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Abstract: Conventional wastewater treatments are not usually effective in the remediation of specific landfill leachates due to their high content in toxic and recalcitrant compounds. Advanced and intensive treatments are needed for the decontamination and possible recycling of these effluents. Here, the combination of advanced oxidation processes (solar photo-Fenton) and an aerobic biological reactor have been applied to treat urban landfill leachates. The effectiveness of the proposed treatment line was also evaluated considering the removal of organic microcontaminants (OMCs) identified in the different phases, which is an innovative practice. The analytical strategy included: (i) a target approach (115 analytes) by liquid chromatography-mass spectrometry (LC-MS/MS); and two suspect approaches using (ii) LC-high-resolution MS (database with >1300 compounds) and (iii) gas-chromatography-MS (database with >900 compounds). OMCs on the treated landfill leachate was reduced up to 94% of the initial concentration. 8 target compounds (mainly pharmaceuticals) out of 155 target analytes represented 85% of the OMC concentration in the raw leachate: cotinine, diclofenac, gabapentin, ketoprofen, lidocaine, mecoprop, nicotine and trigonelline. 3 non-previously reported OMCs were confirmed: di-n-nonyl phthalate, o-phenylphenol and tonalide. Leachate partially oxidized by solar photo-Fenton process can be successfully incorporated to biological systems to complete the treatment by specifically adapted biomass.

1   **Advanced evaluation of landfill leachate treatments by low and high-**

2   **resolution mass spectrometry focusing on microcontaminant removal**

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Abstract

Conventional wastewater treatments are not usually effective in the remediation of specific landfill leachates due to their high content in toxic and recalcitrant compounds. Advanced and intensive treatments are needed for the decontamination and possible recycling of these effluents. ~~In this study~~Here, the combination of advanced oxidation processes (solar photo-Fenton) and an aerobic biological reactor have been applied to treat urban landfill leachates. The effectiveness of the proposed treatment line was also evaluated considering the removal of organic microcontaminants (OMCs) identified in the different phases, which is an innovative practice. The analytical strategy included: (i) a target approach (115 analytes) by liquid chromatography-mass spectrometry (LC-MS/MS); and two suspect approaches using (ii) LC-high-resolution MS (database with >1300 compounds) and (iii) gas-chromatography-MS (database with >900 compounds). OMCs on the treated landfill leachate was reduced up to 94% of the initial ~~quantified~~ concentration. 8~~Eight~~ target compounds (mainly pharmaceuticals) out of 155 target analytes represented 85% of th~~eis~~ OMC concentration in the raw leachate: cotinine, diclofenac, gabapentin, ketoprofen, lidocaine, mecoprop, nicotine and trigonelline. ~~Three~~ 3 non-previously reported OMCs were confirmed: di-*n*-nonyl phthalate, *o*-phenylphenol and tonalide. ~~The study demonstrated that l~~Leachate partially oxidized by solar photo-Fenton process can be successfully incorporated to biological systems to complete the treatment by means of specifically adapted biomass.

Keywords: advanced oxidation processes; landfill leachate; mass spectrometry; organic microcontaminants; suspect and target analysis.

1. Introduction

Urban landfills are the destination of many products and household waste. The leachates generated in controlled landfills are collected for their subsequent treatment considering them as wastewater. As complex and hazardous wastewater, landfill leachates contain high levels of toxic and recalcitrant compounds, including organic microcontaminants (OMCs) considered highly threatening to the environment and human health [1]. Consequently, landfill leachates are not efficiently treated by conventional processes [1]. The release to the environment of leachates non-adequately treated leads to the contamination of groundwater as a first consequence [2].

In general, leachates from landfills in methanogenic phase (stabilized and relatively old) are specially bio-recalcitrant with a very low biological oxygen demand (BOD)/ chemical oxygen demand (COD) ratio (<0.1) and COD values below 3000 mg/L [3]. On the contrary, young landfills produce leachates with considerably higher CODs (around 10000 mg/L) and with low to medium biodegradability [4]. Therefore, conventional physical-chemical and biological treatments could be inefficient also for the remediation of young landfill leachates due to the possible presence of biorefractory compounds [5,6]. In consequence, new advanced remediation technologies are required to face the treatment of this type of complex wastewater. In this sense, in the last years, advanced oxidation processes (AOPs) have been applied as a potential alternative strategy to conventional technologies to treat leachates [7,8]. Among the different AOPs, the solar photo-Fenton process (SPF) is currently one of the most attractive treatments for different kinds of complex wastewaters, considering reaction rate, operating costs and environmental impact [9]. More in detail, the possible combination of a SPF process with a biological post-treatment, once improved the biocompatibility of leachates, will mean a significant reduction on related operating costs with the added value of using a renewable source of UV photons [10,11].

OMCs have been investigated in landfill leachates by applying different strategies. In general, a target approach has been used and the focus has been put on a specific class of organic contaminants [12–18]. Other studies increased the scope to several families with a variable number of monitored target compounds [7,19,20]. However, when using target strategies, there is always missed information that can only be increased with the use of non-target and screening approaches. Some studies have applied liquid chromatography coupled to low resolution mass spectrometry (LC-LRMS) and gas chromatography coupled to LRMS (GC-LRMS) in the full scan mode to carry out

screening analysis of leachates [1,21]. Other authors performed the characterization of landfill leachates using a screening strategy by GC coupled to high-resolution MS (GC-HRMS), focusing on GC-amenable OMCs [22]. However, sensitivity of HRMS instruments cannot be compared to that of the modern LRMS instruments (triple quadrupole or quadrupole-lineal ion trap, QqLIT). Bearing this in mind, the application of combined target and non-target approaches using both HRMS and LRMS and LC and GC seem to be an adequate strategy to deal with complex landfill leachates and wide-scope analyses.

The present study aims the characterization of landfill leachates which were subjected to a combination of a physical-chemical pre-treatment, an AOP (SPF) and an aerobic biological treatment. Therefore, the effectiveness of the decontamination line proposed in each separate stage was evaluated not only by monitoring classical parameters (such as COD, TOC, biodegradability, etc.), but also enriched with a detailed study including several advanced analytical techniques for OMC determination. Thus, raw leachate and the effluents obtained after coagulation/flocculation step, SPF pre-oxidation and the final aerobic biological treatments were submitted to target analysis by LC-QqLIT-MS/MS, suspect analysis by LC coupled to quadrupole-time-of-flight MS (LC-QTOF-MS, for LC-amenable compounds) and screening analysis by GC coupled to quadrupole MS (GC-Q-MS, for GC-amenable compounds). The information was used to evaluate the performance of the whole proposed treatment line with respect to OMC elimination.

