

## **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 and 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, HNO<sub>3</sub>, 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 (CO<sub>2</sub>)

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 (HNO<sub>3</sub>)

Line 206: sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)

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

Line 288-289: phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>)

Line 460: potassium oxide (K<sub>2</sub>O)

**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>*

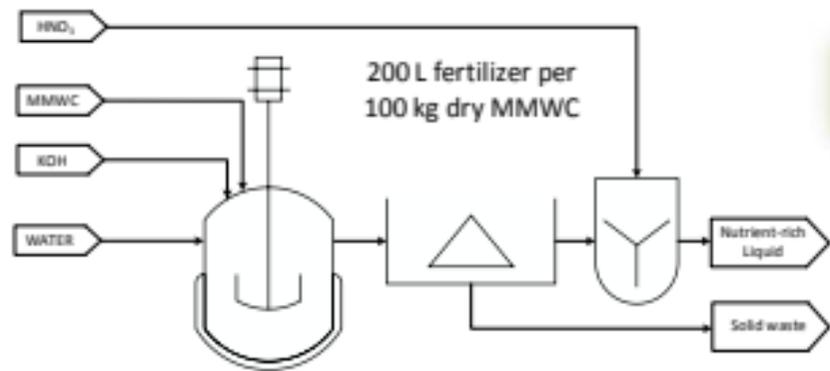
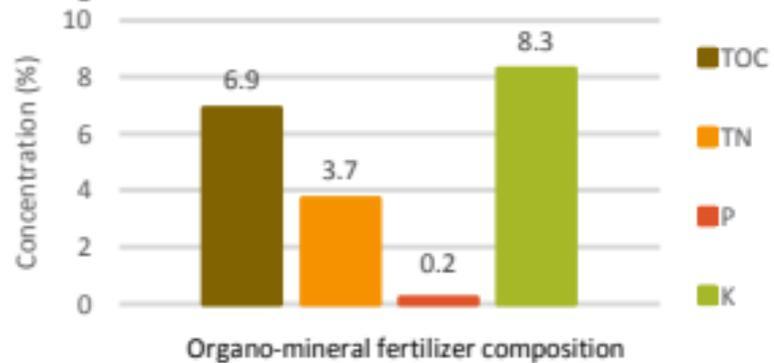
Ozkaynak Kanmaz was replaced by Kanmaz, E.O. in the manuscript and References section.

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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21 **Word count: 8119**

22 **Abstract**

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

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

## 47 **Keywords**

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

## 50 **1. Introduction**

51 **Soil organic carbon** (SOC) is an essential compound for agriculture. SOC  
52 improves physical soil conditions, nutrient retention, bacterial diversity, and  
53 fertility. Moreover, SOC has a primal relevance for the mitigation of global  
54 warming. Small losses in SOC significant impacts on **carbon dioxide (CO<sub>2</sub>)**  
55 concentration in the atmosphere (Matschullat et al., 2018). A typical organic  
56 carbon source is the application of humic substances, which can be used in  
57 agricultural lands to enhance plant growth and water holding capacity as well as  
58 for their bactericidal and fungicidal properties (**Kanmaz, 2019**).

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

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

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

77 The EU produced nearly 250 Mt of municipal solid waste per year, 486 kg per  
78 capita (Eurostat, 2019b). Mechanical biological treatment (MBT) is the most  
79 widespread alternative for processing mixed municipal waste. In 2017, there  
80 were about 570 MBT plants throughout Europe, with a treatment capacity of 55  
81 Mt (Ecoprog, 2017). The organic fraction of municipal waste recovered in MBT  
82 is usually stabilized through composting. The resulting stabilized residue is of  
83 low quality, and the application of the European regulations will restrict its use in  
84 agriculture as an end-product fertilizer (European Commission, 2018a). So, if no  
85 agricultural use is envisaged, such bad quality compost will be disposed of in  
86 landfills (Ribeiro et al., 2017). Landfill restrictions will be significantly  
87 strengthened to reflect the EU's ambition to shift to a circular economy. By 2035  
88 the amount of municipal waste landfilled should be lower than 10% of the total  
89 quantity (by weight) generated (European Commission, 2018b). Thus, the  
90 development of alternatives for valorization of MMWC from MBT plants is an  
91 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

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

## 127 **2. Materials and Methods**

### 128 2.1. Raw material

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

### 132 2.2. Extraction

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

140 supernatants were carefully recovery through filtration (Filter-lab 1300/80 0.45  
141  $\mu\text{m}$ , Filters AOIA S.A., Spain) and stored at 4°C until being analyzed.

