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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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(Article begins on next page)

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

Silvia Tabasso^a, Marco Ginepro^a, Lorenzo Tomasso^a, Enzo Montoneri^{b*}, Roberto Nisticò^c, Matteo Francavilla^d

^aUniversità di Torino, Dipartimento di Chimica, Via P. Giuria 7, 10125 Torino, Italy.

^bUniversità di Torino, Dipartimento di Scienze Agrarie, Forestali e Alimentari, Largo P. Braccini 2, 10095 Grugliasco, Italy.

^cPolytechnic of Torino, Department of Applied Science and Technology DISAT, C.so Duca degli Abruzzi 24, 10129 Torino, Italy.

^dSTAR Integrated Research, University of Foggia, Via Gramsci, 89-91, 71121, Foggia, Italy

ABSTRACT

Municipal biowaste (MBW) provide a range of polymeric biosurfactants (BPS) with different chemical nature depending on the sourcing biowaste. Three different BPS were isolated from MBW sourced from 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 aromatic moieties and several different acid and basic functional groups. The BPS were used in aqueous 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 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 and Pb). A new process was studied. It comprises use of the BPS solutions for washing the polluted soil and treating the recovered solutions by acidification and membrane filtration to separate a pollutant concentrate from water for further use. On the basis of the results BPS appear a valid alternative to conventional processes.

Keywords

Biopolymers; Municipal biowaste; Heavy metals; Soil washing

Abbreviations: BPS, polymeric biosurfactants; MBW, municipal biowastes; AN, anaerobic; AE, aerobic; WWT, urban waste water treatment; LBG, landfill biogas; FORSUD, digestate from bio-organic (humid) fraction of solid urban waste AN reactor; HS, humic substances; V, home gardening and park trimmings residues; F, sewage sludge; CVT230, V composted for 230 days; CVDF, 35/55/10 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 sulphate.

1. Introduction

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, (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 long time. Depending on their behaviour, they are a potential threat to the ecosystem and human health.

* Corresponding author.

E-mail address: enzo.montoneri@gmail.com (E. Montoneri).

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

65 Humic substances (HS), naturally occurring in soils, sediments, waters and fossils (Thurman,
66 1986), have also been considered for use in soil remediation (Perminova and Hatfield, 2005). They are
67 soil endogenous compounds and capable to bind metal ions by the presence of carboxylic and phenolic
68 groups. The complexation of trace metals by HS in soil has been much investigated (Wu et al., 2002).
69 No adverse environmental impact is expected from these materials. Extraction of natural HS for use in
70 large scale remediation of contaminated sites is not economically viable due to the low concentration in
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.
75 Composts may produce multiple environmental benefits. Municipal biowaste (MBW) is the most
76 sustainable worldwide abundantly available source of compost. The MBW is rich in organic matter.
77 Collection costs are covered by tax payers. It is defined negative cost feedstock (Sheldon-Coulson,
78 2011). Fermentation of MBW under controlled anaerobic and aerobic conditions allows reducing the
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
81 used to amend and/or fertilize soil. Composts have been much investigated as auxiliaries for soil
82 remediation. Added to contaminated soil, they can bind metal pollutants. They have great potential to
83 reduce mobility (Geebelen et al., 2002), bioavailability and toxicity of trace elements (Smith et al.,
84 2009). Compost production and use has therefore multipurpose potential environmental sustainable
85 benefits in the sectors of biowaste managements, soil fertilization and remediation (Nwachukwu et al.,
86 2008). Composts may be effective by several processes, which include raising soil pH, complexation
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
89 remain in soil for long time. In the long term, due to the slow dissolution of organic matter, some
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
94 feedstock for the production of soluble value-added biopolymers. A recent review (Montoneri, 2017)
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
100 mixture of molecules with molecular weight from 5 to over 500 kDa molecular weight. These contain a
101 wide variety of aliphatic and aromatic C chains, substituted by several acid and basic functional groups

