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Integrated biochemical and chemical processing of municipal bio-waste to obtain bio based products for multiple uses. The case of soil remediation

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Wastes to clean waste. Urban biowastes-derived biopolymers to wash soil contaminated by heavy metals from industrial factory.

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ABSTRACT

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Municipal biowaste (MBW) provide a range of polymeric biosurfactants (BPS) with different chemical 16 nature depending on the sourcing biowaste. Three different BPS were isolated from MBW sourced from 17 18 a waste management plant located in Pinerolo (Italy). These products had molecular weight ranging from 5 to over 750 kDa. They were characterized by the presence of aliphatic C chains substituted by 19 20 aromatic moieties and several different acid and basic functional groups. The BPS were used in aqueous 21 solution to wash soil sampled from a dismissed heavily contaminated industrial site in North Italy, containing metal pollutants. Multiple extractions on the same soil sample were performed, in order to 22 23 compare the different types of BPS with conventional commercial products (EDTA, DTPA, sodium dodecyl sulfate). The recovered washing solutions were analyzed heavy metals (i.e., Cd, Cu, Cr, Ni, Zn 24 and Pb). A new process was studied. It comprises use of the BPS solutions for washing the polluted soil 25 26 and treating the recovered solutions by acidification and membrane filtration to separate a pollutant 27 concentrate from water for further use. On the basis of the results BPS appear a valid alternative to 28 conventional processes.

30 Kevwords

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31 Biopolymers; Municipal biowaste; Heavy metals; Soil washing 32

33 Abbreviations: BPS, polymeric biosurfactants; MBW, municipal biowastes; AN, anaerobic; AE, aerobic; WWT, urban waste water treatment; LBG, landfill biogas; FORSUD, digestate from bio-34 organic (humid) fraction of solid urban waste AN reactor; HS, humic substances; V, home gardening 35 36 and park trimmings residues; F, sewage sludge; CVT230, V composted for 230 days; CVDF, 35/55/10 37 w/w/w FORSUD/V/F mix composted for 110 days; Al/Ar, aliphatic-to-aromatic C ratio; EDTA, ethylenediaminetetraacetic acid; DTPA, diethylenetriaminepentaacetic acid; SDS, sodium dodecyl 38 39 sulphate.

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41 1. Introduction

42 Heavy metals contamination in soils is widespread across the world. Soil remediation is a difficult task (Wuana and Okieimen, 2011). It relies on various reactions, such as complexation, ion exchange, 43 44 (ad)sorption and desorption, precipitation and dissolution reactions. It is affected by the soil nature and the metals' behaviour in the target environment. Heavy metals, once introduced into the soil, remain for 45 46 long time. Depending on their behaviour, they are a potential threat to the ecosystem and human health.

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53 With the growing population, industrial production and consumption of resources, the anthropogenic environmental impact has become a primary social concern. The demand for soil 54 55 treatment techniques is consequently growing. The development of new efficient economically and environmentally sustainable remediation processes has become a key research activity (Nisticò, 2017). 56 Various approaches have been suggested for the remediation of metal-contaminated sites. These include 57 58 soil washing using particle size separation and chemical extraction with aqueous solutions of surfactants 59 and mineral acids (Kuhlman and Greenfield, 1999) and/or chelating compounds (Leštan et al., 2008). Sodium dodecyl sulphate (SDS; Ahmadi et al., 1995), ethylenediaminetetraacetic acid (EDTA), and 60 diethylenetriaminepentaacetic acid (DTPA) are very effective agents for this purpose. Unfortunately, at 61 the end of the treatment they remain as exogenous substances in the treated soil. Depending on toxicity 62 and recalcitrancy to biodegradability, they may end up causing a secondary environmental impact 63 64 (Chaturvedi and Kumar, 2010).

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Humic substances (HS), naturally occurring in soils, sediments, waters and fossils (Thurman, 65 1986), have also been considered for use in soil remediation (Perminova and Hatfield, 2005). They are 66 soil endogenous compounds and capable to bind metal ions by the presence of carboxylic and phenolic 67 68 groups. The complexation of trace metals by HS in soil has been much investigated (Wu et al., 2002). No adverse environmental impact is expected from these materials. Extraction of natural HS for use in 69 large scale remediation of contaminated sites is not economically viable due to the low concentration in 70 71 soil or not environmentally sustainable due to the consequent depletion of fossil sources (Montoneri, 72 2017).