142 Experiments were performed in duplicate.

### 143 2.3. Optimization based on Taguchi experimental design

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

151 A series of preliminary experiments were carried out to simplify the optimization  
152 of nutrient extraction conditions through a Taguchi experimental design. The  
153 influence of the type of solvent (water or 0.5 M KOH), agitation (100, 200 and  
154 300 rpm) and temperature (30, 45 and 60 °C) was studied. All other parameters  
155 remained constant: S:L ratio 1:2.5, 24 h extraction time and mixture particle size  
156 (MMWC not separated by particle sizes). From the preliminary experimental  
157 results, the most critical factors regarding nutrient extraction were identified and  
158 used to build a Taguchi experimental design.

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

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

164 concentrations in the extracts. Four factors, with three different levels, were  
165 selected in the experimental design. The factor and levels were: A = S:L ratio  
166 (1:2.5, 1:10, 1:20; dimensionless), B = solvent (distilled water, 0.5 M KOH, 1 M  
167 KOH), C = time (24, 48, 72 h) and D = particle size (< 1 mm, mixture, > 1 mm).  
168 The experiments were carried out in duplicate, leading to a total of 18 runs.

169 Finally, in order to verify the results obtained in the experimental design, a  
170 confirmatory run was carried out under the optimal conditions obtained in the  
171 Taguchi design, varying only the particle size of the raw material (<1 mm,  
172 mixture, > 1 mm).

#### 173 2.4. Phytotoxicity study

174 The germination test determinates the phytotoxic effects of organic extracts  
175 from MMWC for agriculture use. Zucconi et al. (1981) developed a method of  
176 phytotoxicity analysis through seed germination and plant growth, being  
177 evaluated through the germination index (GI). If the GI ranges between 80 and  
178 100%, it means that germination is not affected by phytotoxic substances. In the  
179 interval of 50 to 80%, phytotoxic substances affect germination moderately.  
180 Finally, values lower than 50% means that there is a considerably amount of  
181 these substances.

182 In this case, the seeds chosen were *Lepidium sativum*. Germination tests were  
183 conducted by evenly spacing ten seeds in a Petri dish containing a filter paper  
184 (Filter-lab 1300/80 0.45 µm, Filters AOIA S.A., Spain) as support. Firstly, the  
185 organic extract without dilution was adjusted to pH 6.5 with nitric acid (HNO<sub>3</sub>)  
186 69% (3 mL per 100 mL of extract). Subsequently, 25 mL of distilled water  
187 (control) or the organic extract without dilution or water diluted to 1/10, 1/100,

188 1/1000, and 1/10000 were added to the Petri dish. Each test was carried out in  
189 triplicate. The Petri dishes were then incubated under dark conditions at 27 °C  
190 for 120 h. After that, germinated seeds were counted, and the root and shoot  
191 lengths were measured. The relative seed germination (RSG) and the relative  
192 root growth (RRG) indexes were calculated. The values of RSG and RRG allow  
193 the GI to be determined by the following equations (Eq. 1-3), according to  
194 Tiquia et al. (1996).

$$195 \quad RSG (\%) = (\text{number of seeds germinated in liter extract}) / (\text{number of seeds} \\ 196 \quad \text{germinated in control}) * 100 \quad (1)$$

$$197 \quad RRG (\%) = (\text{mean root length in liter extract}) / (\text{mean root length in control}) * 100 \quad (2)$$

$$198 \quad GI (\%) = (RSG) * (RRG) / 100 \quad (3)$$

## 199 2.5. Analytical methods

### 200 2.5.1. Solid samples

201 The dried samples of MMWC were sieved to determinate the particle size  
202 distribution (sieves CISA ISO-3310.1 and .2). The humidity and volatile solids  
203 (VS) were determined by gravimetry (at 100 °C and 550 °C, respectively).  
204 Elementary composition (carbon and nitrogen contents) was analyzed by a  
205 LECO CHN-2000 analyzer (LECO Instruments, Spain). Phosphorus was  
206 characterized by wet digestion with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and HNO<sub>3</sub> followed by  
207 phosphorus measurement in extracts by spectrophotometry (HITACHI UV 2000  
208 spectrophotometer, Hitachi Healthcare Americas, United States) according to  
209 the molybdenum blue method (APHA, 2012). Macro, micronutrients and heavy  
210 metals were analyzed by ICP Optical Emission Spectrometry (ICP-MS with  
211 Agilent HP 7500c Octopolar Reaction System, Agilent, United States) and ICP

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212 Mass Spectrometry (Atomic emission spectrophotometer ICP-OES Radial  
213 Simultaneous Agilent 725-ES, Agilent, United States) after microwave digestion  
214 (Milestone Ultrawave, Milestone, Italy) for 10 min at 250 °C with 2 mL HNO<sub>3</sub>.

