5	62.0 ± 2.1	49.2 ± 0.9
(C)						
0.5 M KOH	30	200	3.3 ± 0.2	30.6 ± 2.2	39.1 ± 2.1	26.6 ± 2.2
	45		4.2 ± 0.1	45.1 ± 2.8	50.4 ± 1.3	39.3 ± 6.0
	60		4.6 ± 0.1	52.9 ± 2.3	54.9 ± 1.0	46.4 ± 2.3

3.2.1. Effect of the extraction solvent

The effect of extraction solvents (water and 0.5 M KOH) was studied. When the extraction was conducted with water, the TOC and TKN concentrations were 17.2 g/L and 2.4 g/L, respectively. However, when 0.5 M KOH was used as extractant, the concentrations increased significantly to 56.5 g TOC/L and 5.2 g TKN/L. In contrast, the concentrations of phosphorus expressed as phosphorus pentoxide (P_2O_5) did not exceed 0.04 g/L in the aqueous extracts and 2 g/L in the KOH extracts (data not shown). The concentrations of nutrients extracted with 0.5 M KOH were 3.5-fold higher than those reached when water was used as a solvent. These results agree with those previously reported for sewage sludge. Ma et al. (2019) observed that increasing the pH to 10 promoted the dissolution of OM in the form of proteins, humic, and lignin-like substances. Lin et al. (2018b) concluded that alkaline conditions could improve the solubilization of humic substances because of the reduction of particle size, making the organic particles more accessible for hydrolysis. So, the alkaline extraction is more useful to extract organic carbon and nitrogen from MMWC. Keeling et al. (2003) studied the recovery of nitrogen by extracting compost from mature green waste with water to enhance fertilizer uptake in wheat and rapeseed. The best results were obtained at a S:L ratio of 1:3, improving root and shoot weight by more than 65% compared to the application of a commercial N-fertilizer. Szögi et al. (2015) studied the influence of pH on the extraction of phosphorus and nitrogen and proved that to extract phosphorus from organic waste such as pig manure, the pH must be acidic since under alkaline conditions the extraction of this compound is inefficient. However, the concentration of nitrogen extracted

from the manure was not affected by the pH of the extractant liquid. The conclusion was that extraction with KOH was more effective than with water, because it has a higher power of solubilization and, therefore, improves the extraction of OM and nutrients. However, the concentration of KOH in the extractant has to be limited due to the economic cost that it involves as a solvent. From the experimental results, the type of solvent was included as a parameter in the design of experiments in order to study its effect on the extraction of nutrients.

3.2.2. Effect of agitation

Three levels of agitation (100, 200 and 300 rpm) were studied using 0.5 M KOH as a solvent. The effect of agitation on the extraction of organic carbon and TKN from MMWC (Table 2) indicates that as agitation increased up to 300 rpm, the concentrations obtained were higher (5.2 g TKN/L and 56.5 g TOC/L). However, there were no significant differences ($p > 0.05$) between performing the extraction at 200 rpm and 300 rpm. Therefore, the most favorable agitation for the extraction of nutrients, in this case, was 200 rpm, obtaining under these conditions 4.6 g TKN/L and 52.9 g TOC/L (Table 2). The corresponding extraction yields were 54.9% TKN and 46.4% TOC. It should be noted that the maximum concentration of phosphorus in the extracts was lower than 2 g P_2O_5/L (data not shown). Several studies have confirmed that particle-liquid mass transfer is enhanced when agitation rate increases (Pangarkar et al., 2002). However, a compromise between the improvement of nutrient concentrations and electricity costs associated with agitation has to be reached. An increase in agitation from 200 to 300 rpm allows the TOC extraction yield to be improved by 6%. However, the agitation power multiplies by a factor of 3.4

(data not shown). From these experimental results, an agitation of 200 rpm was chosen for the design of experiments. In this way, mass transfer is not limiting, and energy costs could be maintained as low as possible.

3.2.3. *Effect of temperature*

The efficiency of three extraction temperatures (30, 45, and 60°C) was compared using 0.5 M KOH as extractant. The experimental results concluded that a remarkable increase in TKN and TOC concentrations was achieved when increasing the extraction temperature. The maximum concentrations (4.6 g TKN/L and 52.9 g TOC/L) were reached at the highest temperature (60 °C). The corresponding extraction yields were 54.9% TKN and 46.4% TOC. Table 2 showed that the TKN concentrations increased from 3.3 g/L to 4.2 g/L when the temperature rose from 30 °C to 45 °C. Similarly, Tortosa et al. (2014) addressed nutrient extraction from olive oil processing waste with 1 M KOH at 25 °C and 70 °C and concluded that the more suitable extraction temperature was 70 °C in order to recover 80% of the soluble carbon. It is well-known that an increase in extraction temperature enhances the solubility of extractable compounds, matrix-analyte interactions are more easily broken, and a higher diffusion rate is achieved. Also, viscosity and surface tension of solvent are reduced, and it can penetrate more efficiently into the solid (Mosca et al., 2018). However, significant differences were not observed ($p > 0.05$) when the temperature was further increased from 45 °C to 60 °C and nitrogen concentration remained almost constant. On the other hand, the TOC concentration in the extracts was enhanced after increasing temperature from 30 °C to 60 °C (30.6 g/L to 52.9 g/L) (Table 2), but the differences between performing extraction at 45 °C or 60 °C were not significant ($p > 0.05$). Therefore, the operation at high temperatures

(60 °C) would not be necessary, since mild temperatures (45 °C) allow to reach similar extraction yields. As it was previously observed, the maximum concentration of phosphorus in the extracts was lower than 2 g P₂O₅/L (data not shown). In general, an increase in temperature improves the kinetics of solubilization. However, within the range of temperatures studied, no significant differences ($p > 0.05$) were observed between TOC and TKN extraction yields reached at 45 °C and 60 °C (Table 2). From the point of view of energy costs, a temperature of 45 °C is recommended to reach reasonable high nutrient recoveries. Therefore, an extraction temperature of 45 °C was chosen to carry out the design of experiments.