2. Experimental

2.1. Leachate samples origin and characterization

Landfill leachate samples were collected from an urban landfill placed on Vila Real (North of Portugal). This landfill receives 75000 ton/year of municipal solid wastes for a population of around 50000 people and it started operating in the year 2000. The leachates used in this study presented a pH of 8.5, 95.7 NTU of turbidity and 31.4 mS/cm of conductivity. The values of COD, total nitrogen (TN) and dissolved organic carbon (DOC) were 9387 mg O_2/L, 4854 mg N/L and 1860 mg C/L, respectively. These leachates showed the following ionic concentrations: 2603 mg/L of Cl^-, 3048 mg/L of NH_4^+, 84 mg/L of NO_3^-, 117 mg/L of PO_4^{3-} and 211 mg/L of SO_4^{2-}, apart from other inorganic ions. 85% of acute toxicity (and non-biodegradable) was measured by

110 activated sludge from a municipal wastewater treatment plant (MWWTP) in a
111 respirometer (by monitoring oxygen uptake rate) [23].

112

113 *2.2. Analytical methods*

114 *2.2.1. Landfill leachate characterization*

115   DOC was measured with a Shimadzu TOC-VCN analyzer (Kyoto, Japan) after
116 filtering samples through 0.2-μm syringe-driven filters. TN was quantified in a TC-
117 TOC-TN analyzer coupled with a TNM-1 unit (model TOC-VCSH, Shimadzu). Anion
118 concentrations were determined with a Metrohm 872 Extension Module 1 and 2 ion
119 chromatography (IC) system (Herisau, Switzerland) configured for gradient analysis.
120 Cation and ammonium concentrations were determined with a Metrohm 850
121 Professional IC configured for isocratic analysis. COD was determined using
122 commercial kits (Spectroquant™, Merk, Darmstadt, Germany). Total iron concentration
123 was measured using the 1,10-phenantroline method following ISO 6332. Hydrogen
124 peroxide was analyzed by using titanium (IV) oxysulfate according to DIN 38402H15.
125 Turbidity was measured in a Hach 2100 N turbidimeter (Loveland, CO, USA). Sulfuric
126 acid (95-97%, J.T. Baker, Deventer, The Netherlands), hydrogen peroxide (35% *w/v*,
127 reagent-grade, J.T. Baker), titanium oxysulphate (1.9-2.1%, Sigma Aldrich, Steinheim,
128 Germany) and ferric chloride anhydrous (97%, Panreac, Barcelona, Spain) were also
129 used.

130

131 *2.2.2. Target analysis of OMCs by LC-QqLIT-MS/MS*

132   Samples were analyzed according to a previously validated method using the direct
133 injection (DI) technique [24]. This method was able to monitor 115 OMCs including
134 pharmaceuticals and pesticides at the ng/L level. Briefly, samples were filtered (0.22
135 μm, PTFE, Millipore, Cork, Ireland) and injected directly into the LC system. [13]C-
136 Caffeine was used as injection standard (purity >98%, Sigma-Aldrich). Appropriate
137 dilution (normally 1:10 or 1:100 *v/v*) was applied when signal saturation was observed.
138 The chromatographic separation was accomplished using a Zorbax Eclipse XDB C18
139 analytical column (50 mm × 4.6 mm, 1.8-μm particle size, Agilent Technologies, Foster
140 City, CA, USA). The LC-QqLIT-MS/MS system consisted of an Agilent 1200
141 chromatograph (Agilent Technologies) coupled to a 5500 QTRAP™ from Sciex (Foster
142 City, CA, USA) equipped with an electrospray (ESI) source (TurboIon™ Spray). The

143   Schedule MRM Algorithm™ was applied for data acquisition (SRM mode, selected

144   reaction monitoring). More information regarding the LC gradient, MS/MS conditions

145   and software has been already reported [24].

146

2.2.3. Suspect analysis of OMCs by LC-QTOF-MS

148   To increase the scope of the analysis, a subsequent determination using HRMS was

149   carried out. Filtrated leachate samples (0.22 µm, PTFE) were analyzed using a

150   previously developed strategy [25] and also a DI technique. Briefly, a suspect list of

151   >1300 OMCs frequently found in wastewater was used to investigate the presence of

152   other OMCs out of the target method [26]. The separation by LC was performed by a

153   Poroshell 120 EC-C18 column (50 mm x 4.6 mm, 2.7-µm particle size, Agilent

154   Technologies). The LC-QTOF-MS system consisted of an Agilent 1260 chromatograph

155   (Agilent Technologies) coupled to a Triple TOF 5600+™ from Sciex equipped with a

156   dual source (ESI for sample injection and atmospheric-pressure chemical ionization

157   (APCI) for calibrant delivery). The TOF-MS survey scan mode followed by four IDA

158   events (information dependent acquisition) were applied (m/z 100-2000; mass resolving

159   power, 30000). Further information about LC gradient, MS settings, screening

160   workflow and software can be found in the cited reference.

161

2.2.4. Suspect analysis of OMCs by GC-Q-MS

163   500 mL of raw samples were extracted by liquid-liquid extraction (LLE) with

164   dichloromethane and *n*-hexane (see Supporting Material for extraction method details).

165   4 different extracts with a concentration factor of 500 were obtained for each leachate

166   sample in order to cover a wide range of polarity and to extract as many OMCs as

167   possible. Samples were submitted to analysis in a GC-Q-MS system for the suspect

168   analysis of >900 compounds. The GC-MS system consisted of a 7890B chromatograph

169   interfaced to a quadrupole (Q) analyzer 5977A (Agilent Technologies, Palo Alto, CA,

170   USA). The separation was carried out with an HP-5MS UI capillary column (30 m ×

171   0.25 mm i.d. × 0.25 µm film thickness). Retention times (RT) were locked using

172   chlorpyrifos methyl. Data was acquired in the full scan mode. Identification was carried

173   out using the data from the commercial library (Agilent Technologies) [27] and the

174   NIST library 2.2 (Ed. 2014). This database includes pesticides, endocrine disruptors,

175   transformation products, musk compounds, and persistent organic pollutants (POPs),

176 among others. It applies two main features: (i) the use of locked RTs so that the RTs of

177 the compounds included in the library can be precisely reproduced when using the same

178 column; and (ii) the application of mass spectral matching and deconvolution software

179 tools. Additional information can be found in the Supporting Material.

180

181 *2.3. Treatment line for landfill leachate*

182 All studies were performed at pilot plant scale at Plataforma Solar de Almería (PSA,

183 Spain). It began with a coagulation/flocculation step by using ferric chloride anhydrous

184 at 0.5 g/L according to previous experience with similar wastewaters [11,28–30]. The

185 plant consisted of a 200-L conical mixer coupled to a filtration system: a silex filter of

186 75 μm and two microfilters of 25 μm and 5 μm. Firstly, the adjustment of the raw

187 landfill leachate at pH 5 was carried out. Then, ferric chloride anhydrous was added and

188 3 min of rapid mixing at 100 rpm for coagulation, slow mixing at 30 rpm during 30 min

189 for flocculation, and 30 min of settling provoking solids sedimentation were applied.