#### 215 2.5.2. Liquid samples

216 TOC was determined by a TOC-V 5000 analyzer (Shimadzu, Japan). Total  
217 Kjeldahl nitrogen (TKN) was analyzed by acid digestion with H<sub>2</sub>SO<sub>4</sub> and  
218 distillation (KjelFlex K-360 distillatory, BUCHI, Mexico) and ammonium ion  
219 (NH<sub>4</sub><sup>+</sup>) was characterized by distillation without previous digestion (APHA,  
220 2012). Nitrate ion concentrations (NO<sub>3</sub><sup>-</sup>) were obtained by liquid  
221 chromatography with an ICPak™ Anion HC column (Waters, United States)  
222 coupled with a conductivity detector (Waters 432) feeding 2.0 mL/min of a  
223 borate/gluconate/acetonitrile solution as eluent at 30 °C. Samples were filtered  
224 through a 0.22 µm membrane before injection. Organic nitrogen (ON) was  
225 obtained by the difference between TKN, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>. Phosphorus, macro  
226 and micronutrients, and heavy metals were analyzed as previously described in  
227 section 2.5.1.

#### 228 2.6. Data analysis

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

235 **3. Results and discussion**

236 3.1. Characterization of the raw material

237 The physicochemical characteristics of the MMWC were firstly analyzed.  
238 Regarding the particle size, the 0.04% of MMWC had a particle size greater  
239 than 20 mm; the 0.76% was between 10 mm and 20 mm, the 4.18% was  
240 between 5 mm and 10 mm, the 46.13% was between 1 mm and 5 mm, and the  
241 rest was under 1 mm.

242 The composition of MMWC was compared with previously published data on  
243 the characteristics of compost obtained from municipal waste in Italy (Cesaro et  
244 al., 2019) and the data published by Lin et al. (2018a). Comparing the  
245 characteristics (Table 1), it can be seen that the OM content of the MMWC  
246 (543.2 g/kg) compares well with the values reported by Lin et al. (2018a) for  
247 municipal compost. TOC content (287.2 g/kg) is also within the typical range  
248 reported. Analyzing the primary and secondary nutrients, total nitrogen (TN),  
249 phosphorus (P) and potassium (K) contents (21 g TN/kg, 6.5 g P/kg and 15.5 g  
250 K/kg) are within the range of the values reported for MMWC. Calcium  
251 concentration (69.2 g/kg) was above the maximum expected value (50 g/kg),  
252 whereas magnesium and sodium exhibited concentrations within the expected  
253 intervals. Therefore, due to its composition, the MMWC used in this study is a  
254 potential source of organic carbon and other nutrients, which can be recovered  
255 to obtain liquid fertilizers.

256 Table 1. Comparison of the composition of different MMWCs.

Parameters	Units	MMWC (this work)	Cesaro et al. (2019)	Lin et al. (2018a)
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pH		7.1	7.07	7.1-8.5
Moisture <sup>(a)</sup>	%	23.5	18.8	--
Ash content <sup>(a)</sup>	%	35.0	--	--
<b>Organic compounds <sup>(b)</sup></b>				
OM	g/kg	543.2	--	330-720
TOC	g/kg	287.2	245	280-380 <sup>(c)</sup>
Acid Lignin	g/kg	344.8	--	--
Cellulose	g/kg	137.7	--	--
Hemicellulose	g/kg	22.8	--	--
<b>Principal and secondary nutrients <sup>(b)</sup></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
<b>Micronutrients and heavy metals <sup>(b)</sup></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

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

258 <sup>(a)</sup> Total weight basis.

259 <sup>(b)</sup> Dry weight basis.

260 <sup>(c)</sup> Referred to **TC**.

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

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

### 270 3.2. Preliminary experiments

271 Preliminary experiments were carried out to analyze the effect of extraction  
 272 parameters such as type of solvent used (water or 0.5 M KOH), agitation (100,  
 273 200 and 300 rpm) and temperature (30, 45 and 60 °C) on the extraction of  
 274 organic carbon and nitrogen from MMWC. The S:L ratio was set at 1:2.5 to  
 275 check if maximum TOC and TKN concentrations reached in the extract could  
 276 comply with EU requirements for liquid organo-mineral fertilizers. Results from  
 277 the preliminary experiments are shown in Table 2.