3.3. Taguchi methodology for optimization of extraction parameters

After the preliminary study about the influence of the main extraction parameters, the Taguchi methodology, described in section 2.3, has been applied to optimize experimental conditions. Table 3 summarizes the results obtained for the nine experiments carried out in duplicate. The effect of controlled factors on TOC and TKN concentrations in the organic extracts is shown in Figure 1. As can be seen, the effect of the controlled factors presents a similar trend for TOC and TKN concentrations, because the organic nitrogen prevails. The main influence is attributed to the S:L ratio, although the other factors also exerted a considerable effect on TOC and TKN concentrations. As it was expected, the nutrient concentrations increase as the amount of liquid used in the extraction decreases. The highest TOC and TKN concentrations were achieved at the highest S:L ratio (1:2.5), the highest extraction time (72 h) and particle size (> 1 mm) using the most concentrated KOH solution (1 M) as

extractant. Regarding the influence of other experimental factors, higher concentrations of nutrients are expected as extraction time and KOH concentration in solvent increases (Genuino et al., 2017). Moreover, higher concentrations of nutrients are expected with smaller particle size because the contact surface is favored (Jahongir et al., 2018).

Table 3. Taguchi experimental design. $L_9(3^4)$ orthogonal array. TKN and TOC extraction concentrations.

Trial	S:L (g/g)	KOH (M)	Time (h)	Particle size	TKN (g/L)	TOC (g/L)
1	1:2.5	0	24	< 1 mm	2.3 ± 0.2	14.2 ± 0.1
2	1:2.5	0.5	48	Mixture*	4.9 ± 0.1	52.4 ± 0.7
3	1:2.5	1	72	> 1 mm	7.5 ± 0.3	67.1 ± 2.7
4	1:10	0	48	> 1 mm	1.0 ± 0.2	5.0 ± 0.2
5	1:10	0.5	72	< 1 mm	2.0 ± 0.1	14.8 ± 0.2
6	1:10	1	24	Mixture*	2.1 ± 0.4	15.9 ± 0.1
7	1:20	0	72	Mixture*	0.5 ± 0.2	2.2 ± 0.1
8	1:20	0.5	24	> 1 mm	1.0 ± 0.1	8.2 ± 0.1
9	1:20	1	48	< 1 mm	1.0 ± 0.2	7.3 ± 0.2

*Mixture: MMWC not separated by particle size before extraction

An analysis of variance (ANOVA) was performed to analyze experimental results (Table 4). The analysis of the F-ratio (variance ratio) revealed that all factors studied were statistically significant (at 95% confidence level), both for the TKN and for the TOC concentrations in the organic extracts. When calculating the contribution of each factor to the responses, the most influential factor was the S:L ratio, contributing 58.28% for TKN and 53.57% for TOC. The S:L ratio is critical for the extraction because a higher concentration of nutrients was obtained when higher solid loadings were used. The solvent used in the extraction is also significant and contribute to the responses by 18.70% (TKN) and 18.95% (TOC). The experimental design proves that the increase in the molarity of KOH in the solvent (0-0.5-1.0 M), rose the concentrations of TKN

and TOC (Figure 1). Finally, the extraction time and the particle size are the factors with a lower contribution, which does not exceed 9% for both the TKN and the TOC concentrations. This fact could mean that to reach adequate final nutrient concentrations in the liquid extracts, it is not necessary separating the MMWC by particle sizes before the extraction process. Finally, the ANOVA analysis reveals that the contribution of the residual error of TKN and TOC is 7.39% and 11.42%, respectively. These error percentages show that the observed variability can be attributed to the experimental errors and the composition of the raw material.

Table 4. Results of analysis of variance (ANOVA) for (A) TKN concentration and (B) TOC concentration.

Variation source	Sum of squares	Degrees of freedom	Mean Square	F-Ratio	P-Value	Contribution (%)
(A)						
A: S:L ratio	49.1	1	49.1	102.6	0.0000	58.3
B: solvent	15.7	1	15.7	32.9	0.0001	18.7
C: time	7.1	1	7.12	14.9	0.0020	8.5
D: particle size	6.0	1	6.0	12.6	0.0036	7.2
Total error	6.2	13	0.5			7.4
Total (corrected)	84.2	17				
(B)						
A: S:L ratio	4484.9	1	4484.9	61.0	0.0000	53.6
B: solvent	1586.4	1	1586.4	21.6	0.0005	19.0
C: time	697.9	1	697.9	9.5	0.0088	8.3
D: particle size	646.0	1	646.0	8.8	0.0110	7.7
Total error	956.4	13	73.6			11.4
Total (corrected)	8371.6	17				

Statistical analysis reveals that the optimal combination of factors that maximize the nutrient concentrations (7.5 g TKN/L and 67.1 g TOC/L) corresponded to trial 3 when the fraction of particles of higher size (> 1 mm) was used.

3.4. Influence of MMWC particle size

As it can be verified in Table 3, the combination of factors found as optimal (A1-B3-C3-D3: S:L ratio 1:2.5, solvent: 1 M KOH, 72 h extraction time and particle size > 1 mm) led to the highest nutrient concentrations. Accordingly, it was necessary to perform a confirmatory experiment to probe the accuracy of the results and to ensure if separation of the MMWC by particle sizes before extraction could improve nutrient recoveries.