102 bonding the mineral elements. The BPS may be obtained in a wide variety of chemical composition and
103 properties depending on the MBW sourcing material. They have been demonstrated suitable for a wide
104 variety of applications in the chemical industry, agriculture, and animal husbandry. Similar range of
105 performances from the sourcing digestate and composts is not possible, due to their insolubility. Since
106 BPS derive from natural organic matter as HS, no adverse environmental impact is expected from their
107 use. Investigation of BPS for remediation of soil contaminated by heavy metals has not been carried out
108 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
112 (CV), and of the compost of a mix of food waste digestate, gardening residues and sewage sludge
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
115 properties, such as the solubility at $\text{pH} > 4$, the capacity to yield micelle with large hydrodynamic
116 diameter in solution, and the insolubility at acid pH. These properties allowed developing a new two-
117 step process comprising washing the soil at $\text{pH} > 4$ and cleaning up the recovered washing solution by
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.

122 123 **2. Methods**

124 125 *2.1. BPS and other reagents*

126 127 The investigated BPS were available from previous work (Montoneri, 2017). They were sourced
128 from MBW sampled from the process lines of *ACEA Pinerolese Industriale S.p.A.* waste treatment plant
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 $\text{pH} 13$ and $60\text{ }^\circ\text{C}$ to yield the BPS. Solutions of
132 BPS at different concentrations were obtained by dissolving the BPS in water. All solutions were stored
133 at $4\text{ }^\circ\text{C}$ before use. They were analyzed for metal content by Inductively Coupled Plasma - Atomic
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
138 dilutions (from $25\text{ }\mu\text{g L}^{-1}$ to $30,000\text{ }\mu\text{g L}^{-1}$) of a multi elemental solution ($1,000\text{ mg L}^{-1}$). The
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.

141 142 *2.2. Soil treatment and characterization*

143 144 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 catalyts.

148 149 *2.3. Equilibrium partition time measurement*

150

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

161 2.4. Multiple extractions

162 Five consecutive washing trials were run on each soil sample (1 g) with 10 mL of the following
163 washing solutions in deionized water: BPS (10 g L⁻¹), EDTA (6.25 mM), DTPA (5 mM), DTPA/CaCl₂
164 5 mM/0.01 M, SDS (5 g L⁻¹). These washing solutions were analysed following the same procedure
165 reported in the above section.
166

167 2.5. Secondary treatment of after use recovered washing solution

168 An aliquot (10 mL) of solutions containing the same amount of metals as the washing solutions
169 was acidified with concentrated HCl (37%) to pH 1.5-3.0, and centrifuged (15 min., 4,000 rpm). The
170 supernatant was analyzed for heavy metal as described above. Alternatively, the solutions were filtered
171 under 4 bar pressure with a Millipore Stirred Ultrafiltration Cell (Amicon Bioseparations) through M-
172 PE5-GPET membranes with 5 kDa cut-off. The permeate was analyzed for heavy metal as described
173 above.
174
175

176 3. Results

177 3.1. BPS characterization

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

191 Data for FORSUD, CV and CVDF BPS have already been published (Rosso et al., 2015). Table 1
192 lists selected data, which are relevant to understand the different chemical composition, properties and
193 performance in the intended application of the investigated BPS. The aliphatic to aromatic C ratio
194 (Af/Ar) indicates the type of lipophilicity (mostly aliphatic or mainly aromatic) of the BPS. The amine
195 (NR), phenol (PhOH) and carboxylic (COOH) groups are relevant for their property to chelate metal
196 ions. The surface tension data provide hints on the solution conformation of the BPS. The data show
197 that the FORSUD and CV BPS exhibit the largest differences. The former has the lowest values for the
198 ash content and for the content of COOH acid groups, while exhibiting the highest values for the Af/Ar
199
200

parameter and the amine functional groups. This indicates FORSUD as the most lipophilic, aliphatic and least acidic material. At the other extreme of such empirical rating chemical scale, CV has the highest content of total PhOH and COOH acid groups, and the lowest amount of amine functional groups. As likely consequence of its chemical composition, FORSUD exhibits the lowest CMC and γ_{CMC} values. This indicates that FORSUD molecules in solution aggregate to form micelles at lower concentration than the CV and CVDF molecules.