190 Afterwards, SPF process (pH adjusted to 2.8-3 with sulfuric acid) was studied as a

191 second stage in a compound parabolic collector (CPC) pilot plant. This pilot plant (total

192 volume: 82 L) consists of a recirculation tank with one centrifugal pump for water flow,

193 4.16 m^2 of CPC total irradiated area, being 44.6 L the illuminated volume inside the

194 solar collector absorber tubes [9]. The addition of iron was not necessary as a

195 concentration of 30 mg/L of Fe (III) remained dissolved after the

196 coagulation/flocculation step. An initial dose of 200 mg/L of hydrogen peroxide was

197 added, mixed in the dark and the CPC uncovered, starting the SPF process. Hydrogen

198 peroxide was continuously added as consumed in the reaction bulk. The temperature

199 inside the reactor was set and controlled at 35 ºC.

200 The pH of the SPF effluent was adjusted to 7 and the treatment was completed in an

201 advanced biological pilot plant based on an aerobic immobilized biomass reactor (IBR)

202 operated in continuous mode. This system is composed of a 200-L conditioning tank

203 and a 20-L recirculation tank connected to the 20-L IBR filled in with K1 supports

204 (AnoxKaldnes, diameter: 9.1 mm; surface area for biofilm growth: approximately

205 500 m^2/m^3; density 0.95 kg/dm^3) that were colonized by active sludge from the

206 MWWTP of El Toyo (Almeria) and a final 20-L collecting conic tank. Biomass

207 adsorbed on the supports generated biofilms after 4 days of feeding with influent of the

MWWTP. Dissolved oxygen (always >2 mg/L), pH and temperature were recorded automatically.

3. Results and Discussion

3.1. Landfill leachate treatment

Coagulation/flocculation pre-treatment, after the addition of 0.5 g/L of anhydrous $FeCl_3$, reduced 53% of the turbidity and eliminated 30% of the initial DOC. The subsequent SPF process was extended till a drastic reduction of toxicity and improvement of biodegradability were attained (data not shown) and thus, a combination with an aerobic biological treatment could be considered feasible to complete the treatment. At this stage, 43% of DOC was eliminated (final DOC of 750 mg/L) after 6.7 h of illumination time (Fig. 1). The partially treated landfill leachate showed an increase in biodegradability (from 0.06 to 0.62) which was enough to start the adaptation phase of an aerobic biological process and to finish the wastewater treatment. For that purpose, increasing volumes of the pre-treated landfill leachates were fed (mixed with the influent of a conventional MWWTP) to the biological reactor in batch mode. After 12 days of operation the complete adaptation of the biosystem was attained and continues mode operation in the bioreactor began. Then, feeding flow was continuously increased from 0.16 L/h until attaining the maximum treatment capacity at 0.58 L/h after 10 days of operation (2.8 days of hydraulic retention time), obtaining a maximum DOC elimination rate of 1.9 mg/L·min, and TN elimination rate of 8.3 mg/L· min.

Different studies have reported also the combination of AOPs with aerobic biological systems for landfill leachates treatment obtaining similar results to those shown in the present work. Combination of technologies previously assessed by other authors for the treatment of landfill leachate were photo-Fenton [31] or electro-Fenton [32] with biological treatments, Fenton combined with passive aerated inmobilized biomass reactor [33], photo-electro-Fenton with membrane bioreactors [34], etc., all of them showing COD elimination percentages from 83 to 98% in line with the results observed in the treatment line proposed in this work (97% of total COD removal). Specifically, better results in terms of biodegradabilidy enhancement were obtained with the application of photo-Fenton process in the proposed treatment line compared to O_3/H_2O_2 (0.29) [35].

3.2. Target analysis of OMCs by LC-QqLIT-MS/MS

Leachate and effluents from the three treatment stages were submitted to analysis (raw, coagulated-flocculated, SPF and IBR) using the method previously described to monitor 115 OMCs [24]. The main advantage of the DI technique is the absence of losses in sample extraction. The DI technique is adequate when using sensitive MS systems, such as the QqLIT analyzer, and considering that for many of these samples, a dilution stage was required. The results are summarized in Fig. 2. Different types of OMCs (up to 43 compounds, 37% of the monitored OMCs) were detected in the samples (Table A.1, Supporting Information) at concentrations from ng/L to µg/L. A significant decrease in the OMC load was observed during the treatment stages, with a total removal of 94%, from an initial total load in the raw leachate of 624.3 µg/L.

8 out of the 43 OMCs in the raw leachate represent 85% of the total load: cotinine (nicotine metabolite), diclofenac (nonsteroidal anti-inflammatory agent), gabapentin (antiepileptic drug, treatment of neuropathic pain), ketoprofen (nonsteroidal anti-inflammatory agent), lidocaine (local anesthetic, anti-arrhythmia agent), mecoprop (herbicide), nicotine (toxic alkaloid from tobacco) and trigonelline (metabolite of niacin or vitamin B3, biomarker for coffee consumption, antidiabetic properties, also found in legumes and soy products). Some of these compounds (cotinine, lidocaine and nicotine) were also reported at very high levels (>50 µg/L) and high frequency of detection in leachates from the U.S. [20] The 8 OMCs pointed out also represented 87% of the total load in the coagulated-flocculated leachate. After the SPF stage (87% of removal), three out of these eight compounds represented 98% of the total (gabapentin, nicotine and trigonelline). After the biotreatment (94% removal) still gabapentin, nicotine and trigonelline represented 60% of the load but a substantial elimination was obtained in the treatment. The concentration of gabapentin, nicotine and trigonelline was 319.5, 27.9 and 37.2 µg/L, respectively, in the raw leachate and 15.1, 4.4 and 1.1 µg/L, after the biotreatment.

It is important to notice that the SPF effluent was transferred to an aerobic IBR, being mixed during continuous operation with influent from a MWWTP for a proper adaptation of the biomass. Consequently, the leachate was diluted, firstly with the aim of adapting the biomass and secondly, to enhance the treatment efficiency. The mixture with the influent of the MWWTP provoked a small increment of the concentrations of

some OMCs in the outlet of the IBR (e.g. gabapentin, Table A.1). In any case, the degradation of OMCs from leachate throughout the different treatment stages was still higher than 94%. Indeed, from the 34 OMCs detected after the biotreatment stage (see Table A.1), 27 came from influent of the MWWTP mixed with effluent from SPF (note effluent from SPF contained only 7 OMCs), but a very low concentration levels.

In summary, the OMC content in the raw landfill leachate was clearly eliminated after the treatment line, with a final global concentration of 34.440.5 µg/L, similar to the one that can be measured in a typical urban biological effluent (primary + secondary treatment).[24,316] Despite only a few works have been published about this topic, the proposed treatment line achieved better effectiveness, in terms of OMCs degradation, than the results reported by, for instance, Rocha et al. [7]. In this study, the presence of 40 OMCs (considering GC and LC-amenable analytes) were confirmed in leachates submitted to a photo-Fenton process, with a complete elimination of only 24 OMCs.