To this end, the effect of particle size (< 1 mm, mixture and > 1 mm) was studied under the optimal conditions. The analysis of these fractions of different particle size did not show significant differences regarding the TOC and TKN compositions of the initial material (data not shown). Figure 2 shows that the highest concentrations of TOC and TKN are obtained when the smallest particle size was used (7.8 g TKN/L and 77.7 g TOC/L). This result was expected since the decrease in particle size improves the specific area of contact, and the mass transfer in the extraction (Ma and Mu, 2016). Comparing the results of trial 3 (7.5 g TKN/L and 67.1 g TOC/L) and those obtained in the confirmatory experiment (Figure 2), particle size > 1 mm cannot be considered as an optimal factor, because the nutrient concentrations were higher when the particle size was smaller (particle size < 1 mm). Regarding TOC concentration, the differences were significant ($p < 0.05$) for mixture MMWC (69.0 g/L) and the material with a particle size smaller than 1 mm (77.7 g/L). However, no significant differences were observed for the TKN concentration (7.5 – 7.8 g/L). Therefore, separating the MMWC by fractions of different sizes before the extraction process is not recommended because the concentration of extracted

nutrients did not improve considerably. In this way, it is possible to reduce the production costs associated with the separation of the material without significantly reducing the concentrations of nutrients obtained in the extraction process.

Taking into account the Taguchi results and the confirmatory experimental runs about the influence of particle size, it could be concluded that the most favorable conditions for the extraction process, in the range of the operating conditions tested, are: S:L ratio 1:2.5, solvent 1 M KOH, 72 h extraction time, particle size mixture, 45 °C extraction temperature and an agitation of 200 rpm.

3.5. Utilization of the organic extracts as liquid fertilizers

To assess if the nutrient-rich extract obtained under the optimal conditions is in compliance with the legal requirements to be commercialized as liquid fertilizer, a complete characterization of the extract, including the analysis of micronutrients and metals, was carried out. Table 5 compares the composition of the liquid extract obtained under optimal conditions with the requirements of the Regulation (EU) 2019/1009 of the European Parliament and of the Council on CE marked fertilizing products (European Commission, 2019) as liquid organo-mineral fertilizers.

Regarding TOC and principal nutrients (N, P, K), the EU Regulation dictates that the minimum TOC content must be 3% w/w, and the liquids have to reach at least one of the three minimum nutrient concentrations (2% TN of which 0.5% is ON, 2% P as P₂O₅ and/or 2% w/w K as potassium oxide (K₂O)). As it was shown in Table 5, the liquid extracted under optimal conditions shows the following composition: TOC: 6.9%, TN: 0.8%, ON: 0.7%, P₂O₅: 0.2% and K₂O:

8.3%. Additionally, the humic acids percentage in the liquid was 47.6% TOC/TOC_{total}, which is of the same order as those reported by De Souza and Bragança (2018), who extracted 68.8% TOC/TOC_{total} from coal using 0.5 M NaOH and S:L ratio of 1:10. On the other hand, Kanmaz (2019) performed a subcritical water extraction of food by-products at 200 °C for 15 min, and the recovery of humic acids was 59.2% TOC/TOC_{total}. The use of humic substances provides physical, chemical, and biological benefits in soil.

Moreover, the concentration of contaminants must not exceed the quantities established in the EU Regulation. The concentrations detected were 0.4 mg Cd/kg, 0.02 mg Hg/kg, 9.2 mg Ni/kg, and 6.6 mg Pb/kg, under the limits of the EU Regulation. The extraction of heavy metals such as Ni, Cd, Cr, and Pb is usually favored at acidic or neutral conditions (pH < 7). If alkaline solvents such as NaOH are used, the extraction of these metals is ineffective (Smith, 2009). On the other hand, pathogens (*E. coli* and *Salmonella* spp.) were below the limits of EU regulation. Table 5 shows that the organic extract is in compliance with the EU Regulation regarding TOC, nutrients, pathogens, and heavy metals concentrations, and thus, it could be considered as a fertilizer with European Conformity (CE) mark.

Table 5. Comparison between the composition of the nutrient-rich liquid obtained under the optimal conditions and the Regulation 2019/1009 of the European Parliament and of the Council on CE marked fertilizing products.

Parameters	Units	Extract liquid ^(a)	EU Regulation
pH		6.51	--
Total Organic Carbon			
TOC	% w/w	6.9	3
Humic acids	% TOC/TOC _{total}	47.6	--

Fulvic acids	% TOC/TOC _{total}	52.4	--
Principal nutrients			
TN	% w/w	3.7	2
ON	% w/w	0.7	0.5
NH ₄ ⁺	% w/w	0.1	--
NO ₃ ⁻	% w/w	2.9	--
P as P ₂ O ₅	% w/w	0.2	2
K as K ₂ O	% w/w	8.3	2
Secondary nutrients			
Ca	g/kg	4.8	--
Mg	g/kg	0.8	--
Na	g/kg	2.4	--
Micronutrients			
Fe	g/kg	1.3	--
Mn	mg/kg	43.8	--
Heavy metals			
Cd	mg/kg	0.4	3
Hg	mg/kg	0.02	1
Ni	mg/kg	9.2	50
Pb	mg/kg	6.6	120
Cu	mg/kg	16.8	600
Zn	mg/kg	108.4	1500
As	mg/kg	1.3	40
Cr	mg/kg	5.3	--
Pathogens			
<i>Escherichia coli</i>		n.d.	0 in 25 mL
<i>Salmonella</i> spp.		< 10	< 1000 in 1 mL

n.d.: no detected

^(a)Optimal extraction conditions: S:L ratio 1:2.5, solvent: 1 M KOH, time: 72 h, particle size: mixture, temperature: 45°C and agitation: 200 rpm.

3.6. Valorization of the solid residue after extraction

The solid residue obtained after the extraction process can be further valorized.

Under optimal operating conditions, the OM content of the residue is relatively high (114.72 ± 1.72 g TOC/kg). The residue contains a higher heating value (HHV_v) of 7.79 MJ/kg and a lower heating value (LHV_v) of 7.25 MJ/kg.

According to these data, the solid residue could be used in situ in the liquid

fertilizer production industrial plant, either through the production of biochar (Wang and Wang, 2019) or to satisfy heating needs of the plant.