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

Type of solvent	T (°C)	$\omega$ (rpm)	Concentrations (g/L)		Extraction yield (%)	
			TKN	TOC	TKN	TOC
<b>(A)</b>						
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>(B)</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
<b>(C)</b>						
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

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283 *3.2.1. Effect of the extraction solvent*

284 The effect of extraction solvents (water and 0.5 M KOH) was studied. When the  
285 extraction was conducted with water, the TOC and TKN concentrations were  
286 17.2 g/L and 2.4 g/L, respectively. However, when 0.5 M KOH was used as  
287 extractant, the concentrations increased significantly to 56.5 g TOC/L and 5.2 g  
288 TKN/L. In contrast, the concentrations of phosphorus expressed as **phosphorus**  
289 **pentoxide (P<sub>2</sub>O<sub>5</sub>)** did not exceed 0.04 g/L in the aqueous extracts and 2 g/L in  
290 the KOH extracts (**data not shown**). The concentrations of nutrients extracted  
291 with 0.5 M KOH were 3.5-fold higher than those reached when water was used  
292 as a solvent. These results agree with those previously reported for sewage  
293 sludge. Ma et al. (2019) observed that increasing the pH to 10 promoted the  
294 dissolution of **OM** in the form of proteins, humic, and lignin-like substances. Lin  
295 et al. (2018b) concluded that alkaline conditions could improve the solubilization  
296 of humic substances because of the reduction of particle size, making the  
297 organic particles more accessible for hydrolysis. So, the alkaline extraction is  
298 more useful to extract organic carbon and nitrogen from MMWC. Keeling et al.  
299 (2003) studied the recovery of nitrogen by extracting compost from mature  
300 green waste with water to enhance fertilizer uptake in wheat and rapeseed. The  
301 best results were obtained at a **S:L ratio** of 1:3, improving root and shoot weight  
302 by more than **65%** compared to the application of a commercial N-fertilizer.  
303 Szögi et al. (2015) studied the influence of pH on the extraction of phosphorus  
304 and nitrogen and proved that to extract phosphorus from organic waste such as  
305 pig manure, the pH must be acidic since under alkaline conditions the extraction  
306 of this compound is inefficient. However, the concentration of nitrogen extracted

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

### 315 *3.2.2. Effect of agitation*

316 Three levels of agitation (100, 200 and 300 rpm) were studied using 0.5 M KOH  
317 as a solvent. The effect of agitation on the extraction of organic carbon and TKN  
318 from MMWC (Table 2) indicates that as agitation increased up to 300 rpm, the  
319 concentrations obtained were higher (5.2 g TKN/L and 56.5 g TOC/L). However,  
320 there were no significant differences ( $p > 0.05$ ) between performing the  
321 extraction at 200 rpm and 300 rpm. Therefore, the most favorable agitation for  
322 the extraction of nutrients, in this case, was 200 rpm, obtaining under these  
323 conditions 4.6 g TKN/L and 52.9 g TOC/L (Table 2). The corresponding  
324 extraction yields were 54.9% TKN and 46.4% TOC. It should be noted that the  
325 maximum concentration of phosphorus in the extracts was lower than 2 g  
326  $P_2O_5/L$  (data not shown). Several studies have confirmed that particle-liquid  
327 mass transfer is enhanced when agitation rate increases (Pangarkar et al.,  
328 2002). However, a compromise between the improvement of nutrient  
329 concentrations and electricity costs associated with agitation has to be reached.  
330 An increase in agitation from 200 to 300 rpm allows the TOC extraction yield to  
331 be improved by 6%. However, the agitation power multiplies by a factor of 3.4

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(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

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357 (60 °C) would not be necessary, since mild temperatures (45 °C) allow to reach  
358 similar extraction yields. As it was previously observed, the maximum  
359 concentration of phosphorus in the extracts was lower than 2 g P<sub>2</sub>O<sub>5</sub>/L (data not  
360 shown). In general, an increase in temperature improves the kinetics of  
361 solubilization. However, within the range of temperatures studied, no significant  
362 differences ( $p > 0.05$ ) were observed between TOC and TKN extraction yields  
363 reached at 45 °C and 60 °C (Table 2). From the point of view of energy costs, a  
364 temperature of 45 °C is recommended to reach reasonable high nutrient  
365 recoveries. Therefore, an extraction temperature of 45 °C was chosen to carry  
366 out the design of experiments.