73 Humic-like substances are present in composts. These materials may be produced in large 74 quantities as a mean to handle the increasing amount of biowastes from anthropogenic source. Composts may produce multiple environmental benefits. Municipal biowaste (MBW) is the most 75 sustainable worldwide abundantly available source of compost. The MBW is rich in organic matter. 76 77 Collection costs are covered by tax payers. It is defined negative cost feedstock (Sheldon-Coulson, 2011). Fermentation of MBW under controlled anaerobic and aerobic conditions allows reducing the 78 79 weight and volume of the biowaste. It produces biogas to use as fuel and stable solid material 80 containing residual recalcitrant organic matter (Montoneri, 2017). Digestates and composts may be used to amend and/or fertilize soil. Composts have been much investigated as auxiliaries for soil 81 remediation. Added to contaminated soil, they can bind metal pollutants. They have great potential to 82 reduce mobility (Geebelen et al., 2002), bioavailability and toxicity of trace elements (Smith et al., 83 2009). Compost production and use has therefore multipurpose potential environmental sustainable 84 benefits in the sectors of biowaste managements, soil fertilization and remediation (Nwachukwu et al., 85 2008). Composts may be effective by several processes, which include raising soil pH, complexation 86 87 (Brown et al., 2004), sorption, precipitation, or a combination of them (Brown et al., 2003). However, 88 their use in soil remediation has some drawbacks. Composts are insoluble in water. Exhausted composts remain in soil for long time. In the long term, due to the slow dissolution of organic matter, some 89 90 elements, in particular Cu (Temminghoff et al., 1997), which are associated to the dissolved organic 91 matter, may be mobilized (Zhou et al., 2001). The same may occur after compost organic matter 92 mineralization.

93 In the last fifteen years, anaerobic digestates and compost have also been studied as sustainable feedstock for the production of soluble value-added biopolymers. A recent review (Montoneri, 2017) 94 95 reports that MBW are a readily available cost effective source of soluble bio-organic polymeric 96 substances (BPS) bearing chemical similarities with HS (Palma et al., 2018). The BPS are obtained by 97 alkaline hydrolysis of composts from different of urban kitchen, gardening and sewage sludge wastes. 98 They contain organic and mineral matter representing the memory of the pristine biowaste 99 polysaccharide, protein, fats, lignin and mineral constituents. The organic matter is constituted by a mixture of molecules with molecular weight from 5 to over 500 kDa molecular weight. These contain a 100 wide variety of aliphatic and aromatic C chains, substituted by several acid and basic functional groups 101

bonding the mineral elements. The BPS may be obtained in a wide variety of chemical composition and properties depending on the MBW sourcing material. They have been demonstrated suitable for a wide variety of applications in the chemical industry, agriculture, and animal husbandry. Similar range of performances from the sourcing digestate and composts is not possible, due to their insolubility. Since BPS derive from natural organic matter as HS, no adverse environmental impact is expected from their use. Investigation of BPS for remediation of soil contaminated by heavy metals has not been carried out so far.

109 The present work reports the performance of three different MBW sourced BPS in the 110 remediation of a heavily contaminated dismissed italian industrial site. The BPS were obtained by 111 hydrolysis of the anaerobic digestate of food waste (FORSUD), of the compost of gardening residues (CV), and of the compost of a mix of food waste digestate, gradening residues and sewage sludge 112 113 (CVDF). In addition to the capacity of chelating metals, which was expected on basis of the content of 114 carboxylic, phenolic and amino groups, the BPS presented some intriguing chemical and physical properties, such as the solubility at pH > 4, the capacity to yield micelle with large hydrodynamic 115 diameter in solution, and the insolubility at acid pH. These properties allowed developing a new two-116 step process comprising washing the soil at pH > 4 and cleaning up the recovered washing solution by 117 118 separating the pollutants' concentrate from clean water for further re-use. Such process could not be 119 carried out with the sourcing compost and digestate of the BPS, due to their insolubility in the whole pH 120 range. The soil washing performance of BPS was therefore assessed by comparison with the 121 conventional SDS, EDTA and DTPA commercial compounds.