3.7. Germination test

Germination tests were conducted to evaluate the phytotoxicity of the nutrient-rich extract. The GI determines the maximum germination potential of the seed and evaluates the fertilizer phytotoxicity. The germination of the plant is influenced by the presence of organic acids of lower molecular weight, NH_4^+ , salinity, and heavy metals (Luo et al., 2018). Germination test results are summarized in Figure 3. The extract without dilution shows a GI of 0%, which means that the liquid could present phytotoxic substances (Nurdiawati et al., 2015). On the other hand, the 1/100 dilution resulted in a GI of around 80%, which indicates that the amount of potentially phytotoxic substances in the dilute extracts has no significant effect on germination. However, the 1/1000 and 1/10000 dilutions have a GI around 70%, which could indicate that the low concentration of nutrients due to the dilution is not enough for germination of seeds.

4. Economic analysis

A preliminary study of the nutrient extraction process for the valorization of MMWC was carried out for determining the overall economic viability of the process. An industrial plant with a processing capacity of 300 kg/h of MMWC with a humidity of 25% w/w was selected as the basis for calculation. Considering this MMWC flowrate, the inputs were 424 L/h of water, 49 kg/h of KOH 50% w/v, and 20 L/h of HNO_3 50% w/v. Taking into account the production

yield at lab-scale (200 L of fertilizer per 100 kg of dry MMWC) an output of 450 L/h of liquid fertilizer could be obtained. The Lang factors method, widely used in industrial engineering to calculate the capital and operating costs, has been applied for this preliminary economic study. A complete description of the method can be found in the literature (Sinnott, 2005). The corresponding item costs are summarized in Table 6.

Table 6. Main costs estimated with Lang method for an industrial plant producing liquid fertilizers from MMWC by alkaline extraction.

Item	Cost (k€)
PCE ¹	350
Equipment Erection	155
Piping	155
Instrumentation	55
Electrical	35
Buildings, process	35
Utilities	155
Storages	70
Site development	20
Ancillary buildings	70
PPC ²	1,100
Design and Engineering	270
Contractor's fee	50
Contingency	110
FCC ³	1,530
Working Capital	70
TIC ⁴	1,600

1. PCE: Equipment Cost. They were estimated with CAPCOST software.

2. PPC: Physical Plant Cost. $PPC = PCE * (1+f_1+f_2+...+f_9) = PCE * 3.15$

3. FCC: Fixed Capital Cost. $FCC = PPC * (1+f_{10}+f_{11}+f_{12}) = PPC * 1.40$

4. TIC: Total Investment Cost. $TIC = FCC * (1+f_{13}) = PPC * 1.05$

The equipments considered in the extraction process were storage tanks for raw materials and final products, extraction tanks, centrifuge, pumps, conveyors, and neutralization system with HNO₃. Regarding the costs of raw materials, the following prices were considered: MMWC: 12 €/t (Resíduos do Nordeste, 2019), process water: 3.16 €/m³ (Aquavall, 2017), KOH 50% w/v: 1.2 €/L, and HNO₃ 50% w/w: 300 €/t (Sinnott, 2005). Therefore, taking into account that the yearly working hours are 8,000 h/y and that the plant will operate for 10 years, the plant would make it profitable for a fertilizer sale price above 1 €/L. A net present value (NPV) of 880 k€ with an interest rate of 10% and an internal return rate (IRR) of 22% in six years was calculated.

The proposed industrial plant produced a fertilizer with a competitive price (1 €/L). The market price of liquid organic fertilizers currently available can vary over a wide range (0.5-10 €) due to the variability in their formulation, the raw material, the production process and the size and materials used for packaging, among other factors.

5. Conclusions

This study proposed an efficient extraction process for the recovery of organic carbon and other nutrients using an abundant residue, MMWC, as a renewable resource. Appropriate operating conditions for extraction were selected from a Taguchi experimental design. The nutrient rich extract complies with the requirements to be considered as liquid organo-mineral fertilizer. TOC concentration reached 6.9%, value more than two-fold higher than the minimum stated in European regulations (3%). The concentration of humic acids accounted for 47.6% of TOC. Germination tests showed successful germination

of **Garden** cress (*Lepidium sativum*) after proper dilution of the organic liquid.

The preliminary economic study shows that a plant with a capacity of 300 kg/h of wet MMWC needs a total investment cost of **1,600** k€. The sale price of liquid fertilizer should be higher than 1 €/L to be economically profitable. Overall, the proposed valorization process operates under moderate conditions and allows to produce a liquid extract that could be used as an organo-mineral fertilizer according to the European regulations. **The solid residue could be used to produce biochar or to satisfy heating needs, in an approach of circular economy.** In this way, MMWC can be successfully recycled, minimizing waste and the amount taken to landfill. The use of organic fertilizers rich in humic substances reduces the dependence on **fossil-based products, such as** inorganic fertilizers and, consequently, contributes to mitigate their negative effects on the environment. Further investigations will be focused on performing growth assays under controlled conditions to check the effects of the liquid extracts on the growth of plants in soil.

Acknowledgements

Authors wish to acknowledge to the Programme of Cooperation INTERREG V-A Spain-Portugal (POCTEP) 2014-2020 and EU-FEDER for providing financial support (project 0119_VALORCOMP_2_P). Authors also acknowledge the support of the regional government of Castilla y León and the EU-FEDER (UIC 129, CLU 2017-09). M. Fernández-Delgado also thanks Junta de Castilla y León for providing her PhD grant (E-47-2019-0114592). Authors thank Francisco Lafuente (Department of Agroforestry Sciences, University of

Valladolid) and Marisol Vega (Department of Analytical Chemistry, University of Valladolid) for their technical assistance.

References

APHA, 2012. Standard Methods for the Examination of Water and Wastewater, 21th ed. American Public Health Association, Washington, DC, USA.