### 367 3.3. Taguchi methodology for optimization of extraction parameters

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

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

386 Table 3. Taguchi experimental design.  $L_9(3^4)$  orthogonal array. TKN and TOC  
 387 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

388 \*Mixture: MMWC not separated by particle size before extraction

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

400 and TOC (Figure 1). Finally, the extraction time and the particle size are the  
 401 factors with a lower contribution, which does not exceed 9% for both the TKN  
 402 and the TOC concentrations. This fact could mean that to reach adequate final  
 403 nutrient concentrations in the liquid extracts, it is not necessary separating the  
 404 MMWC by particle sizes before the extraction process. Finally, the ANOVA  
 405 analysis reveals that the contribution of the residual error of TKN and TOC is  
 406 7.39% and 11.42%, respectively. These error percentages show that the  
 407 observed variability can be attributed to the experimental errors and the  
 408 composition of the raw material.

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

Variation source	Sum of squares	Degrees of freedom	Mean Square	F-Ratio	P-Value	Contribution (%)
<b>(A)</b>						
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>(B)</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				

411  
 412 Statistical analysis reveals that the optimal combination of factors that maximize  
 413 the nutrient concentrations (7.5 g TKN/L and 67.1 g TOC/L) corresponded to  
 414 trial 3 when the fraction of particles of higher size (> 1 mm) was used.

### 415 3.4. Influence of MMWC particle size

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3 416 As it can be verified in Table 3, the combination of factors found as optimal (A1-  
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5 417 B3-C3-D3: S:L ratio 1:2.5, solvent: 1 M KOH, 72 h extraction time and particle  
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8 418 size > 1 mm) led to the highest nutrient concentrations. Accordingly, it was  
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10 419 necessary to perform a confirmatory experiment to probe the accuracy of the  
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12 420 results and to ensure if separation of the MMWC by particle sizes before  
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14 421 extraction could improve nutrient recoveries.

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18 422 To this end, the effect of particle size (< 1 mm, mixture and > 1 mm) was  
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20 423 studied under the optimal conditions. The analysis of these fractions of different  
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22 424 particle size did not show significant differences regarding the TOC and TKN  
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24 425 compositions of the initial material (data not shown). Figure 2 shows that the  
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26 426 highest concentrations of TOC and TKN are obtained when the smallest particle  
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28 427 size was used (7.8 g TKN/L and 77.7 g TOC/L). This result was expected since  
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30 428 the decrease in particle size improves the specific area of contact, and the  
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32 429 mass transfer in the extraction (Ma and Mu, 2016). Comparing the results of  
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34 430 trial 3 (7.5 g TKN/L and 67.1 g TOC/L) and those obtained in the confirmatory  
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36 431 experiment (Figure 2), particle size > 1 mm cannot be considered as an optimal  
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38 432 factor, because the nutrient concentrations were higher when the particle size  
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40 433 was smaller (particle size < 1 mm). Regarding TOC concentration, the  
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42 434 differences were significant ( $p < 0.05$ ) for mixture MMWC (69.0 g/L) and the  
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44 435 material with a particle size smaller than 1 mm (77.7 g/L). However, no  
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46 436 significant differences were observed for the TKN concentration (7.5 – 7.8 g/L).  
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48 437 Therefore, separating the MMWC by fractions of different sizes before the  
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50 438 extraction process is not recommended because the concentration of extracted  
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439 nutrients did not improve considerably. In this way, it is possible to reduce the  
440 production costs associated with the separation of the material without  
441 significantly reducing the concentrations of nutrients obtained in the extraction  
442 process.

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

### 23 448 3.5. Utilization of the organic extracts as liquid fertilizers

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

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

463 **8.3%**. Additionally, the humic acids percentage in the liquid was **47.6%**  
 464 **TOC/TOC<sub>total</sub>**, which is of the same order as those reported by De Souza and  
 465 Bragança (2018), who extracted **68.8% TOC/TOC<sub>total</sub>** from coal using 0.5 M  
 466 NaOH and S:L ratio of 1:10. On the other hand, Kanmaz (2019) performed a  
 467 subcritical water extraction of food by-products at 200 °C for 15 min, and the  
 468 recovery of humic acids was **59.2% TOC/TOC<sub>total</sub>**. The use of humic substances  
 469 provides physical, chemical, and biological benefits in soil.

