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

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Abstract

In line with the Green Supply Chain Management, Sustainable Supply Chain Management and Natural-Resource-Based Views (NRBV), the present study is as further step of a long range research program initiated in 2004. The project aims to demonstrate municipal bio-waste (MBW) as feedstock to produce bio based chemicals alternative to fossil sourced products. Previous work demonstrated MBW as source of polymeric biosurfactants (BPS) with multiple properties for use in chemical and agriculture sectors. The present paper reports now a new BPS feature, i.e. that BPS are efficient active principles for soil remediation. The study involves three BPS obtained by alkaline hydrolysis from different streams of an MBW treatment plant: the anaerobic digestate of food kitchen waste (FORSUD), the compost (CV) of gardening residues and the compost (CVDF) of a mix of gardening residues, digestate and sewage sludge. The BPS have 5 to over 750 kg/mol molecular weight, characterized by the presence of aliphatic C chains substituted by aromatic moieties and several different acid and basic functional groups. They were used at 0.1-100 g/L in aqueous solution to wash soil sampled from an Italian metal polluted site. Collected data statistical analysis was carried out by ANOVA. The recovered washing solutions were analyzed for Cu, Cr, Ni, Zn, Pb. The 50-100 g/L CVDF BPS solutions exhibited 98-81% extraction efficiency, compared to 70-60% for CV and FORSUD. Compared to conventional commercial extractants, CVDF BPS extraction efficiency ranked as CVDF = diethylene triamine pentaacetic acid > ethylene diamine tetraacetic acid > sodium dodecyl sulphate. A new two steps process was studied: (1) use of BPS solution for washing the polluted soil; (2) treating the recovered solution by acidification and membrane filtration to separate a pollutant concentrate from water for further use. Results indicate membrane filtration more efficient and/or sustainable. They confirm BPS as value added products upgrading MBW from societal cost to source of benefits.

Keywords: Biopolymers; Municipal bio-waste; Heavy metals; Soil washing.

1. Introduction

The present paper falls within the frame work of the Green Supply Chain Management (GSCM) and Sustainable Supply Chain Management (SSCM) concepts (de Oliveira et al., 2018). It deals with the valorization of wastes, specifically municipal bio-wastes (MBW), as natural resources to produce new value added bio based chemicals. It has necessarily an empirical approach, because of the complex composition of the materials dealt with, which stems from their biological nature. It is one step of a long range research program (Montoneri, 2017) initiated in 2004 with two objectives: build up scientific knowledge on the nature of these materials; develop sustainable, standardized, reproducible processes and products adoptable by chemical industry.

The paper reports the specific case study of polluted soil from a dismissed industrial site, which is remediated by applying a polymeric bio surfactant (BPS) obtained from MBW. The study is not motivated merely by environmental reasons. It tries not only to assess the performance and environmental benefits of BPS, but also its economic sustainability. Indeed, it is quite unlikely that environmental benefits became real if not economically sustainable. The 2004 started project aims to develop MBW as feedstock for a bio refinery producing biofuel and bio based chemicals. The project relies on a number of features associated to MBW. The first is that MBW contain all components (e.g. polysaccharides, fats, proteins and lignin) that have originated the fossil sources of the current commercial products. The second is that MBW are the most abundant negative-cost worldwide available C source on earth. The third is that the problem to valorise bio-waste as source of bio based value added products is not feedstock availability, but the development of sustainable processes. When this issue will be solved, feedstock to produce consumers' products will not be any longer a strategic source owned by few countries as fossils are now.

Good environmental practices and sustainable development are two issues addressed by the GSCM and SSCM concepts, respectively. In the chemical field, the principal actors to make real the transition from a fossil-based economy to a bio-based more ecofriendly economy are major chemical companies. These exist only if they can realize profit, reduce costs, increase business competitiveness and value. Several major chemical companies are engaged since years in the development of bio based products. These efforts are supported also by many EU programs co-funding R&D. Notwithstanding the efforts, the bio based economy has not developed yet as expected. A recent literature review (de Oliveira et al., 2018) reports the main barriers to the bio based economy implementation. One is the resistance to the adoption of advanced technology. The authors of the present paper are convinced that, in the fuel and chemicals sectors, this technology related barrier stems from a number of factors, including feedstock availability and processing.