123 **2. Methods**

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125 *2.1. BPS and other reagents* 126

127 The investigated BPS were available from previous work (Montoneri, 2017). They were sourced from MBW sampled from the process lines of ACEA Pinerolese Industriale S.p.A. waste treatment plant 128 129 in Pinerolo (Italy). These were the anaerobic digestate of food kitchen waste (FORSUD), the compost 130 CV of gardening residues and the compost CVDF made from a mix of gardening residues, FORSUD 131 and sewage sludge. These materials were hydrolysed at pH 13 and 60 °C to yield the BPS. Solutions of 132 BPS at different concentrations were obtained by dissolving the BPS in water. All solutions were stored at 4°C before use. They were analyzed for metal content by Inductively Coupled Plasma - Atomic 133 134 Emission Spectrometer (ICP-OES) Liberty series II Varian®. The analyzed elements and selected 135 emission wavelengths were Cr 267.716 nm, Ni 231.604 nm, Cu 327.393 nm, Zn 206.200 nm, Cd 136 228.802 nm, Pb 220.353 nm, Mn 257.610 nm, Na 589.592 nm, K 766.490 nm, Ca 317.933 nm, Mg 137 285.213 nm, Al 396.253 nm, Fe 238.204 nm. Ten standard solutions were prepared by successive dilutions (from 25 μ g L⁻¹ to 30,000 μ g L⁻¹) of a multi elemental solution (1,000 mg L⁻¹). The 138 139 concentration of the trace elements (Cr, Ni, Cu, Zn, Cd, Pb) was registered in mg L⁻¹. Hereinafter, the 140 raw BPS are identified by the acronym of the sourcing material, i.e. CV, CVDF and FORSUD.

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142 2.2. Soil treatment and characterization

144 The investigated soil was sampled, sieved and analysed according to official Italian procedures 145 (Presidente della Repubblica, 2006) from a 1970 dismissed industrial site located in North Italy, near 146 the city of Novara. In this site an acetaldehyde and a sulphuric acid production plants had been 147 operating, respectively using acetylene and pyrites as starting materials, and Hg and V based catalysts.

- 148
- 149 2.3. Equilibrium partition time measurement
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151 A soil aliquot (1 g), taken randomly from the 0.5 mm sieved homogenized lot, was suspended in 5, 10, 30 ml washing solutions containing 10 g L^{-1} BPS. The suspensions were shaken for 1, 9, 12, 24, 152 31, 36, or 48 hours, in an end-over-end shaker. They were then centrifuged (15 min, 3,000 rpm), filtered 153 154 using a 2.5 µm filter paper (Whatman No. 42) and analyzed for the heavy metals' content as above. The metal content found in the after use recovered BPS washing solution was corrected for the metal content 155 contributed by the neat BPS in the solution. The calculated net amount of metal extracted from the soil 156 157 by the BPS solution was used to calculate the % metal recovery in solution referred to the starting amount of metal in soil before washing. Total organic C, in the after use recovered washing solutions, 158 159 was measured according to according Italian official methods of analysis (Ministero delle Politiche 160 Agricole, 1999b).

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162 2.4. Multiple extractions

Five consecutive washing trials were run on each soil sample (1 g) with 10 mL of the following washing solutions in deionized water: BPS (10 g L⁻¹), EDTA (6.25 mM), DTPA (5 mM), DTPA/CaCl₂ 5 mM/0.01 M, SDS (5 g L⁻¹). These washing solutions were analysed following the same procedure reported in the above section.

168 2.5. Secondary treatment of after use recovered washing solution

An aliquot (10 mL) of solutions containing the same amount of metals as the washing solutions was acidified with concentrated HCl (37%) to pH 1.5-3.0, and centrifuged (15 min., 4,000 rpm). The supernatant was analyzed for heavy metal as described above. Alternatively, the solutions were filtered under 4 bar pressure with a Millipore Stirred Ultrafiltration Cell (Amicon Bioseparations) through M-PE5-GPET membranes with 5 kDa cut-off. The permeate was analyzed for heavy metal as described above.

177 **3. Results**

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179 *3.1. BPS characterization*180

181 The BPS used for the present work were available from previous research (Montoneri et al., 2017) carried out to assess their performance in several other uses as fertilizers, supplement for animal diet, 182 surfactants and components of plastic materials. As raw hydrolysates of fermented biowaste, they 183 184 cannot be characterized as well as synthetic molecules. The number and diversity of molecules 185 composing their molecular pool makes rather hard to isolate and identify each single molecule. For 186 these products, an analytical protocol was developed including elemental analysis, 13C NMR 187 spectroscopy, molecular weight measurements, potentiometric titration and surface tension 188 measurements. This allows determining the content of mineral elements, organic C and N, and several 189 organic C moieties. Obviously, these data are not enough to assess definite unequivocal molecular 190 structures. Nevertheless, from the practical point of view they have been proven helpful to assess 191 differences between BPS sourced from different biowaste, which relate to chemical composition, 192 molecular conformation in solution and performance in investigated applications.