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

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

Parameters	Units	Extract liquid <sup>(a)</sup>	EU Regulation
pH		6.51	--
<b>Total Organic Carbon</b>			
TOC	<b>% w/w</b>	6.9	3
Humic acids	<b>% TOC/TOC<sub>total</sub></b>	47.6	--

	Fulvic acids	% TOC/TOC <sub>total</sub>	52.4	--
1	<b>Principal nutrients</b>			
2	TN	% w/w	3.7	2
3		ON	% w/w	0.7
4		NH <sub>4</sub> <sup>-</sup>	% w/w	0.1
5		NO <sub>3</sub> <sup>-</sup>	% w/w	2.9
6	P as P <sub>2</sub> O <sub>5</sub>	% w/w	0.2	2
7	K as K <sub>2</sub> O	% w/w	8.3	2
8	<b>Secondary nutrients</b>			
9	Ca	g/kg	4.8	--
10	Mg	g/kg	0.8	--
11	Na	g/kg	2.4	--
12	<b>Micronutrients</b>			
13	Fe	g/kg	1.3	--
14	Mn	mg/kg	43.8	--
15	<b>Heavy metals</b>			
16	Cd	mg/kg	0.4	3
17	Hg	mg/kg	0.02	1
18	Ni	mg/kg	9.2	50
19	Pb	mg/kg	6.6	120
20	Cu	mg/kg	16.8	600
21	Zn	mg/kg	108.4	1500
22	As	mg/kg	1.3	40
23	Cr	mg/kg	5.3	--
24	<b>Pathogens</b>			
25	<i>Escherichia coli</i>		n.d.	0 in 25 mL
26	<i>Salmonella</i> spp.		< 10	< 1000 in 1 mL
27	484	n.d.: no detected		

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

### 488 3.6. Valorization of the solid residue after extraction

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

490 Under optimal operating conditions, the OM content of the residue is relatively  
491 high (114.72 ± 1.72 g TOC/kg). The residue contains a higher heating value  
492 (HHV<sub>v</sub>) of 7.79 MJ/kg and a lower heating value (LHV<sub>v</sub>) of 7.25 MJ/kg.

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

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

### 496 3.7. Germination test

497 Germination tests were conducted to evaluate the phytotoxicity of the nutrient-  
498 rich extract. The GI determines the maximum germination potential of the seed  
499 and evaluates the fertilizer phytotoxicity. The germination of the plant is  
500 influenced by the presence of organic acids of lower molecular weight,  $\text{NH}_4^+$ ,  
501 salinity, and heavy metals (Luo et al., 2018). Germination test results are  
502 summarized in Figure 3. The extract without dilution shows a GI of 0%, which  
503 means that the liquid could present phytotoxic substances (Nurdiawati et al.,  
504 2015). On the other hand, the 1/100 dilution resulted in a GI of around 80%,  
505 which indicates that the amount of potentially phytotoxic substances in the dilute  
506 extracts has no significant effect on germination. However, the 1/1000 and  
507 1/10000 dilutions have a GI around 70%, which could indicate that the low  
508 concentration of nutrients due to the dilution is not enough for germination of  
509 seeds.

## 510 4. Economic analysis

511 A preliminary study of the nutrient extraction process for the valorization of  
512 MMWC was carried out for determining the overall economic viability of the  
513 process. An industrial plant with a processing capacity of 300 kg/h of MMWC  
514 with a humidity of 25% w/w was selected as the basis for calculation.  
515 Considering this MMWC flowrate, the inputs were 424 L/h of water, 49 kg/h of  
516 KOH 50% w/v, and 20 L/h of  $\text{HNO}_3$  50% w/v. Taking into account the production

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

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

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

- 525 1. PCE: Equipment Cost. They were estimated with CAPCOST software.  
526 2. PPC: Physical Plant Cost.  $PPC = PCE * (1+f1+f2+...+f9) = PCE * 3.15$   
527 3. FCC: Fixed Capital Cost.  $FCC = PPC * (1+f10+f11+f12) = PPC * 1.40$   
528 4. TIC: Total Investment Cost.  $TIC = FCC * (1+f13) = PPC * 1.05$

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529 The equipments considered in the extraction process were storage tanks for  
530 raw materials and final products, extraction tanks, centrifuge, pumps,  
531 conveyors, and neutralization system with HNO<sub>3</sub>. Regarding the costs of raw  
532 materials, the following prices were considered: MMWC: 12 €/t (Resíduos do  
533 Nordeste, 2019), process water: 3.16 €/m<sup>3</sup> (Aquavall, 2017), KOH 50% w/v: 1.2  
534 €/L, and HNO<sub>3</sub> 50% w/w: 300 €/t (Sinnott, 2005). Therefore, taking into account  
535 that the yearly working hours are 8,000 h/y and that the plant will operate for 10  
536 years, the plant would make it profitable for a fertilizer sale price above 1 €/L. A  
537 net present value (NPV) of 880 k€ with an interest rate of 10% and an internal  
538 return rate (IRR) of 22% in six years was calculated.