Aquavall, 2017. Supply Service Fees. http://aquavall.es/wp-content/uploads/2017/06/tarifas_agua_2017.pdf (accessed 27 June 2019).

Cesaro, A., Conte, A., Belgiorno, V., Siciliano, A., Guida, M., 2019. The evolution of compost stability and maturity during the full-scale treatment of the organic fraction of municipal solid waste. *J. Environ. Manag.* 232, 264–270. <https://doi.org/10.1016/j.jenvman.2018.10.121>

Daliakopoulos, I.N., Tsanis, I.K., Koutroulis, A., Kourgialas, N.N., Varouchakis, A.E., Karatzas, G.P., Ritsema, C.J., 2016. The threat of soil salinity: A European scale review. *Sci. Total Environ.* 573, 727–739. <https://doi.org/10.1016/j.scitotenv.2016.08.177>

De Souza, F., Bragança, S.R., 2018. Extraction and characterization of humic acid from coal for the application as dispersant of ceramic powders. *J. Mater. Res. Technol.* 7, 254–260. <https://doi.org/10.1016/j.jmrt.2017.08.008>

Ecoprogram, 2017. The Market for Mechanical Biological Waste Treatment in Europe. https://www.ecoprogram.com/fileadmin/user_upload/leseproben/extract_MBT_Europe_2017_ecoprogram.pdf (accessed 30 September 2019).

598 European Commission, 2018a. Directive (EU) 2018/851 of the European
 599 Parliament and of the Council of 30 May 2018 amending Directive 2008/98/EC
 600 on waste. [https://eur-lex.europa.eu/legal-](https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32018L0851&from=EN)
 601 [content/EN/TXT/PDF/?uri=CELEX:32018L0851&from=EN](https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32018L0851&from=EN) (accessed 3
 602 December 2018).
 603 European Commission, 2018b. Directive (EU) 2018/850 of the European
 604 Parliament and of the Council of 30 May 2018 amending Directive 1999/31/EC
 605 on the landfill of waste. [https://eur-lex.europa.eu/legal-](https://eur-lex.europa.eu/legal-content/ES/TXT/PDF/?uri=CELEX:32018L0850&from=EN)
 606 [content/ES/TXT/PDF/?uri=CELEX:32018L0850&from=EN](https://eur-lex.europa.eu/legal-content/ES/TXT/PDF/?uri=CELEX:32018L0850&from=EN) (accessed 30
 607 September 2019).
 608 European Commission, 2019. Regulation 2019/1009 of the European
 609 Parliament and of the Council laying down rules on the making available on the
 610 market of CE marked fertilising products and amending Regulations (EC) No
 611 1069/2009 and (EC) No 1107/2009.
 612 http://www.europarl.europa.eu/doceo/document/TA-8-2019-0306_EN.html
 613 (accessed 30 May 2019).
 614 Eurostat, 2019a. Consumption of inorganic fertilizers.
 615 [http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=aei_fm_usefert&lang](http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=aei_fm_usefert&lang=en)
 616 [=en](http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=aei_fm_usefert&lang=en) (accessed 27 March 2019).
 617 Eurostat, 2019b. Municipal waste statistics.
 618 [https://ec.europa.eu/eurostat/statistics-](https://ec.europa.eu/eurostat/statistics-explained/index.php/Municipal_waste_statistics)
 619 [explained/index.php/Municipal_waste_statistics](https://ec.europa.eu/eurostat/statistics-explained/index.php/Municipal_waste_statistics) (accessed 21 October 2019).

620 Fernández-Delgado, M., Benito, C., Coca, M., González-Benito, G., García-
 621 Cubero, M.T., Lucas, S., 2018. Obtaining liquid fertilizers from mixed municipal
 622 waste compost, in: Proceedings of VI Conference of the Spanish Composting
 623 Network, Valencia, Spain, pp. 395–400.
 624 Genuino, D.A.D., Bataller, B.G., Capareda, S.C., De Luna, M.D.G., 2017.
 625 Application of artificial neural network in the modeling and optimization of humic
 626 acid extraction from municipal solid waste biochar. *J. Environ. Chem. Eng.* 5,
 627 4101–4107. <https://doi.org/10.1016/j.jece.2017.07.071>
 628 Islam, M.K., Yaseen, T., Traversa, A., Ben Kheder, M., Brunetti, G., Coccozza,
 629 C., 2016. Effects of the main extraction parameters on chemical and microbial
 630 characteristics of compost tea. *Waste Manag.* 52, 62–68.
 631 <https://doi.org/10.1016/j.wasman.2016.03.042>
 632 Jahongir, H., Miansong, Z., Amankeldi, I., Yu, Z., Changheng, L., 2018. The
 633 influence of particle size on supercritical extraction of dog rose (*Rosa canina*)
 634 seed oil. *J. King Saud Univ. Eng. Sci.* 31, 140-143.
 635 <https://doi.org/10.1016/j.jksues.2018.04.004>
 636 Keeling, A.A., McCallum, K.R., Beckwith, C.P., 2003. Mature green waste
 637 compost enhances growth and nitrogen uptake in wheat (*Triticum aestivum* L.)
 638 and oilseed rape (*Brassica napus* L.) through the action of water-extractable
 639 factors. *Bioresour. Technol.* 90, 127–132. <https://doi.org/10.1016/S0960->
 640 8524(03)00125-1