193 Data for FORSUD, CV and CVDF BPS have already been published (Rosso et al., 2015). Table 1 194 lists selected data, which are relevant to understand the different chemical composition, properties and 195 performance in the intended application of the investigated BPS. The aliphatic to aromatic C ratio 196 (Af/Ar) indicates the type of lipophilicity (mostly aliphatic or mainly aromatic) of the BPS. The amine 197 (NR), phenol (PhOH) and carboxylic (COOH) groups are relevant for their property to chelate metal 198 ions. The surface tension data provide hints on the solution conformation of the BPS. The data show 199 that the FORSUD and CV BPS exhibit the largest differences. The former has the lowest values for the 200 ash content and for the content of COOH acid groups, while exhibiting the highest values for the Af/Ar 201 parameter and the amine functional groups. This indicates FORSUD as the most lipophilic, aliphatic 202 and least acidic material. At the other extreme of such empirical rating chemical scale, CV has the 203 highest content of total PhOH and COOH acid groups, and the lowest amount of amine functional 204 groups. As likely consequence of its chemical composition, FORSUD exhibits the lowest CMC and 205 γ_{CMC} values. This indicates that FORSUD molecules in solution aggregate to form micelles at lower 206 concentration than the CV and CVDF molecules.

207

208 **Table 1**.

209 Chemical composition, molecular weight and surface tension data for BPS

	FORSUD	CVDF	CV
Ash, w/w % ^a	15.4	27.3	27.9
C, w/w % ^a	45.1	35.5	38.3
Af/Ar ^b	3.4	1.3	1.8
NR, % of total C ^b	9.9	7.8	7.2
PhOH, % of total C ^b	2.3	5.9	5.2
COOH, % or total C ^b	6.7	9.4	12.1
$\gamma CMC, ^{c}mN m^{-1}$	48.8	61.8	61.2
CMC, ^c g L ⁻¹	1.0	3.1	2.1

210 ^[a]Concentration values referred to dry matter. ^[b]Aliphatic (Af),), amine (NR), phenol (PhOH),

211 carboxylic acid (COOH) C content. ^[c]Critical micellar concentration (CMC) and surface tension at the 212 CMC (γ CMC).

213 Rosso et al. (2015) report also other data on the hydrolysis of MBW, which are particularly relevant 214 in relation to the objective of the present work. They show that the hydrolysis of the BPS sourcing 215 digestate and composts yields the BPS and the corresponding insoluble residue. The content of the trace metals (Cu, Ni, Zn, Cr, Pb, Hg) in the FORSUD BPS is lower than in the pristine digestate. Most of the 216 pristine metal content is recovered with the insoluble hydrolysate residue. The CVDF and CV BPS 217 218 exhibit one exception. They contain significantly more Pb than their pristine composts and insoluble 219 hydrolysate. This suggests several considerations. Trace metals are strongly bonded to the pristine 220 organic matter. The alkaline hydrolysis breaks the hydrolysable covalent bonds in the pristine organic matter, yields hydrolysed soluble molecular fragments, but is not capable to break the organo-metal 221 222 bonds in the soluble hydrolysates. The higher Pb content in the CVDF and CV BPS, compared to the 223 pristine composts and insoluble hydrolysates, may imply that the BPS obtained from the composts are 224 strong complexing agents, particularly for Pb.

Overall, the data in Table 1 indicate that all three BPS, for their chemical composition and capacity to yield micellar aggregates, have potential as trace metal sequestering agents to use in ex-situ washing of metal polluted soil.

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- 229 *3.2. Soil washing.*230

The investigated soil was a franco sandy soil/franco type. As result of the industrial activity carried on it, the soil contained high level of organic C (6.72 w/w %) and Cu (1900 ppm). The other major trace metals (Pb, Zn, Ni, Cr) were present in lower concentration (280-870 ppm).

A preliminary experiment was performed washing the soil for 24 h with the solutions of the three investigated BPS at nearly their maximum solubility concentration, i.e., CVDF and CV at 100 g L⁻¹, and

FORSUD at 50 g L⁻¹. Each BPS was investigated in the raw form, i.e. as isolated from the hydrolysis 236 237 reaction and characterized by the chemical composition data in Table 1, and in the de-ashed form 238 containing less than 1 % ash (Montoneri and Nisticò, 2019). De-ashing BPS by HCl/HF treatment (see 239 section 2.1) was carried out to free the chelating functional groups present in the pristine BPS and increase the number of these groups available to complex the trace metals present in the investigated 240 soil. The results (Fig. 1S in the supplementary material SM file) showed that, compared to the raw BPS, 241 242 the de-ashed derivatives exhibit 10-20 % higher washing efficiency. In the authors' opinion, the higher performance level of the de-ashed BPS does not justify the additional complexity of their preparation 243 244 deriving from using and handling the strong corrosive HCl and HF reagents (see section 2.1) and the 245 effort to make the process economically and environmentally sustainable. Further experiments were carried out only with the raw BPS containing 15-27 wt.% ash. 246