Table 1.

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, % of total C ^b	6.7	9.4	12.1
γ_{CMC} , ^c mN m ⁻¹	48.8	61.8	61.2
CMC, ^c g L ⁻¹	1.0	3.1	2.1

^[a]Concentration values referred to dry matter. ^[b]Aliphatic (Af), amine (NR), phenol (PhOH), carboxylic acid (COOH) C content. ^[c]Critical micellar concentration (CMC) and surface tension at the CMC (γ_{CMC}).

Rosso et al. (2015) report also other data on the hydrolysis of MBW, which are particularly relevant in relation to the objective of the present work. They show that the hydrolysis of the BPS sourcing 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 pristine metal content is recovered with the insoluble hydrolysate residue. The CVDF and CV BPS exhibit one exception. They contain significantly more Pb than their pristine composts and insoluble hydrolysate. This suggests several considerations. Trace metals are strongly bonded to the pristine 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 bonds in the soluble hydrolysates. The higher Pb content in the CVDF and CV BPS, compared to the pristine composts and insoluble hydrolysates, may imply that the BPS obtained from the composts are strong complexing agents, particularly for Pb.

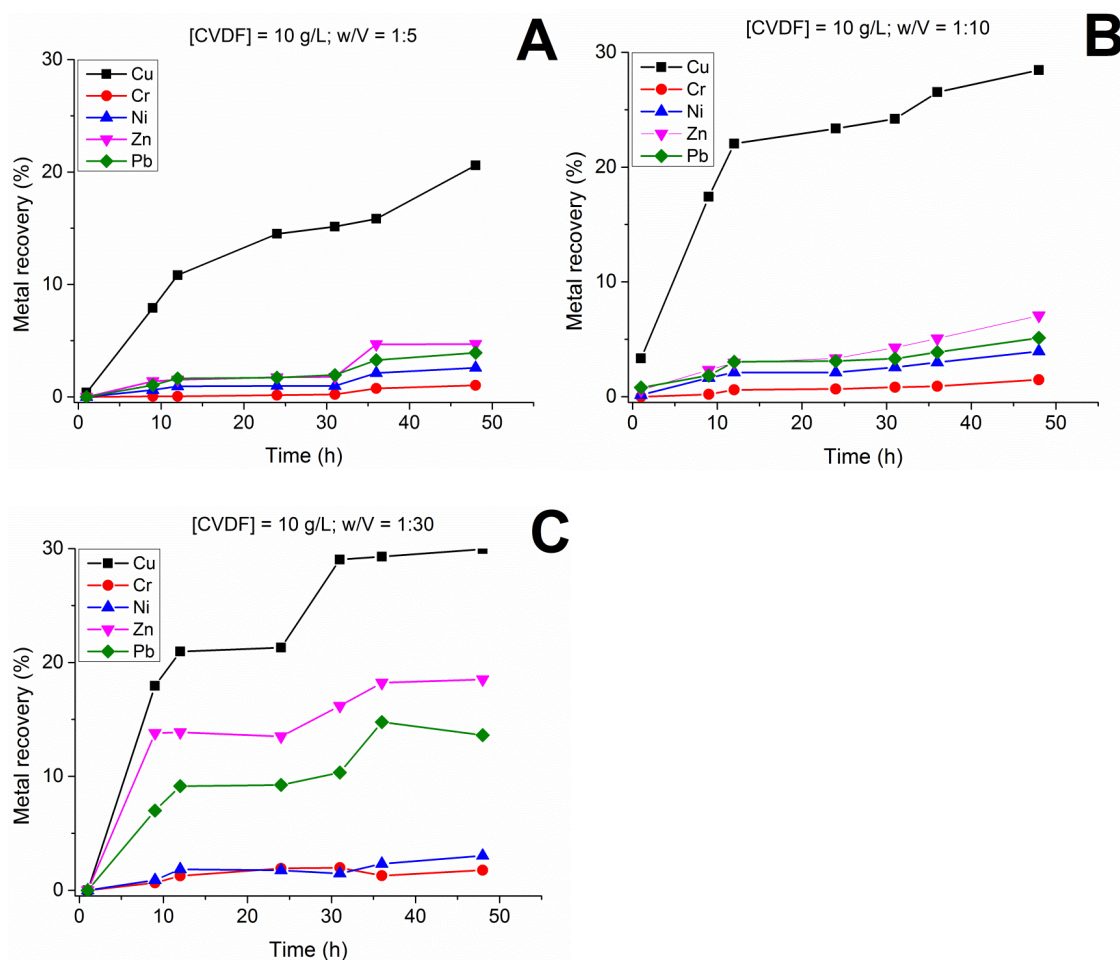
Overall, the data in Table 1 indicate that all three BPS, for their chemical composition and capacity to yield micellar aggregates, have potential as trace metal sequestering agents to use in ex-situ washing of metal polluted soil.