641 Liang, B., Zhao, W., Yang, X., Zhou, J., 2013. Fate of nitrogen-15 as influenced
 642 by soil and nutrient management history in a 19-year wheat–maize experiment.
 643 Field Crop. Res. 144, 126–134. <https://doi.org/10.1016/j.fcr.2012.12.007>
 644 Lima, J.Z., Raimondi, I.M., Schalch, V., Rodrigues, V.G.S., 2018. Assessment
 645 of the use of organic composts derived from municipal solid waste for the
 646 adsorption of Pb, Zn and Cd. J. Environ. Manag. 226, 386–399.
 647 <https://doi.org/10.1016/j.jenvman.2018.08.047>
 648 Lin, L., Xu, F., Ge, X., Li, Y., 2018a. Improving the sustainability of organic
 649 waste management practices in the food-energy-water nexus: A comparative
 650 review of anaerobic digestion and composting. Renew. Sust. Energ. Rev. 89,
 651 151–167. <https://doi.org/10.1016/j.rser.2018.03.025>
 652 Lin, L., Li, R., Li, X., 2018b. Recovery of organic resources from sewage sludge
 653 of Al-enhanced primary sedimentation by alkali pretreatment and acidogenic
 654 fermentation. J. Clean. Prod. 172, 3334–3341.
 655 <https://doi.org/10.1016/j.jclepro.2017.11.199>
 656 Luo, Y., Liang, J., Zeng, G., Chen, M., Mo, D., Li, G., Zhang, D., 2018. Seed
 657 germination test for toxicity evaluation of compost: Its roles, problems and
 658 prospects. Waste Manag. 71, 109–114.
 659 <https://doi.org/10.1016/j.wasman.2017.09.023>
 660 Ma, M.M., Mu, T.H., 2016. Effects of extraction methods and particle size
 661 distribution on the structural, physicochemical, and functional properties of
 662 dietary fiber from deoiled cumin. Food Chem. 194, 237–246.
 663 <https://doi.org/10.1016/j.foodchem.2015.07.095>

664 Ma, S., Hu, H., Wang, J., Liao, K., Ma, H., Ren, H., 2019. The characterization
665 of dissolved organic matter in alkaline fermentation of sewage sludge with
666 different pH for volatile fatty acids production. *Water Res.* 164, 114924.
667 <https://doi.org/10.1016/j.watres.2019.114924>

668 Matschullat, J., Reimann, C., Birke, M., dos Santos Carvalho, D., the GEMAS
669 Project Team, 2018. GEMAS: CNS concentrations and C/N ratios in European
670 agricultural soil. *Sci. Total Environ.* 627, 975–984.
671 <https://doi.org/10.1016/j.scitotenv.2018.01.214>

672 Meena, M.D., Yadav, R.K., Narjary, B., Yadav, G., Jat, H.S., Sheoran, P.,
673 Meena, M.K., Antil, R.S., Meena, B.L., Singh, H. V., Singh Meena, V., Rai, P.K.,
674 Ghosh, A., Moharana, P.C., 2019. Municipal solid waste (MSW): Strategies to
675 improve salt affected soil sustainability: A review. *Waste Manag.* 84, 38–53.
676 <https://doi.org/10.1016/j.wasman.2018.11.020>

677 Mosca, F., Hidalgo, G.I., Villasante, J., Almajano, M.P., 2018. Continuous or
678 batch solid-liquid extraction of antioxidant compounds from seeds of *Sterculia*
679 *apetala* plant and kinetic release study. *Molecules* 23, 1-12.
680 <https://doi.org/10.3390/molecules23071759>

681 Nurdiawati, A., Novianti, S., Zaini, I.N., Nakhshinieva, B., Sumida, H.,
682 Takahashi, F., Yoshikawa, K., 2015. Evaluation of hydrothermal treatment of
683 empty fruit bunch for solid fuel and liquid organic fertilizer co-production. *Energy*
684 *Procedia* 79, 226–232. <https://doi.org/10.1016/j.egypro.2015.11.469>

685 Kanmaz, E.O., 2019. Humic acid formation during subcritical water extraction of
 686 food by-products using accelerated solvent extractor. Food Bioprod. Process.
 687 115, 118–125. <https://doi.org/10.1016/j.fbp.2019.03.008>
 688 Pangarkar, V.G., Yawalkar, A.A., Sharma, M.M., Beenackers, A.A.C.M., 2002.
 689 Particle-liquid mass transfer coefficient in two-/three-phase stirred tank reactors.
 690 Ind. Eng. Chem. Res. 41, 4141–4167. <https://doi.org/10.1021/ie010933j>
 691 Paungfoo-Lonhienne, C., Redding, M., Pratt, C., Wang, W., 2019. Plant growth
 692 promoting rhizobacteria increase the efficiency of fertilisers while reducing
 693 nitrogen loss. J. Environ. Manag. 233, 337–341.
 694 <https://doi.org/10.1016/j.jenvman.2018.12.052>
 695 Raposo, J.C., Villanueva, U., Olivares, M., Madariaga, J.M., 2016.
 696 Determination of humic substances in sediments by focused ultrasound
 697 extraction and ultraviolet visible spectroscopy. Microchem. J. 128, 26–33.
 698 <https://doi.org/10.1016/j.microc.2016.04.004>
 699 Resíduos do Nordeste, 2019. Corretivo orgânico Ferti Trás-os-Montes.
 700 <http://www.residuosdonordeste.pt/ferti/> (accessed 27 June 2019).
 701 Ribeiro, R.S., Rodrigues, R.O., Silva, A.M.T., Tavares, P.B., Carvalho, A.M.C.,
 702 Figueiredo, J.L., Faria, J.L., Gomes, H.T., 2017. Hybrid magnetic graphitic
 703 nanocomposites towards catalytic wet peroxide oxidation of the liquid effluent
 704 from a mechanical biological treatment plant for municipal solid waste. Appl.
 705 Catal. B Environ. 219, 645–657. <https://doi.org/10.1016/j.apcatb.2017.08.013>
 706 Sepehri, A., Sarrafzadeh, M.H., 2019. Activity enhancement of ammonia-
 707 oxidizing bacteria and nitrite-oxidizing bacteria in activated sludge process:

metabolite reduction and CO₂ mitigation intensification process. Appl. Water
Sci. 9. <https://doi.org/10.1007/s13201-019-1017-6>

Sinnott, R.K., 2005. Coulson & Richardson's Chemical Engineering, vol. 6,
Chemical Engineering Design fourth ed. Elsevier, Oxford.