3.3. Suspect analysis of OMCs by LC-QTOF-MS

In order to increase the scope of the OMC identification study, the suspect screening previously explained was applied. The list of >1300 chemicals were compiled in the NORMAN suspect list exchange [26] and reported in literature. After assessing the compliance with the proposed identification criteria [25], analytical standards for 4 suspect compounds were purchased for a conclusive confirmation (Table 1). The selected candidates were only found in the coagulated-flocculated and biological effluents (due to the already commented mix during continuous operation with typical influent from MWWTP). Some of them must be also present in the raw leachate, but they were not probably detected because of an intense matrix effect. No suspect compounds were found in the SPF effluent. After the injection of the reference standards, the RT could be evaluated and the following compounds were confirmed in the coagulated-flocculated effluent (Fig. A.1): chlorfenvinphos (pesticide), niflumic acid (analgesic and anti-inflammatory pharmaceutical), tramadol (opioid analgesic) and valsartan (treatment of hypertension).

The variation of the levels of the confirmed compounds after each stage of the treatment line is shown in Table A.2. Removal was >99% for chlorfenvinphos and niflumic acid, whereas lower removals were obtained for tramadol (60%) and valsartan (21%). The full scan chromatogram obtained by LC-QTOF-MS indicated a general

307   decrease of the number of features detected by the system because of the elimination of

308   the organic content, which includes OMCs (Fig. 3).

309

310   *3.4. Suspect analysis of OMCs by GC-Q-MS*

311   Leachate samples had to be extracted and transferred to an organic solvent prior to GC

312   analysis. A typical LLE scheme (Fig. A.2) was applied since it is a non-specific

313   extraction technique and it allows a high pre-concentration of the sample to increase

314   sensitivity. In this case, the Q system operating in the full scan mode is not as sensitive

315   as the QqLIT analyzer operating in the SRM mode, and a preconcentration stage is

316   mandatory. In this sense, LLE is commonly used in different EPA methods for OMC

317   determination, such as EPA Method 508A [37] (screening of polychlorinated

318   biphenyls), EPA Method 508 [38] (analysis of chlorinated pesticides) or the EPA

319   Method 1613 [39] (dioxin analysis) and it is usually considered as a reference

320   extraction technique providing a high sample preconcentration. In order to cover a wide

321   range of polarities, the combination of two different extraction solvents, such as

322   dichloromethane and *n*-hexane, was applied [22]. Besides, a sequential extraction was

323   also used to increase the extraction capability and matrix removal to reduce matrix

324   effect (Fig. A.2). Together with the samples, a reagent blank (analysis performed using

325   reagents and solvents, without sample, which is substituted by MilliQ water) was also

326   extracted to evaluate the background levels of certain substances which may be present

327   in the leachate samples, such as phthalates.

328   The selection of the suspect candidates (Table 2) was accomplished based on the

329   following criteria: (i) the compound was searched in a RT window of ± 0.350 min,

330   except for certain compounds typically showing a high peak width or groups of

331   compounds such as pesticide triadimenol (±0.700 min); (ii) a tolerance of 40% was

332   applied on the relative responses of the qualifiers ions; (iii) a minimum MS library

333   match score of 60% was required to evaluate the compound as a possible candidate. The

334   occurrence of the same suspect compound in the different extracts of the same sample

335   was also considered, as well as the peak shape, which can be very characteristic for

336   certain compounds (e.g. naphthalene). In general, the specific extractions with *n*-

337   hexane, and the sequential extractions with dichloromethane were able to show a higher

338   number of peaks. The list of 19 suspect candidates included plasticizers, pesticides,

339   PAHs and musk compounds, among others (Table 2). Commercial standards of the

selected candidates were acquired and injected in the GC-MS system. 12 out of the 19 candidates were finally confirmed in the samples with concentrations in the range from 0.02 (phenanthrene, PAH) to 4.9 µg/L (diisobutyl phthalate, plasticizer) as it is shown in Fig. 4. Some compounds showed higher concentrations in the coagulated-flocculated effluent than in the raw samples, probably due to a higher matrix effect that induce a signal suppression effect. In any case, a decrease of the OMC concentration at the end of the treatment line was obtained. As expected, phthalate compounds showed very high concentrations, due to their extended use as plasticizers. To our knowledge, 3 compounds have not been previously reported: di-*n*-nonyl phthalate (plasticizer), *o*-phenylphenol (pesticide) (Fig. A.3), and tonalide (musk compound).

When comparing the results with previous studies, the occurrence of phthalate compounds has been often reported [1]. Four phthalate compounds were detected in the raw leachate, ranging from 0.2 (butyl benzyl phthalate) to 4.9 µg/L (diisobutyl phthalate). These concentrations were comparable to the results reported by Castillo et al. [21] (di-*n*-butylphthalate, <1 µg/L) and Marttinen et al. [18] (butyl-benzyl phthalate, <1 µg/L and di-*n*-butylphthalate, <20 µg/L); Rocha et al. [7] reported considerably higher levels (<500 µg/L) for these two phthalates. In the case of PAHs, naphthalene and phenanthrene were confirmed at levels <0.05 µg/L. Similar concentrations have been reported for these two PAHs [18]. Masoner et al. [20] studied leachates with very different waste compositions, ages and geographic/climatic characteristics, and determined higher concentrations for both PAHs with median values of 5 µg/L for naphthalene and 1 µg/L for phenanthrene. DEET (*N,N*-dimethyl-m-toluamide) is a relevant compound frequently reported in leachates at high levels, e.g. 11-202 µg/L [13], 0.03-144 µg/L [19] or 70 µg/L (median value) [20]. The concentration found for DEET in raw leachate studied in this work was low (1.61 µg/L) in comparison to these previous studies. In the case of triphenyl phosphate, the concentration reported by Masoner et al. [20] is quite similar (2 µg/L). Tonalide has been pointed out as one of the most abundant musk compounds in the environment [1] but it was not detected before in former works about leachates.

It must be noticed that despite the analytical characterization included the monitoring of 115 target compounds and around 1300+900 suspect compounds, only a small percentage of the compounds included in the study were finally detected. This can be explained, firstly, because the applied analytical methods were quite generic in order to cover a wide range of OMCs. Thus, it can be expected that these conditions do not suits

With respect to the effectiveness of the treatment line to remove the confirmed compounds, a summary of the results is shown in Fig. 4 and ~~5~~A.4. The full scan chromatograms obtained for the coagulated-flocculated and SPF effluent (Fig. ~~5~~A.4) indicates a clear reduction of the area of the peaks. This can be interpreted as a general reduction of the components of the different effluents, including organic matter, OMCs and other unknown compounds that could be present. In particular, for the suspect compounds confirmed with standards, a reduction of the concentration was observed after the SPF treatment (89%), with an elimination of 92% considering the complete treatment line (Fig. 4). The remaining concentration of di-*n*-nonyl phthalate was somehow high in the SPF effluent (1.18 µg/L) (Table A.3), despite a substantial elimination of 81% compared with the initial load.