1.1. *The authors' view of the current RTD and approach for the valorization of biomass as feedstock to produce bio based chemicals*

Currently, much research is being carried out to valorise biomass from different sources as alternative to fossil feedstock for the production of fuel, chemicals and materials. Contrary to fossils' exploitation based on well-consolidated chemical technologies, biomass valorization is mostly pursued by applying fermentation and/or biotechnology-based processes. Biotechnology is one of the six key enabling technologies (KET) proposed by the EU Commission for the development of the bio-based industry (European Commission, 2019). This choice has social and political roots. In public opinion, chemistry is associated to oil and carbon fossil sources. The environmental concern arising from the exploitation of fossils has generated the diffuse social belief that chemistry is poisonous, whereas biotechnology, being associated to renewable biomass, is safe. Thus, along with social belief, politicians have emphasized and encouraged biotechnology as KET for replacing fossil feedstock with renewable biomass, glossing over chemistry. This attitude and the complexity of biomass chemical composition has discouraged most chemists to work with biomass. Unfortunately, the current technological paradigm based on biotechnology has not yet allowed developing a sustainable bio-based economy to large scale. This is due to a number of reasons connected with feedstock availability, complexity of chemical composition and processing.

1.1.1. *The complexity of biomass*

Compared to petroleum containing hydrocarbon molecules made from few tens of carbon atoms with well-known chemical structure, biomass has more complex composition. Its main components (cellulose, hemicelluloses and lignin) are polymers. Polysaccharides are soluble macromolecules. Their chemical structure is well-known. They are ductile polymers and can be worked out to manufacture a lot of products used in our daily life. On the contrary, lignin is a cross-linked aromatic polymer. It is insoluble and recalcitrant toward chemical and biochemical attacks. It cannot be worked out to obtain ductile materials, since its network of aromatic rings bonded to short aliphatic C chains confers brittleness and rigidity. Compared to polysaccharides, the chemical nature of lignin is not known as well. Lignin in biomass is intimately bonded to polysaccharides. So far, attempts to establish the real chemical nature of lignin are based on pyrolysis. This technique breaks the chemical bonds of the lignin macromolecules and yields small fragments. These are used to reconstruct virtual chemical structural models of the pristine polymer. The same structure-destructive approach has inspired current fermentation-based technology.

1.1.2. The current technological paradigm to process biomass

Fig. 1 synthesizes the main steps of the current technological paradigm. Biomass fermentation needs bio-waste pre-treatments (step 1) to separate (Isikgor and Becer, 2015) polysaccharides (PS) from recalcitrant lignin (LG), since lignin inhibits fermentation. Fermentation of PS (step 2) demolishes the native polysaccharides' structure to simple molecules. These need a second biochemical reaction (step 3) to obtain biopolymers for the manufacture of bioplastic articles for consumer' use (Chen, 2012). The two fermentation steps require selected and/or genetically modified microorganisms. Monomers and biopolymers are obtained in low yield. The microorganisms' production and the products recovery add critical costs. Lignin is incinerated (step 4) to recover its heat value or pyrolysed (step 5) at high temperature to obtain a range of simple molecules to use as building blocks for the manufacture of fine, commodity and speciality chemicals. These processes destroy the functionalities of native lignin, do not allow exploiting its full potential as feedstock of valued-added chemicals, cause fine dust and GHC emission and/or require high energy consumption.

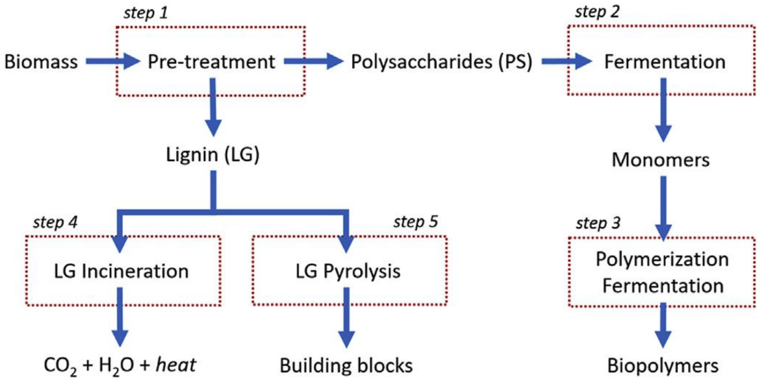

Fig. 1. Main steps of biomass working technology based on fermentation/biotechnology.