Smith, S.R., 2009. A critical review of the bioavailability and impacts of heavy
metals in municipal solid waste composts compared to sewage sludge. Environ.
Int. 35, 142–156. <https://doi.org/10.1016/j.envint.2008.06.009>

Szögi, A.A., Vanotti, M.B., Hunt, P.G., 2015. Phosphorus recovery from pig
manure solids prior to land application. J. Environ. Manag. 157, 1–7.
<https://doi.org/10.1016/j.jenvman.2015.04.010>

Tiquia, S.M., Tam, N.F.Y., Hodgkiss, I.J., 1996. Effects of composting on
phytotoxicity of spent pig-manure sawdust litter. Environ. Pollut. 93, 249–256.
[https://doi.org/10.1016/S0269-7491\(96\)00052-8](https://doi.org/10.1016/S0269-7491(96)00052-8)

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>

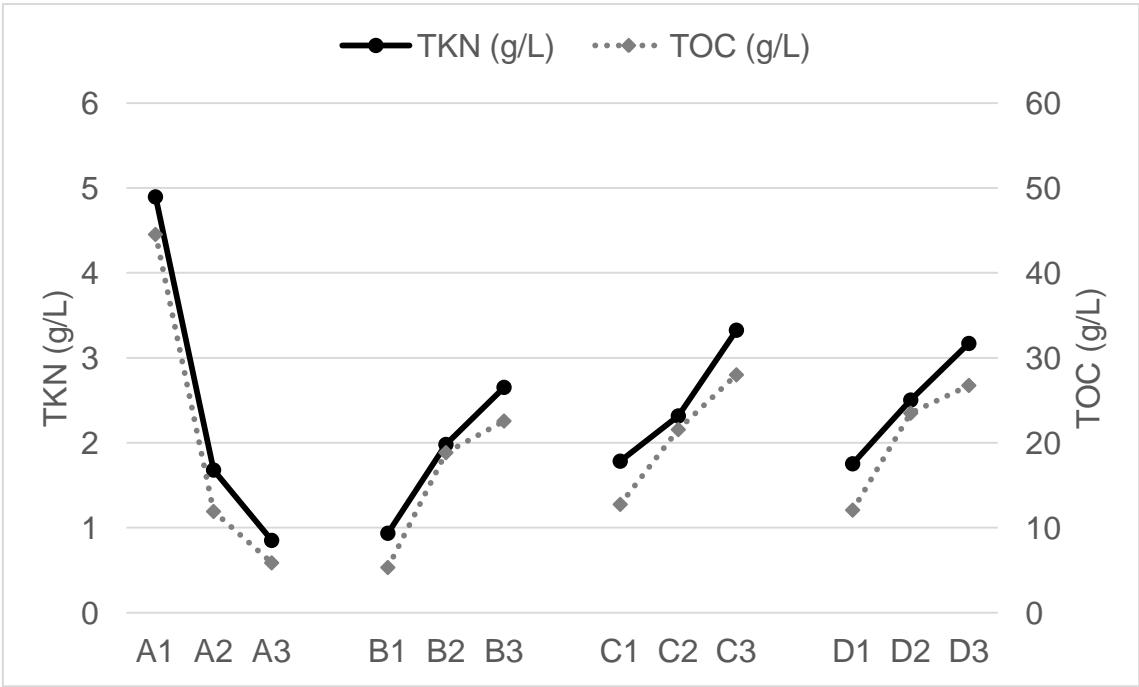
Wang, J., Wang, S., 2019. Preparation, modification and environmental
application of biochar: A review. J. Clean. Prod. 227, 1002–1022.
<https://doi.org/10.1016/j.jclepro.2019.04.282>

Zhu, E., Deng, J., Wang, H., Wang, K., Huang, L., Zhu, G., Belete, M.,
Shahtahmassebi, A., 2019. Identify the optimization strategy of nitrogen
fertilization level based on trade-off analysis between rice production and

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2
3
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9
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11
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13
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47
48
49
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51
52
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60
61
62
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65

731 greenhouse gas emission. J. Clean. Prod. 239, 118060.
732 <https://doi.org/10.1016/j.jclepro.2019.118060>
733 Zucconi, F., Pera, A., Forte, M., De Bertoldi, M., 1981. Evaluating toxicity of
734 immature compost. Biocycle 22, 54–57.

Figure 1



A = **S:L ratio** (1:2.5, 1:10, 1:20; dimensionless), B = solvent (water, 0.5 M KOH, 1 M KOH), C = time (24, 48, 72; h) and D = particle size (< 1 mm, mixture, > 1 mm).