3.2. Soil washing.

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

236 FORSUD at 50 g L^{-1} . Each BPS was investigated in the raw form, i.e. as isolated from the hydrolysis
 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
 240 increase the number of these groups available to complex the trace metals present in the investigated
 241 soil. The results (Fig. 1S in the supplementary material SM file) showed that, compared to the raw BPS,
 242 the de-ashed derivatives exhibit 10-20 % higher washing efficiency. In the authors' opinion, the higher
 243 performance level of the de-ashed BPS does not justify the additional complexity of their preparation
 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
 246 carried out only with the raw BPS containing 15-27 wt.% ash.
 247
 248



251
 252
 253 **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
 254 (A), 1:10 (B), and 1:30 (C). Legend: Cu (black squares), Cr (red circles), Ni (blue up-triangles), Zn (magenta down-
 255 triangles), and Pb (green diamonds)
 256

257 The BPS listed in Table 1, used at the maximum concentrations ($50\text{-}100 \text{ g L}^{-1}$) compatible with
 258 their water solubility at pH 8, gave different results. The highest soil washing efficiency was obtained
 259 with CVDF. This material was therefore used to determine the time to reach the equilibrium partition of
 260 the metals between soil and washing solution as a function of soil/solution ratio. The first experiments
 261 were performed with a 10 g L^{-1} CVDF solution, at three soil/solution w/V ratios. The results of the
 262 washing trials with CVDF under the above conditions are reported in Fig. 1. The data show that, in most
 263 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 range of conventional commercial metal chelating agents was used under the same experimental conditions for comparison. Indeed, the performance of a given chelating agent in extracting metals from 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 Zhang, 2005), DTPA (Hong et al., 2002), SDS (Ahmadi et al., 1995) compounds, which are referral products in the field of environmental remediation. In this work, the DTPA/CaCl₂ solution was also used, since it is recommended by the Italian official method (Presidente della Repubblica, 2006) to assess the bioavailability of heavy metals in non-acid soils.

To compare performance of CVDF with EDTA, DTPA and SDS, multiple extractions (five 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 work, the same concentration was used, and the concentration of the other compounds and BPS were calculated to have the same number of acid groups in the washing solutions as in 5 mM DTPA. Plain water was used as control washing solution. The results are reported in Fig. 2. It may be observed that, based on the % recovery of Cu, Pb and Zn, the performance of BPS runs more or less close to that of 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.