4. Conclusions

The detailed analysis of the leachates obtained after each stage of the treatment line confirmed that a clear reduction of the OMC content was obtained. The results of the target analysis by LC-QqLIT-MS/MS are the most relevant due to the number of monitored and quantified compounds (115) and indicated a reduction of the 94% of the initial OMC load (from the raw to the IBR effluent). The additional suspect analysis by LC-QTOF-MS and GC-Q-MS permitted to evaluate 16 compounds not determined by LC-QqLIT-MS/MS, demonstrating that they were also eliminated in the range from 21% to >99%. LC-QTOF-MS and GC-Q-MS also revealed the presence of non-previously reported OMCs in leachates (di-*n*-nonyl phthalate, *o*-phenylphenol, and tonalide). It has been demonstrated that raw leachate treated by coagulation/flocculation and SPF can be successfully incorporated to a conventional aerobic biological treatment after the specific adaptation of the activated sludge. The overall elimination of the quantified OMCs was 94%. Therefore, leachate treatment based on the combination of different steps (solid separation, advanced oxidation and adapted biotreatment) could be successful not only in COD removal and toxicity reduction, but also in a substantial

406 OMC elimination that deserves to be demonstrated by a proper advanced analytical
407 technique train.
408

409 **Acknowledgements**

415

416 **Appendix A. Supplementary data**

417 Supplementary material related to this article can be found in the online version.
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419

420 **References**

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Figure captions

Fig. 1. DOC elimination throughout the solar photo-Fenton and continuous aerobic biological treatments. H_2O_2 consumption during SPF and TN decrease along the biotreatment are also shown.

Fig. 2. Summary of the results obtained in the target analysis by LC-QqLIT-MS/MS: total OMC load (µg/L), percentage of removal and number of detected OMCs.

Fig. 3. Comparison of the total ion chromatograms (TIC) obtained in the full scan mode by LC-QTOF-MS of raw and treated leachate (coagulated-flocculated, photo-Fenton and aerobic immobilized biomass reactor (IBR) effluent).

Fig. 4. Evolution of the concentrations of the OMCs confirmed by the suspect analysis using GC-Q-MS.

~~**Fig. 5.** Comparison of the total ion chromatograms (TIC) obtained in the full scan mode by GC-Q-MS of coagulated-flocculated and solar photo-Fenton effluent (total area is also shown).~~

Table 1
Summary of the results obtained in the suspect analysis by LC-QTOF-MS.

Leachate	Compound	Formula [M]	RT^a (min)	$[M+H]^+$ (m/z)	Mass error (ppm)	IRD^b (%)	MS/MS library score (%)	>2 PIs^c (<5 ppm)	Standard purchased	Confirmed by standard
Coagulated-flocculated effluent	Chlorfenvinphos	$C_{12}H_{14}Cl_3O_4P$	10.37	358.9768	-2.6	1.7	Sciex (97) Massbank (99)	Yes	Yes	Yes
	Niflumic acid	$C_{13}H_9F_3N_2O_2$	9.77	283.0688	-0.8	3.1	Sciex (93) Massbank (89)	Yes	Yes	Yes
	Tramadol	$C_{16}H_{25}NO_2$	5.94	264.1958	-1.1	2.7	Sciex (90) Massbank (99)	Yes	Yes	Yes
	Valsartan	$C_{24}H_{29}N_5O_3$	8.95	436.2343	-0.2	0.6	Sciex (91) Massbank (99)	Yes	Yes	Yes
IBR^d effluent	Tramadol	$C_{16}H_{25}NO_2$	5.93	264.1958	-0.1	0.6	Sciex (99) Massbank (99)	No	Yes	Yes
	Valsartan	$C_{24}H_{29}N_5O_3$	8.95	436.2343	0.7	3.0	Massbank (73) Chemspider (90)	Yes	Yes	Yes

^{a}RT: retention time; ^{b}IRD: isotopic ratio difference; ^{c}PI: product ion; ^{d}IBR: Aerobic immobilized biomass reactor.

Table 2
Summary of the results obtained in the suspect analysis by GC-Q-MS (data shown for the coagulated-flocculated effluent).

Compound	Stage of the leachate treatment	Type of compound	Previously reported in leachates	Formula [M]	RT[a] (min)	MS library match (%)	Standard purchased	Confirmed by standard
Bisphenol A	C/F[b]	Plastizier	YES	$C_{15}H_{16}O_2$	23.92	89	YES	NO
Butyl-benzyl phthalate	C/F	Plastizier (EPA[c] Priority list)	YES	$C_{19}H_{20}O_4$	27.15	88	YES	YES
Chrysene	C/F	PAH[d] (POPs[e], EPA Priority list)	YES	$C_{18}H_{12}$	28.44	<50	YES	NO
2,4-Dichlorophenol	C/F	Intermediate (EPA Priority list)	YES	$C_6H_4Cl_2O$	5.23	80	YES	YES
DEET[f]	Raw, C/F, SPF[g], IBR[h]	Insect repellent	YES	$C_{12}H_{17}NO$	9.82	97	YES	YES
Diisobutyl phthalate	C/F	Plastizier	YES	$C_{16}H_{22}O_4$	15.95	91	YES	YES
Di-*n*-butyl phthalate	C/F	Plastizier (EPA Priority list)	YES	$C_{16}H_{22}O_4$	18.43	90	YES	YES
Di-*n*-nonyl phthalate	Raw, C/F, SPF, IBR	Plastizier	NO	$C_{26}H_{42}O_4$	33.92	83	YES	YES
Diphenylamine	C/F	Pesticide	YES	$C_{12}H_{11}N$	10.51	90	YES	YES
Fluorene	C/F	PAH (POPs, EPA Priority list)	YES	$C_{13}H_{10}$	9.93	79	YES	NO
Hexachlorobenzene	C/F	Pesticide (POPs, EU[i] Priority list)	YES	C_6Cl_6	12.38	<50	YES	NO
Naphthalene	C/F	PAH (POPs, EPA Priority list, EU Priority list)	YES	$C_{10}H_8$	5.39	65	YES	YES
Naphthalic anhydride	C/F	Pesticide	NO	$C_{12}H_6O_3$	20.13	73	YES	NO
Phenanthrene	Raw, C/F	PAH (POPs, EPA Priority list)	YES	$C_{14}H_{10}$	13.82	82	YES	YES
o-Phenylphenol	C/F	Pesticide	NO	$C_{12}H_{10}O$	8.80	87	YES	YES
Pyrimethanil	C/F	Pesticide	NO	$C_{12}H_{13}N_3$	14.14	72	YES	NO
Sulfur (S8)	C/F	Pesticide	YES	-	20.05	55	YES	NO
Tonalide	Raw, C/F, SPF, IBR	Musk compound	NO	$C_{18}H_{26}O$	10.96	80	YES	YES
Triphenyl phosphate	C/F	Flame retardant, plastizier	YES	$C_{18}H_{15}O_4P$	27.71	83	YES	YES

[a]RT: retention time; [b]C/F: coagulated-flocculated effluent; [c]EPA: Environmental Protection Agency; [d]PAH: polycyclic aromatic hydrocarbon; [e]POP: persistent organic pollutant; [f]DEET: *N,N*-Dimethyl-m-toluamide; [g]SPF: effluent from solar photo-Fenton; [h]IBR: effluent from aerobic immobilized biomass reactor; [i]EU: European Union.