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Fig. 1. Metal recovery (%) in 10 g L⁻¹ CVDF solution as a function of time (hours) at different w/V soil/solution ratio: 1:5
(A), 1:10 (B), and 1:30 (C). Legend: Cu (black squares), Cr (red circles), Ni (blue up-triangles), Zn (magenta down-triangles), and Pb (green diamonds)

The BPS listed in Table 1, used at the maximum concentrations (50-100 g L⁻¹) compatible with their water solubility at pH 8, gave different results. The highest soil washing efficiency was obtained with CVDF. This material was therefore used to determine the time to reach the equilibrium partition of the metals between soil and washing solution as a function of soil/solution ratio. The first experiments were performed with a 10 g L⁻¹ CVDF solution, at three soil/solution w/V ratios. The results of the washing trials with CVDF under the above conditions are reported in Fig. 1. The data show that, in most cases, the CVDF metal recovery reaches a plateau value at 40-50 h soil/solution contact time. Generally, the plateau recovery values increase upon increasing the solution/soil ratio, as expected by
the higher amount of CVDF in contact with the soil. Based on the % recovery values, the metal affinity
for CVDF seems highest for Cu, followed by Zn, Pb, Ni and Cr.

As CVDF is a new product, to assess its value for use as auxiliary in soil washing processes, a 267 268 range of conventional commercial metal chelating agents was used under the same experimental 269 conditions for comparison. Indeed, the performance of a given chelating agent in extracting metals from 270 soil depends on the soil features and on the availability of metals. Thus, the assessment of the performance of CVDF is more fairly carried out by comparison with the well-known EDTA (Lo and 271 272 Zhang, 2005), DPTA (Hong et al., 2002), SDS (Ahmadi et al., 1995) compounds, which are referral 273 products in the field of environmental remediation. In this work, the DTPA/CaCl₂ solution was also 274 used, since it is recommended by the Italian official method (Presidente della Repubblica, 2006) to 275 assess the bioavailability of heavy metals in non-acid soils.

276 To compare performance of CVDF with EDTA, DPTA and SDS, multiple extractions (five 277 consecutive washing trials) were performed with 24 h soil/solution contact time for each trial. Usually, a solution of DTPA 5 mM is used for washing soils contaminated by heavy metals. Accordingly, in this 278 279 work, the same concentration was used, and the concentration of the other compounds and BPS were 280 calculated to have the same number of acid groups in the washing solutions as in 5 mM DTPA. Plain 281 water was used as control washing solution. The results are reported in Fig. 2. It may observed that, based on the % recovery of Cu, Pb and Zn, the performance of BPS runs more or less close to that of 282 283 EDTA and DTPA. However, in the case of Ni and Cr, CVDF yields the highest metal % recovery values. Plain water and the SDS solution appear the least efficient washing media. 284 285



Fig. 2. Effect of different extractants in multiple extraction processes (solution/soil 10 w/V ratio and 24 h contact time) for the heavy metals analyzed. Extractants: bare H₂O, SDS 5 g L⁻¹, EDTA 2 g L⁻¹, DTPA 2 g L⁻¹, DPTA/CaCl₂ 2 g L⁻¹/0.01M, and CVDF 10 g L⁻¹. Legend: Cu (black), Cr (red), Ni (blue), Zn (magenta), and Pb (green).

291 Several other washing trials were carried out with 1 and 0.1 g L^{-1} CVDF solutions at 30, 10 and 5 292 V/w solution/soil ratio and equilibrium contact time. The results are reported in Table 1S and Fig. 2S of the SM file. The highest metal recovery values were recorded for the trials with the highest solution/soil ratio and CVDF concentration in the used solution. The experimental amounts of metals recovered with the washing solutions were elaborated to calculate the specific metal absorption per unit weight of CVDF in solution. These provided useful hints on the behavior of the CVDF molecules in solutions depending on the CVDF concentration in solution and on the solution/soil ratio.