539 The proposed industrial plant produced a fertilizer with a competitive price (1  
540 €/L). The market price of liquid organic fertilizers currently available can vary  
541 over a wide range (0.5-10 €) due to the variability in their formulation, the raw  
542 material, the production process and the size and materials used for packaging,  
543 among other factors.

## 544 **5. Conclusions**

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

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

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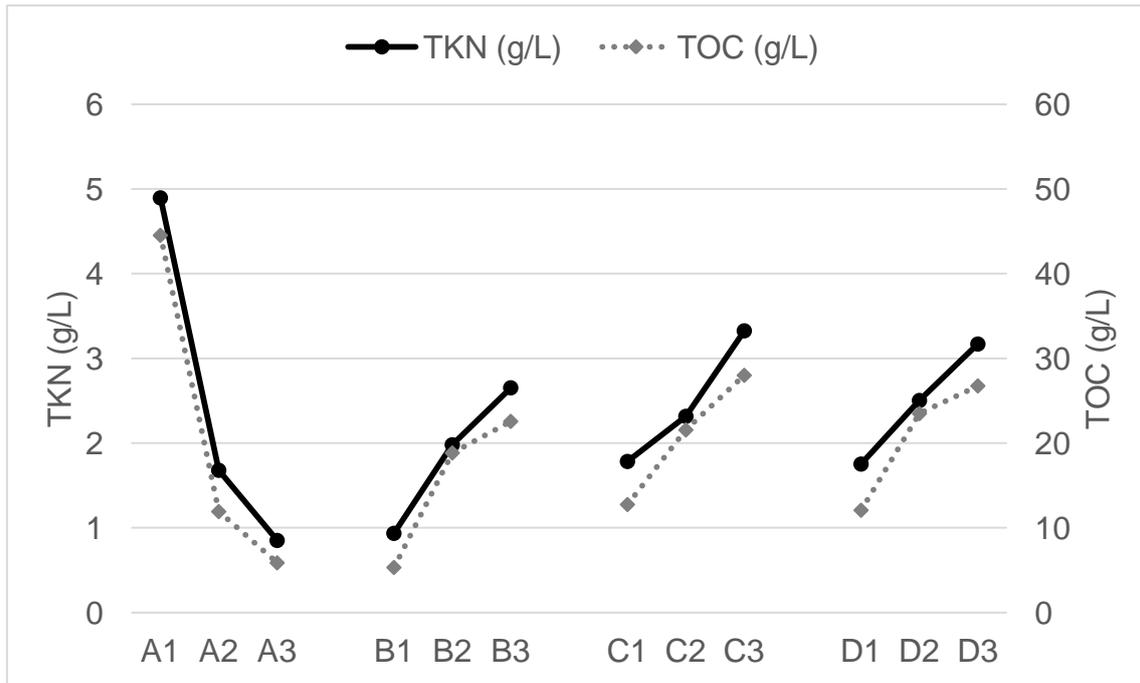
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Figure 1