Figure 4
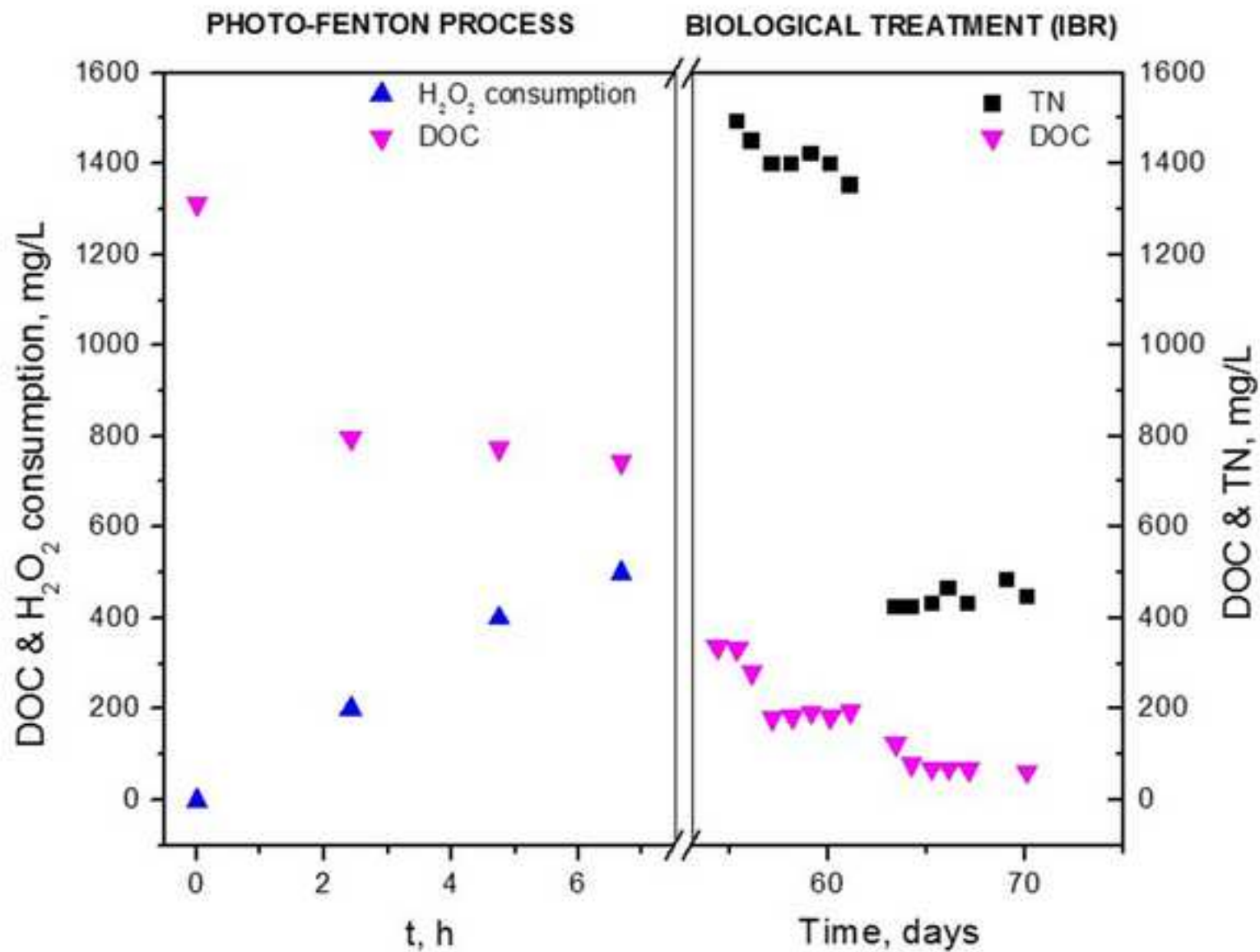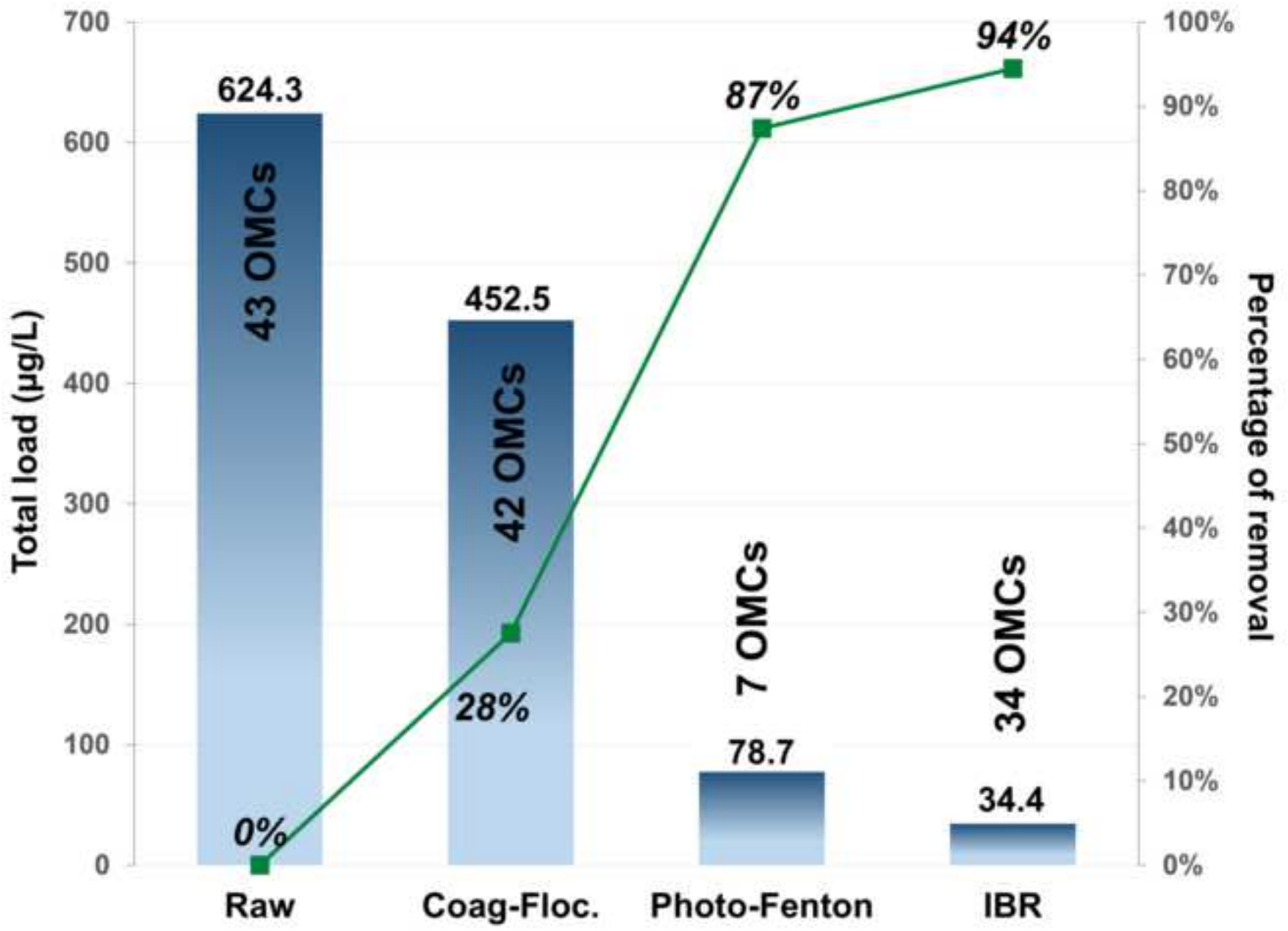