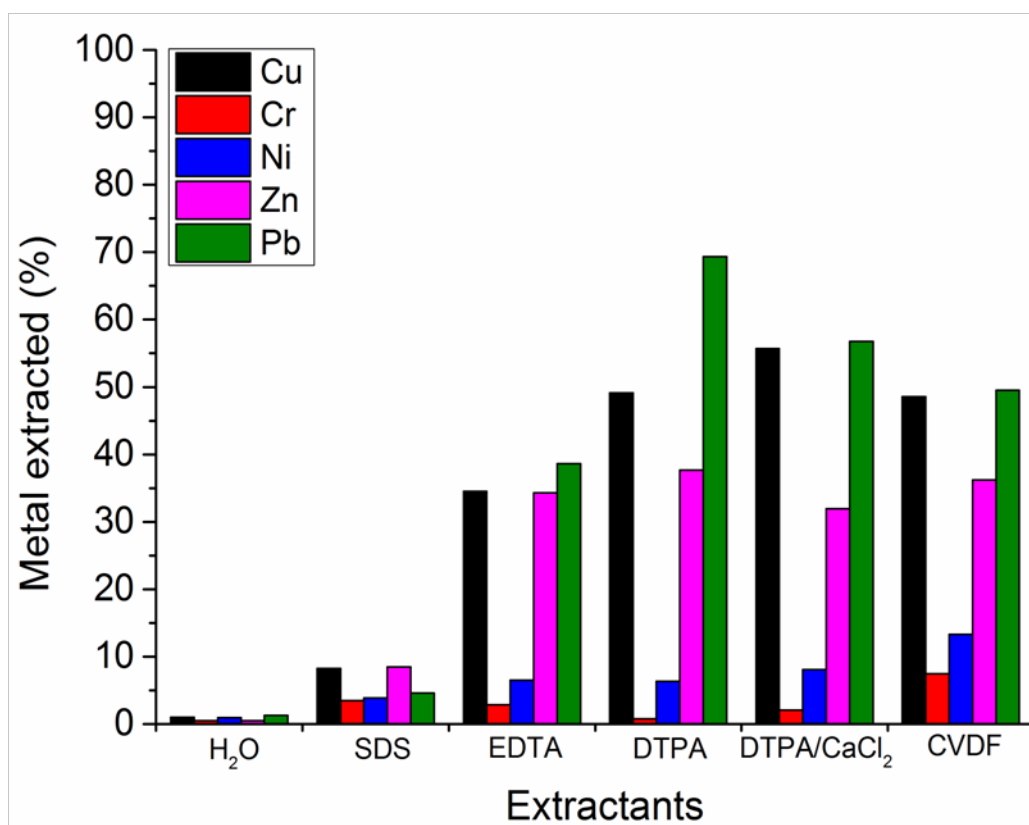


Fig. 2. Effect of different extractants in multiple extraction processes (solution/soil 10 w/V ratio and 24 h contact time) for the heavy metals analyzed. Extractants: bare H₂O, SDS 5 g L⁻¹, EDTA 2 g L⁻¹, DTPA 2 g L⁻¹, DTPA/CaCl₂ 2 g L⁻¹/0.01M, and CVDF 10 g L⁻¹. Legend: Cu (black), Cr (red), Ni (blue),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

Several other washing trials were carried out with 1 and 0.1 g L⁻¹ CVDF solutions at 30, 10 and 5 V/w solution/soil ratio and equilibrium contact time. The results are reported in Table 1S and Fig. 2S of

293 the SM file. The highest metal recovery values were recorded for the trials with the highest solution/soil
294 ratio and CVDF concentration in the used solution. The experimental amounts of metals recovered with
295 the washing solutions were elaborated to calculate the specific metal absorption per unit weight of
296 CVDF in solution. These provided useful hints on the behavior of the CVDF molecules in solutions
297 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
300 upon comparing data at constant volume/solid ratio and decreasing CVDF concentration in solution.
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
303 increase at lower Cs concentration can be explained with the change of the BPS solution molecular
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
308 CVDF-soil interactions. This is a second parameter that, together with the intermolecular interactions
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*

320
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
323 the BPS macromolecularity and insolubility at acid pH. The solutions recovered after 24 h soil washing
324 with 100 g L⁻¹ CV and CVDF, and 50 g L⁻¹ FORSUD (Fig. 1S) were treated by vertical flow membrane
325 filtration under 5 bar pressure, and alternatively by precipitation at acid pH. The two processes allowed
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
328 and secondary treatment, the experimental data in Table 2 are expressed as % recovery of the metal in
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).