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

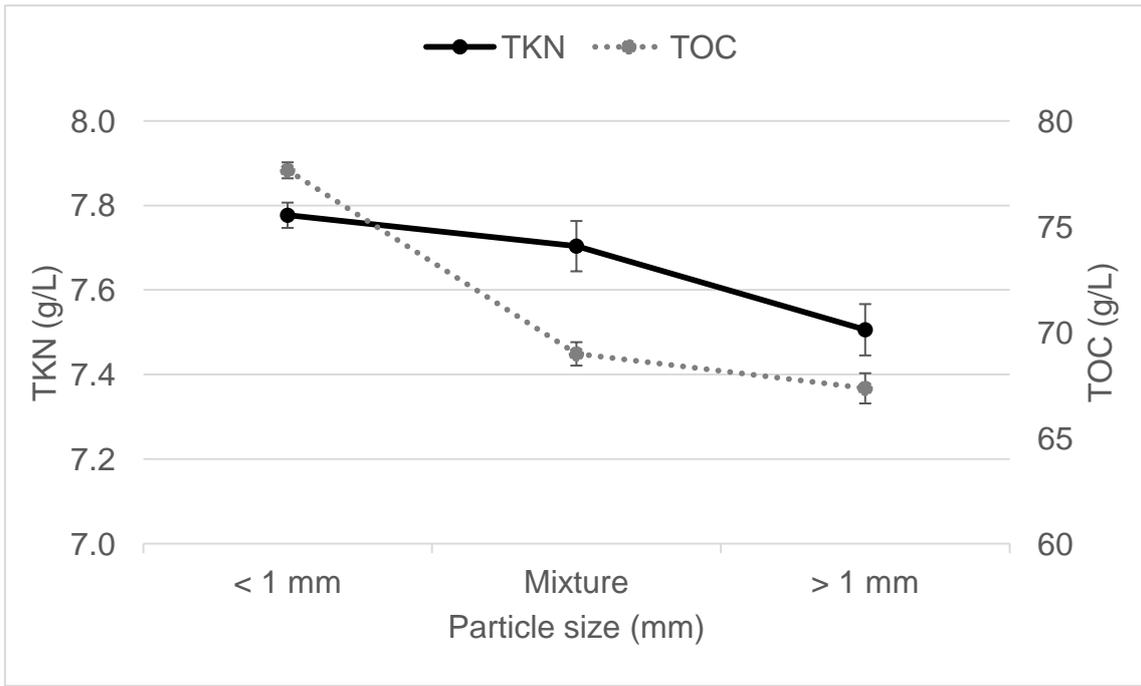


Figure 3

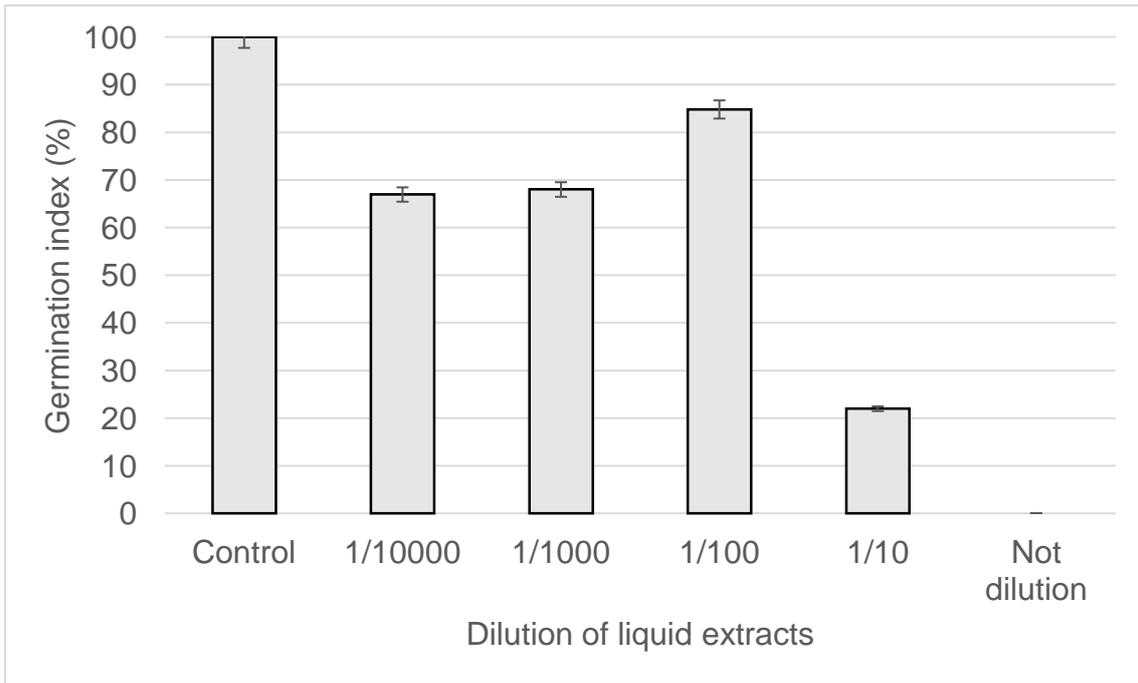


Figure 1. Taguchi experimental design. Effect of control factors (A: S:L ratio, B: solvent, C: extraction time, D: particle size) on TKN and TOC concentrations in extracts.

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.



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## 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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