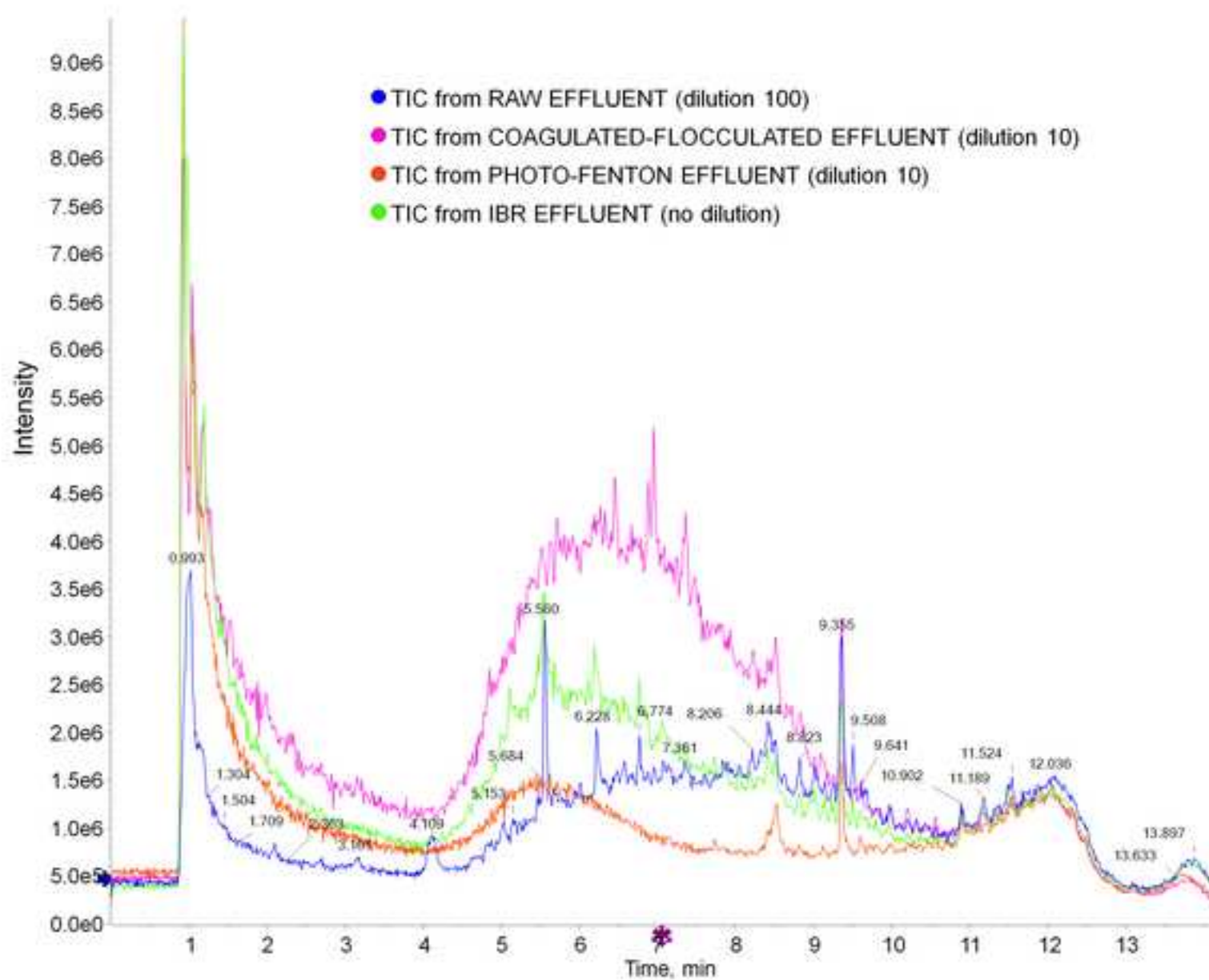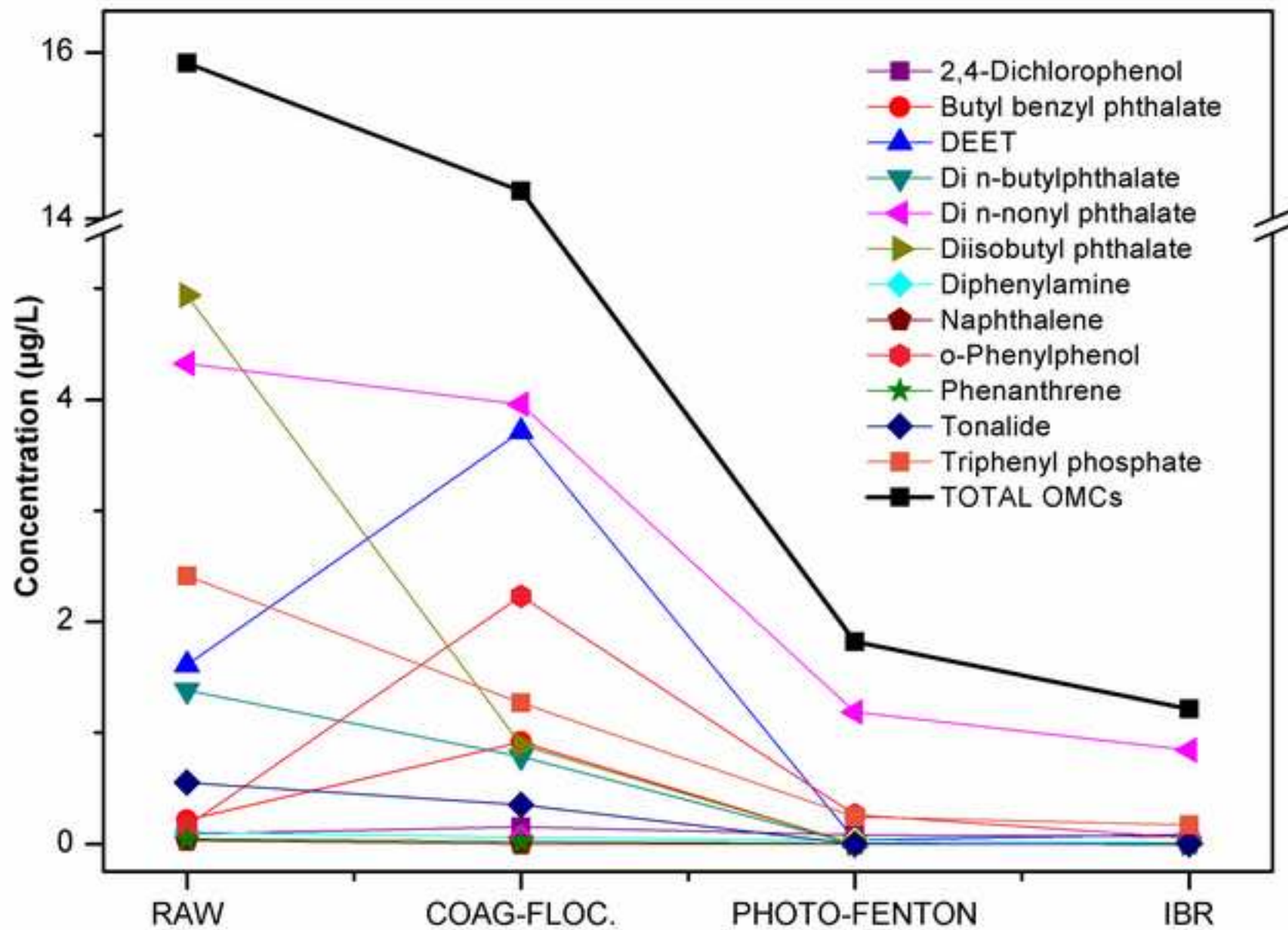
Highlights