Figure 2

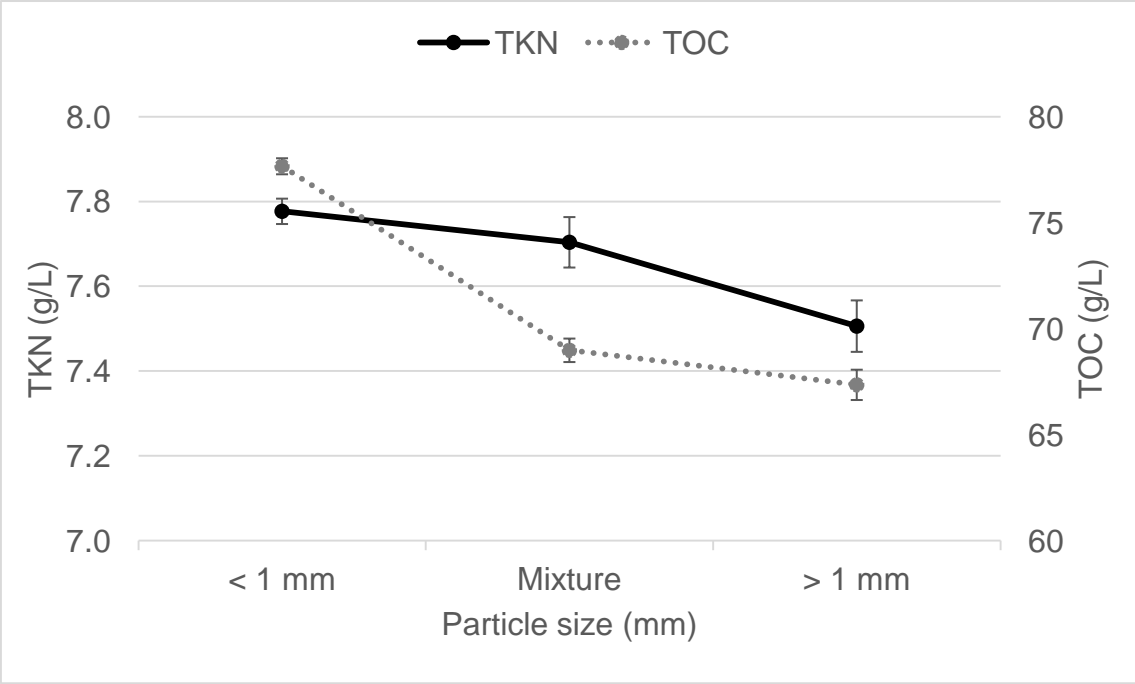


Figure 3

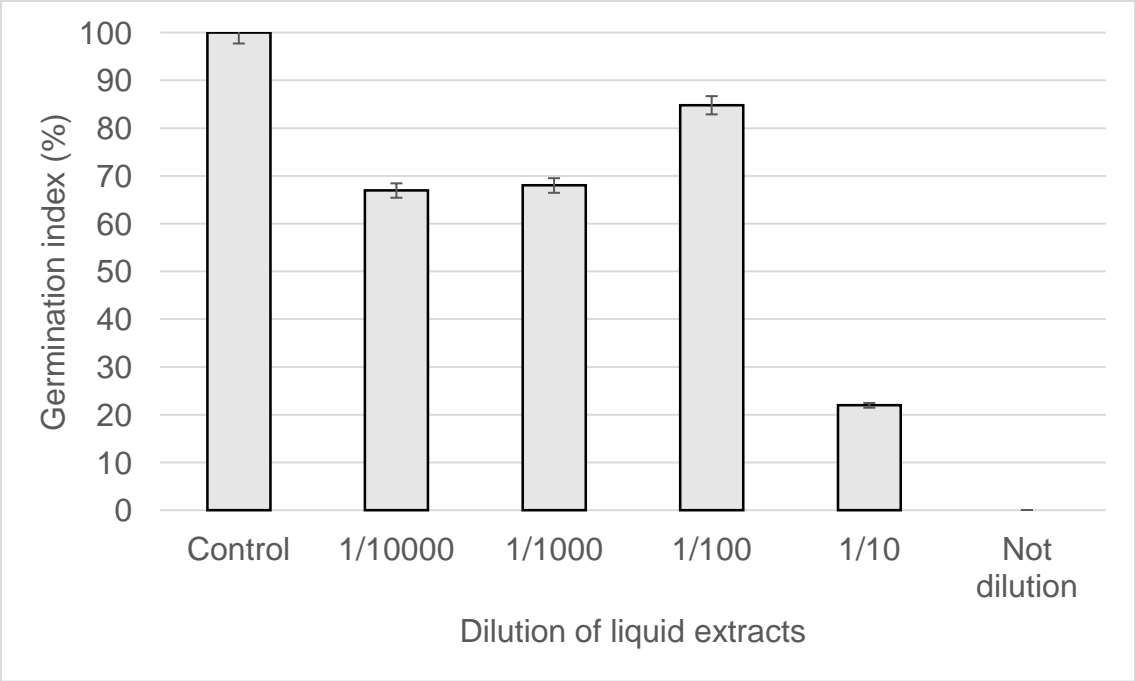


Figure 1. Taguchi experimental design. Effect of control factors (A: S:L ratio, B: solvent, C: extraction time, D: particle size) on TKN and TOC concentrations in extracts.

Figure 2. Effect of particle size on the extraction of nutrients. The experimental conditions were: S:L ratio 1:2.5, solvent: 1 M KOH, time: 72 h, temperature: 45°C and agitation: 200 rpm.

Figure 3. Germination tests. Effect of dilution of liquid extracts on seed germination of Garden cress (*Lepidium sativum*).

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

CRedit author statement

M. Fernández-Delgado: investigation, writing. **E. del Amo-Mateos:** investigation, **S. Lucas:** methodology, Writing - Review & Editing. **M.T. García-Cubero:** conceptualization, methodology. **M Coca:** supervision, Writing - Review & Editing, project administration.



Universidad de Valladolid

Departamento de
Ingeniería Química y
Tecnología del Medio Ambiente

Dr. Jiří Jaromír Klemeš
Editor in Chief Journal of Cleaner Production

15th July, 2019

Dear Dr. Klemeš

I enclose herewith the manuscript entitled **“Recovery of organic carbon from municipal mixed waste compost for the production of fertilizers”** to be considered for publication in the Journal of Cleaner Production.

The paper is about the recovery of organic carbon and other nutrients from mixed municipal waste compost to produce fertilizers. Only about a third of bio-waste produced in the European Union is separately collected. The organic fraction recovered in mechanical biological treatment plants is usually used to produce compost of low quality, whose use in agriculture will be restricted by the application of European policies. The work aims to develop an extraction process for the efficient recovery of mainly organic carbon and others nutrients of compost from unsorted municipal waste to obtain organic fertilizers for agricultural purposes. Turning waste into a resource is an essential part of closing the loop in a circular economy.

The research study is framed in the European Project VALORCOMP, funded by the Cooperation Program INTERREG V-A Spain-Portugal (POCTEP) and the European Regional Development Fund (FEDER).

Yours faithfully,

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