1.1.3. The feedstock issue

The major focus (Iles and Martin, 2013) of the biotechnology-based paradigm has been on developing biofuels (e.g., bioethanol) and bio-based building blocks for the manufacture of bioplastics. Residues from agriculture and the food industry have been target feedstock.

Bioethanol plants are operating in few countries (Neto et al., 2018). Bioethanol has commercial production success in Brazil, where sugarcane as sustainable feedstock is abundant and easy available. In the large majority of countries, bioethanol production has not reached commercial level due to lower availability of sustainable biomass as feedstock, but also because of poor valorization of the lignin residue. The heat value recovered by incineration of lignin is roughly worth 0.06-0.13 €/kg, not enough to compensate for the cost of the fermentation process.

Currently, bioplastics represent approximately 1% of the 300 Mt/yr of plastics produced (Tsagaraki et al., 2017). They are manufactured from bio-based polymers based entirely or partly on monomers obtained by fermentation (Chen, 2012). They are 2-7 times more expensive than traditional fossil originated polymers (Nisticò et al., 2017).

Surfactants constitute also a major category of chemicals to produce consumers' goods. Bio surfactants (Tsagaraki et al., 2017) are produced from plants or animal fats, or various microorganisms. The global bio surfactants' demand is estimated 400,000 t/yr. Raw materials' cost accounts for 10-30% of total production costs. Rhamnolipids and sophorolipids are key product segments of the microbial bio surfactants market. Due to the exceptional performance (Randhawa and Rahman, 2014), their 30-150 €/kg price (Connolly et al., 2010) is much higher than the 1.5-5.5 €/kg (Rust and Wildes, 2008) of fossil sourced synthetic or oleo chemical natural surfactants.

Building blocks are used (Tsagaraki et al., 2017) as base chemicals in industrial manufacturing processes to be transformed into new families of useful molecules or materials. Most bio-based chemicals have higher production costs than their counterparts from fossil source. Market prices range from 0.6 €/kg for acetic acid to over 3.0 €/kg for 1,4-butanediol. By comparison, prices for fossil sourced counterparts range from 0.6 €/kg for acetic acid to 1.8 €/kg for 1,4-butanediol. The indicative future bio-based production cost targeted by several companies is 1.0 €/kg, once the relevant conversion technologies have been successfully commercialised.

1.1.4. The authors view and approach to develop a bio-waste based chemical industry

The above highlighted technological factors for the fermentation/biotechnology-based paradigm and the biomass collection costs are criticalities that need to be overcome to develop the bio-based chemicals economy to larger scale. Currently, major chemical companies (e.g. DuPont, BASF, SABIC, Dow Chemical, LyondellBasell, and Mitsubishi Chemical) are engaged in the production of bio-based chemicals. There are no questions that they will have a major role in spurring the bio-based economy. However, it seems that they were reluctant to undertake fermentation technology as core business (Iles and Martin, 2013) for several reasons. One is the complexity inherent to maintained alive biological systems. The other is the need to use energy intensive separation processes. Third is the fact that copying with the challenges of biochemical processes diverges from the procedures to optimize chemical reaction that chemical companies are familiar with. Under these circumstances, the authors of the present paper are convinced that, to overcome the criticalities of the current technological paradigm, RTD should move from a biotechnology vision toward an approach more based on chemical processes, which is closer to the chemical companies' core business and traditional expertise. The authors envision a different technological paradigm built on two elements: municipal bio-waste (MBW) as feedstock; chemical technology to convert MBW to value-added products.

The MBW-chemical processing paradigm has several potential environmental, economic and social benefits, connected to improving MBW waste management and spurring bio-based economy. Undoubtedly, its realization is a hard task. Compared to biomass, petroleum is a less complex and more exploitable feedstock as it is concentrated in large quantities in confined spaces, contains less water, and more concentrated and simpler organic matter, which can be fractionated by distillation into individual hydrocarbons with well-defined chemical composition and structure. On the other hand, biomass organic matter is richer in O and N than fossil matter. The former contains many acid and basic functional groups that are responsible of the performance of current commercial chemicals obtained from fossil source through synthetic chemical reactions. Biomass contains native polymers, which properly modified could allow obtaining plastic articles we need in our daily life. It is therefore a pity to demolish the native organic matter present in biomass as it occurs in the biotechnology-based route represented in Fig. 1.