- Addition of landfill leachates treated by solar photo-Fenton to biological systems.
- Treatment effectiveness: evaluation of organic microcontaminant (OMC) removal.
- Evaluation using target and suspect analysis by LC-MS/MS, LC-QTOF-MS and GC-MS.
- Treated leachate: reduction of 94% of the initial quantified OMC concentration.
- Detection of 3 non-reported OMCs: di-*n*-nonyl phthalate, *o*-phenylphenol and tonalide.

STATEMENT OF NOVELTY

This study describes the development of a specific treatment for landfill leachates using a solar photo-Fenton process to reduce toxicity and increase biodegradability, and a subsequent biological treatment. The treatment effectiveness was evaluated considering organic microcontaminant removal, which is highly novel regarding the few related works. This information is also relevant for the potential design of specific treatments for leachates. A combined target and suspect strategy were applied using low and high-resolution mass spectrometry tools. The treated leachate shows a reduction of 94% of the initial quantified OMC concentration. 3 non-reported OMCs were detected: di-*n*-nonyl phthalate, *o*-phenylphenol and tonalide.

Revised Supplementary Material

Click here to download Supplementary Material: Revised Supplementary_Material.pdf

Revised Graphical Abstract
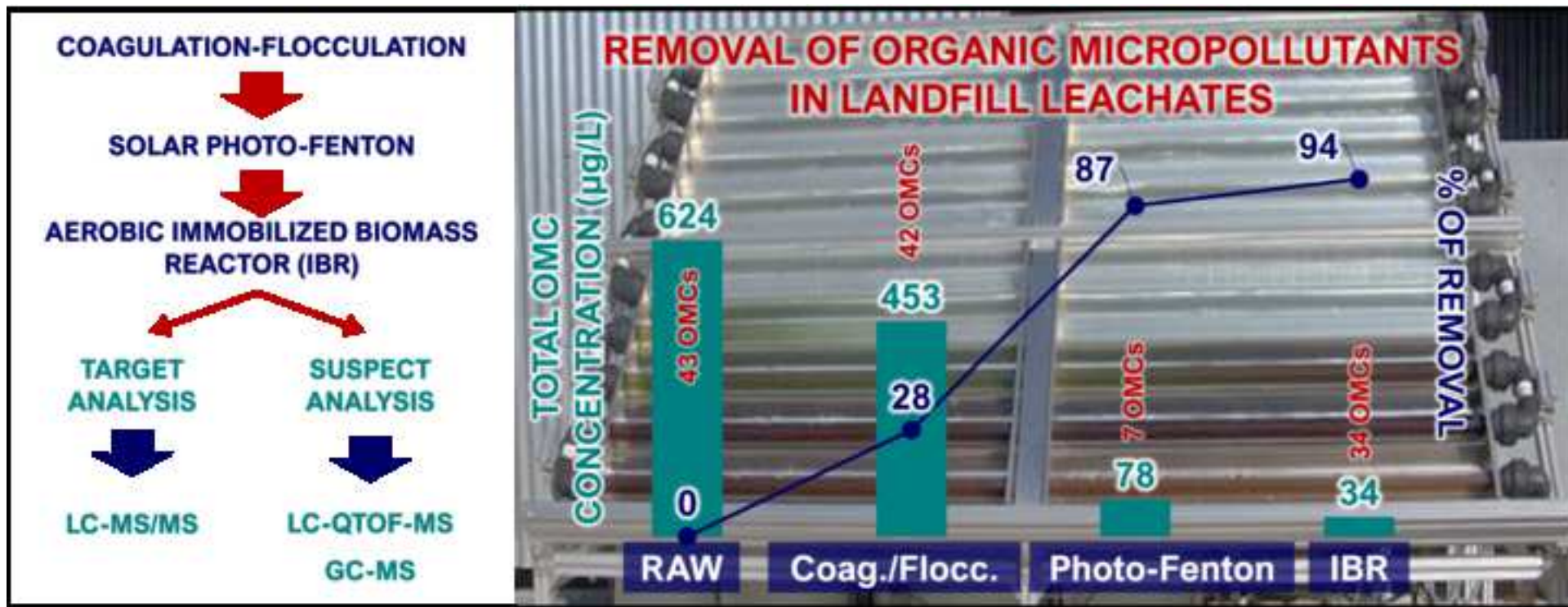
1   **Abstract**

2   Conventional wastewater treatments are not usually effective in the remediation of

3   specific landfill leachates due to their high content in toxic and recalcitrant compounds.

4   Advanced and intensive treatments are needed for the decontamination and possible

5   recycling of these effluents. ~~In this study~~Here, the combination of advanced oxidation

6   processes (solar photo-Fenton) and an aerobic biological reactor have been applied to

7   treat urban landfill leachates. The effectiveness of the proposed treatment line was also

8   evaluated considering the removal of organic microcontaminants (OMCs) identified in

9   the different phases, which is an innovative practice. The analytical strategy included:

10   (i) a target approach (115 analytes) by liquid chromatography-mass spectrometry (LC-

11   MS/MS); and two suspect approaches using (ii) LC-high-resolution MS (database with

12   >1300 compounds) and (iii) gas-chromatography-MS (database with >900 compounds).

13   OMCs on the treated landfill leachate was reduced up to 94% of the initial ~~quantified~~

14   concentration. 8~~Eight~~ target compounds (mainly pharmaceuticals) _out of 155 target_

15   _analytes_ represented 85% of th~~eis~~ OMC concentration _in the raw leachate_: cotinine,

16   diclofenac, gabapentin, ketoprofen, lidocaine, mecoprop, nicotine and trigonelline.

17   ~~Three~~ 3 non-previously reported OMCs were confirmed: di-n-nonyl phthalate, o-

18   phenylphenol and tonalide. ~~The study demonstrated that l~~Leachate partially oxidized by

19   solar photo-Fenton process can be successfully incorporated to biological systems to

20   complete the treatment by means of specifically adapted biomass.

21