298 The data in Fig. 2S evidence a definite trend for the specific absorption of metals to increase upon 299 decreasing the CVDF concentration in the washing solution from 10 to 0.1 g L⁻¹. This appears clearly upon comparing data at constant volume/solid ratio and decreasing CVDF concentration in solution. 300 301 The only exception to this trend is the specific absorption of Cr reaching the maximum value at Cs 1 g 302 L^{-1} and decreasing at Cs 0.1 g L^{-1} . Aside from this case, the overall trend of the specific absorption to increase at lower Cs concentration can be explained with the change of the BPS solution molecular 303 304 configuration from large aggregates of macromolecules to smaller micelles where the complexing 305 functional groups are more accessible by the metal ions. There seems to be also a trend for the specific 306 absorption to increase upon decreasing the volume/solid ratio at constant Cs value. This implies 307 decreasing the CVDF/soil ratio. It must be concluded that the CVDF/soil ratio affects the interaction CVDF-soil interactions. This is a second parameter that, together with the intermolecular interactions 308 309 among the BPS macromolecules in solution, is likely to affect the BPS molecular conformation and 310 accessibility of its complexing functional groups by the soil metal ions. The available data do not allow 311 rationalizing definitely the contribution of the CVDF concentration in solution and the solution/soil 312 ratio to the CVDF soil washing performance. Given the complexity of the BPS molecular pool, it is 313 unlikely that this could be ever established by identifying the active complexing molecules, and their 314 chemical composition, solution behavior and role in sequestering metal ions. Nevertheless, further 315 experimental work could assess empirical relationships between the types of BPS and soils, and the soil 316 washing parameters, in order to optimize the process for large scale application in real operational 317 environment.

319 3.3. Secondary Treatment of After Use Washing Solutions

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321 The scope of the secondary treatment was to dewater the recovered washing solution by 322 separating a BPS-metal concentrate from clean water. Two processes were investigated by exploiting the BPS macromolecularity and insolubility at acid pH. The solutions recovered after 24 h soil washing 323 with 100 g L⁻¹ CV and CVDF, and 50 g L⁻¹ FORSUD (Fig. 1S) were treated by vertical flow membrane 324 filtration under 5 bar pressure, and alternatively by precipitation at acid pH. The two processes allowed 325 326 obtaining 95 % of the starting aqueous solution in the permeate or chloride phase, and a residual 327 slurry/wet solid phase as membrane retentate or acid insoluble BPS metal concentrate. For each metal and secondary treatment, the experimental data in Table 2 are expressed as % recovery of the metal in 328 329 the permeate or chloride liquid phase, relative to its content in the solution recovered from the primary 330 soil washing treatment. Contrary to the case of the primary soil washing treatment, in the secondary 331 treatment of the after use washing solution, the lower is the % recovery of the metal in the liquid 332 (permeate or chloride) phase, the better is the process.

333 In the case of the secondary treatment, the performance of the two processes was found dependant 334 on the type of BPS and metal present in the after use washing solution. Table 2 shows that for the metal 335 polluted FORSUD solution, and for all metals in it, the recovery in the chloride solution of the 336 acidification secondary treatment is significantly higher than in the permeate solution of the membrane 337 filtration secondary treatment. Thus, the membrane filtration treatment allows separating cleaner water 338 (in the permeate) from the BPS metal concentrate (in the retentate). The same is true in the case of the 339 after use CV washing solution, except for the Cr recovery being higher by the membrane filtration 340 treatment. The CVDF data show that for Cr and Cu, the recovery is higher by the membrane filtration 341 than by the acidification treatment. Thus, for the specific cases of Cr in the CV washing solutions, and

of Cu and Cr in the CVDF washing solution, the acid treatment allows separating a cleaner aqueous
 solution (i.e. the chloride phase separated from the insoluble BPS metal concentrate).

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345 **Table 2.** Results of the secondary treatment of the BPS solutions recovered after 24 h soil washing.

346 Percentage of heavy metals recovered in the permeate and chloride phases, relative to the metals'

content in the soil washing	solutions.				
BPS	Cu (%)	Cr (%)	Ni (%)	Zn (%)	Pb (%
CVDF Permeate ^a	42	43	51	37	37
CVDF Chloride ^b	33	13	61	59	51
CV Permeate ^a	23	19	14	30	22
CV Chloride ^b	44	3	42	65	55
FORSUD Permeate ^a	23	6	6	12	12
FORSLID Chloride ^b	62	31	46	57	54

347 content in the soil washing solutions.

^aPermeate after ultrafiltration through a membrane with 5 kDa cut-off.

349 ^bSolution obtained after precipitation with concentrated HCl.