Table 2. Results of the secondary treatment of the BPS solutions recovered after 24 h soil washing. 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
FORSUD Chloride ^b	62	31	46	57	54

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

^bSolution obtained after precipitation with concentrated HCl.

4. Discussion

In this study, three MBW, sampled from different sections of a urban waste treatment plant, were used as sourcing materials of humic-like polymeric biosurfactants (BPS) to be investigated as chelating 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, possessing the highest molar fraction of acidic functional groups (Table 1), shows the highest chelating capacity. The BPS are constituted by a heterogeneous molecular pool. Presumably, the C types and functional groups listed in Table 1 are not homogeneously distributed over the entire molecular pool. 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 metal ions and on the different conformation of the different molecules in solution.

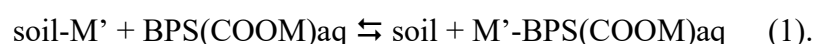
The behavior of BPS macromolecules in solution in the 0.2-100 g L⁻¹ concentration range has been investigated (Montoneri et al., 2010) by measurements of solubility properties in solvents of different polarity, surface activity, power to enhance the water solubility of hydrophobic compounds, and particle size. The results suggest that in the 0.2-2.5 g L⁻¹ range an intramolecular rearrangement of 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 pseudomicelles. Other workers (Du et al., 2001) report that different bivalent (Xu et al., 2007) and trivalent metal ions (Garg et al., 2016) in solution affect significantly the capacity to micellize and solution conformation of the resulting molecular aggregates of typical conventional commercial surfactants, e.g., sodium dodecyl sulphate and hexadecyltrimethyl ammonium chloride. These changes 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 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

in the extraction of Ni and Cr than the synthetic chelating agents (Fig. 2), probably because other 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 with organic compounds (Kabata-Pendias, 2001). Dissolved organic matter can increase Cu mobility by formation of soluble organic complexes. Consistently with the findings of other workers (Tessier et al., 1979), the higher extraction of Cu and Pb (Fig. 2) may be due also to the fact that these elements are in more available and extractable soil fractions, while Cr is present only in residual less extractable soil fractions. The system is complicated by different processes, such as competitive adsorption of other metal ions or anions, competitive adsorption of metals by the organic matter in the soil, stability of the complexes formed with ligands, and adsorption of the chelating agent by soil. These may contribute to 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 and after use. No significant depletion of organic carbon was found in the after use solution, compared to the pristine solutions. Yet, TOC data cannot completely explain the complexity of the processes involved in the kinetic behavior shown in Fig. 1. The TOC can also be influenced by a dynamic exchange between the organic matter present in soil (both as natural and anthropogenic matter) and in the washing solutions. Considering the complexity of the system, in addition to the diversity of metal sorbing components of soil compartments as well as the polyelectrolyte nature of the BPS, the kinetics 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



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.

Although separating the exhausted BPS washing soil for the soil, and repeating over and over again the soil washing step (1) with fresh BPS solution, may allow more cleaning of the soil, this practice will increase the volume of the collected washings, which needs to be disposed. It poses the issue of the secondary treatment to separate clean water for further use from the M'-BPS(COOM)_{aq} complex. To 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



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

Alternatively, due its macromolecular nature, the M'-BPS(COOM)_{aq} complex solution, separated from the clean soil, can be filtered through ultrafiltration membrane as in step



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),
437 where water is recovered with the aqueous chloride phase. The data in Table 2 shows that both the
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 metal-
445 free chloride solution by reaction (2). Moreover, the reaction (2) yields a salt solution which requires
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
448 drying/incineration treatment to yield final concentrates containing only metals for use in the chemical
449 industry or landfill. However, reaction (3) should allow obtaining cleaner water for further use.

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
461 contaminants at acidic pH or ultrafiltration. A smaller volume of the polluted fraction has to be disposed
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
465 results contribute to assessing the hydrolysates of MBW biowastes as value-added products for multiple
466 use and the MBW as sustainable feedstock for the production of renewable biobased chemical
467 specialities for use in place of synthetic chemicals from fossil source.

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470
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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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