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352 4. Discussion353

354 In this study, three MBW, sampled from different sections of a urban waste treatment plant, were 355 used as sourcing materials of humic-like polymeric biosurfactants (BPS) to be investigated as chelating 356 agents for soil remediation. As humic substances, BPS can complex metal ions through carboxyl and phenolic OH groups, thus promoting the binding and removal of heavy metal from soil. The CVDF, 357 358 possessing the highest molar fraction of acidic functional groups (Table 1), shows the highest chelating 359 capacity. The BPS are constituted by a heterogeneous molecular pool. Presumably, the C types and 360 functional groups listed in Table 1 are not homogeneously distributed over the entire molecular pool. 361 This makes rather unfeasible assessing the molecular conformations of the different molecules. Most likely, the BPS chelating capacity depends both on the total content of functional groups capable to bind 362 metal ions and on the different conformation of the different molecules in solution. 363

The behavior of BPS macromolecules in solution in the 0.2-100 g L⁻¹ concentration range has 364 been investigated (Montoneri et al., 2010) by measurements of solubility properties in solvents of 365 different polarity, surface activity, power to enhance the water solubility of hydrophobic compounds, 366 and particle size. The results suggest that in the 0.2-2.5 g L⁻¹ range an intramolecular rearrangement of 367 368 BPS macromolecules from a flat to a more spherical coil conformation occurs. At higher concentration, intermolecular interactions between pseudomicelles take place and yield large aggregates of 369 pesudomicelles. Other workers (Du et al., 2001) report that different bivalent (Xu et al., 2007) and 370 trivalent metal ions (Garg et al., 2016) in solution affect significantly the capacity to micellize and 371 372 solution conformation of the resulting molecular aggregates of typical conventional commercial surfactants, e.g., sodium dodecyl sulphate and hexadecyltrimethyl ammonium chloride. These changes 373 374 are likely to change the accessibility of the chelating functional groups by metal ions. They can well explain the dependence of the metal/CVDF specific absorption on the CVDF concentration in solution 375 376 and on the CVDF/soil ratio shown in Fig. 2S.

The BPS concentration in the washing solution and the BPS/soil ratio are two parameters of crucial importance for the economic and environmental sustainability of *ex-situ* soil washing. Low BPS concentration allow exploiting the potential total complexing capacity of the functional groups. The data in Fig. 1 show that the washing efficiency by a BPS solution at a given concentration increases upon increasing the total amount of BPS in contact with the soil. This implies using a high water volume ratio. Yet, it is not a critical factor for the process sustainability, as pointed out below by the results obtained in the secondary treatment of the washing solution.

Washing trials with multiple extractions show that Cu, Zn and Pb are extracted more efficiently than Ni and Cr, both by BPS and by the synthetic chelating agents. Noteworthy, BPS are more efficient 386 in the extraction of Ni and Cr than the synthetic chelating agents (Fig. 2), probably because other 387 processes (such as, for example, the complexation with phenolic groups) are involved. The recovery of Cu is higher with respect to the other metals. This element has a well-known ability to form chelates 388 389 with organic compounds (Kabata-Pendias, 2001). Dissolved organic matter can increase Cu mobility by 390 formation of soluble organic complexes. Consistently with the findings of other workers (Tessier et al., 391 1979), the higher extraction of Cu and Pb (Fig. 2) may be due also to the fact that these elements are in 392 more available and extractable soil fractions, while Cr is present only in residual less extractable soil 393 fractions. The system is complicated by different processes, such as competitive adsorption of other 394 metal ions or anions, competitive adsorption of metals by the organic matter in the soil, stability of the 395 complexes formed with ligands, and adsorption of the chelating agent by soil. These may contribute to 396 determine the hump-shaped patterns in Fig. 1. To better understand these processes, total organic carbon (TOC) measurements were performed in the present form for the 10 g L⁻¹ BPS washing solutions before 397 398 and after use. No significant depletion of organic carbon was found in the after use solution, compared 399 to the pristine solutions. Yet, TOC data cannot completely explain the complexity of the processes 400 involved in the kinetic behavior shown in Fig. 1. The TOC can also be influenced by a dynamic 401 exchange between the organic matter present in soil (both as natural and anthropogenic matter) and in 402 the washing solutions. Considering the complexity of the system, in addition to the diversity of metal 403 sorbing components of soil compartments as well as the polyelectrolyte nature of the BPS, the kinetics 404 of metal release cannot be directly related to a definite phenomenon.

The data in Fig. 2 show that five sequential extractions, carried out with the CVDF solution, allow washing out 40-50 % of the major elements present (Cu, Pb, Zn) and 10-15 % of the elements present in lower concentration (Ni and Cr). Increasing the number of sequential extractions will allow more cleaning of the contaminated soil by virtue of the complexation reaction

409

410 soil-M' + BPS(COOM)aq \leftrightarrows soil + M'-BPS(COOM)aq (1). 411

In this reaction, the following reagents and products are involved. The BPS(COOM)aq reagent is the BPS alkaline carboxylate prepared by the alkaline hydrolysis of the sourcing CVDF and CV compost or anaerobic FORSUD digestate.(Rosso et al, 2015). The soil-M' substrate is the soil containing the M' trace metals. The water soluble BPS carboxylate, by its complexing/chelating capacity extracts the heavy metal contaminants (M') from soil to yield the M'-BPS(COOM)aq complex and the clean soil.

417 Although separating the exhausted BPS washing soil for the soil, and repeating over and over again 418 the soil washing step (1) with fresh BPS solution, may allow more cleaning of the soil, this practice will 419 increase the volume of the collected washings, which needs to be disposed. It poses the issue of the 420 secondary treatment to separate clean water for further use from the M'-BPS(COOM)aq complex. To 421 this scope, in the present work, two alternative secondary treatments have been investigated

Due to its insolubility at acid pH, the M'-BPS(COOM)aq complex solution, separated from the clean
 soil, can be precipitated at acid pH as in step

425 M'-BPS(COOM)aq + HClaq
$$\leftrightarrows$$
 M'-BPS(COOH)solid + MClaq (2),
426

427 to yield the trace metal-BPS complex in solid form and the chloride aqueous phase.

428 Alternatively, due its macromolecular nature, the

429 M'-BPS(COOM)aq complex solution, separated from the clean soil, can be be filtered through

430 ultrafiltration membrane as in step431

- 432 M'-BPS(COOM)aq membrane filtration \rightarrow M'-BPS(COOM)retentate + permeate (3),
- 433
- to yield a slurry containing the trace metal-BPS retentate and the permeate aqueous phase.

435 Ultrafiltration of BPS has been proven to remove 94% of the water contained in the pristine BPS 436 solution (Negre et al., 2018) and recover it in the permeate phase. The same occurs in reaction (2), where water is recovered with the aqueous chloride phase. The data in Table 2 shows that both the 437 438 chloride and permeate phases contain trace metals. The metals in both phases are likely bonded to BPS 439 molecules with molecular weight lower than the membrane molecular cut off. These are water soluble 440 at acid pH and permeate through the membrane. The permeate phase recovered from step (3) contains 441 significantly less metals than the chloride phase recovered from reaction (2), with few exceptions for Cu 442 in the CVDF and CV permeate and Cr in CVDF permeate. In the present work, step (3) has been carried 443 out with membranes with 5 kDa molecular cut-off. Upon using membranes with lower molecular cut 444 off, it is more likely to obtain permeates with reduced metal content through step (3) than trace metalfree chloride solution by reaction (2). Moreover, the reaction (2) yields a salt solution which requires 445 446 further desalting treatment. Both treatments (2) and (3) yield a trace metal concentrate in the 447 precipitated solid phase and retentate slurry, respectively. These can be treated by a tertiary drying/incineration treatment to yield final concentrates containing only metals for use in the chemical 448 449 industry or landfill. However, reaction (3) should allow obtaining cleaner water for further use.

450 451

452 5. Conclusions

453 454 This paper deals with three environmental issues related to anthropogenic and industrial activities, 455 namely: i) the management of municipal biowastes, ii) the soil washing process of contaminated 456 industrial sites, and iii) the post-processing of the washing solutions.

457 The hydrolysis of municipal biowastes yields polymeric biosurfactants (BPS) with chelating 458 properties which are particularly suitable for removal of heavy metals from the contaminated soil. The 459 present work proposes a new process comprising washing soil contaminated with metal pollutants 460 using the above aqueous BPS solutions and treating the recovered solutions by precipitation of the contaminants at acidic pH or ultrafiltration. A smaller volume of the polluted fraction has to be disposed 461 462 in this way, and the residual chloride or permeate liquid phase can be recycled for further uses. The data 463 provide basic data and offer scope for further development/implementation of the proposed process 464 scheme (reactions 1-3) to sustainable operation in real environment in batch or continuous mode. The results contribute to assessing the hydrolysates of MBW biowastes as value-added products for multiple 465 use and the MBW as sustainable feedstock for the production of renewable biobased chemical 466 467 specialities for use in place of synthetic chemicals from fossil source.

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476 Appendix A. Supplementary material (SM)

- 477 478 Supplementary data related to this article can be found at https://doi.org/..../j.jclepro.2019.....
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