1.1.4.1. Factors encouraging the development of the MBW-chemical route.

MBW is the most competitive potential sustainable feedstock, compared to any other renewable feedstock. As collection and transportation costs are covered by tax payers, MBWis defined negative cost feedstock (Sheldon-Coulson and Thesis, 2011) available worldwide in every urban settlement. More than half of the world population currently lives in cities, which accounts for 75% of natural resource consumption, 50% of global waste production, 60-80% of greenhouse gas emissions (Ellen Macarthur Foundation, 2017). Global

EU MBW production is about 90 Mt/yr (Tsagaraki et al., 2017). Cities are priority environment (Ellen Macarthur Foundation, 2017) to realize transition from mass consumption/undisciplined waste production to a resource-efficiency/waste valorization model. They provide biomass feedstock with excellent reliable long-term availability, in sufficient scale for sustainable production of bio-based chemical products, and not likely to compromise food production as biomass from dedicated plants may do.

In this context, the authors have published over 100 papers since 2004 (Montoneri, 2017) on the valorization of MBW as feedstock for the production of biobased value added products by integrated biochemical-chemical processing. Relevant data have been obtained from work developed on the case study of the ACEA Pinerolese Industriale MBW treatment plant located in Pinerolo, Italy. The plant processes 50,000 t/yr MBW by fermentation producing 4.3 Mm^3 biogas and 4500 compost t/yr. The process cost is 156 €/MBW ton. It is compensated by the revenue of 66 €/t and 1 €/t from biogas and compost sales, respectively, and 90 €/t from tipping fee. The authors have estimated that ACEA MBW availability may yield 4000-15,000 t/yr bio-based products upon applying the patented chemical hydrolysis process (Montoneri, 2017) to the MBW plant feed and compost. The hydrolysis process cost has been estimated 100-200 €/t MBW ton, close to the current ACEA fermentation process. The authors have also demonstrated that the hydrolysis process does not demolish the native organic structure of the biomass components. It yields biopolymers (BPS), which save the memory of the polymeric structure and functionalities of the components of the pristine bio-waste. However, BPS are soluble in water and processable to obtain plastic composite materials. They have been proven experimentally to be efficient as plant bio stimulants in agriculture, diet supplement for animal husbandry, bio surfactants to use in the formulation of detergents, auxiliaries for textile dyeing, emulsifiers, as templates for the fabrication of nanocrystalline materials, as photosensitizers for photoremediation of industrial wastes polluted by organics, as biopolymers for the manufacture of finished consumers' products. The multiple purpose performance stems from the fact that BPS contain the chemical memory of the pristine biomass components coupled to acquired solubility properties. Based on market values of commercial products in the same functional categories, BPS sale value may range from 1500 to 150,000 €/t. This is several order of magnitude higher than the biogas and compost values currently obtained by the case study ACEA plant. The data prospects that ACEA MBW treatment plant could be turned into MBW fed bio refinery with relevant economic and social benefits, including creation of jobs and relief of citizens from taxes covering tipping fees.

1.2. The objective and significance of the present work in the above context

The objective of the present work was to test the performance of the BPS as auxiliaries to remediate a soil polluted by heavy metal as a consequence of industrial activity. The idea of a polluting anthropogenic bio-waste generating a product capable to clean up the environment from anthropogenic pollutants was fascinating. Undoubtedly, it can gain unanimous consensus from citizens and policy makers. This was not the only authors' objective. Consistently with the GSCM-SSCM concepts and the natural-resource based view (Hart and Dowell, 2011), the authors intent was to lay also the basis for a process, which was at the same time environmentally and economically sustainable. For the authors' strategy to promote the MBW-chemical route view, proving BPS efficient auxiliaries for soil remediation widened the range of applications of BPS already demonstrated (Montoneri, 2017). It added value to MBW as feedstock. It paved the way to the development of a MBW based bio refinery. These are far more ambitious motivations than just achieving the objective of soil remediation. The present work is only one of the many steps to add to the many steps already carried out to change the view of MBW from societal cost to resource producing revenue coupled to environmental and social benefits. To the authors' knowledge there is no example of such comprehensive approach for the valorization of MWB as feedstock for new value added bio based products. This constitutes the novelty in relation to the state of art of the bio based industry.

1.3. The BPS within the state-of-art of surfactant assisted soil remediation

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' behavior 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.

With the growing population, industrial production and consumption of resources, the anthropogenic environmental impact has become a primary social concern. The demand for soil treatment techniques is consequently growing. The development of new efficient economically and environmentally sustainable remediation processes has become a key research activity. Various approaches have been suggested for the remediation of metal-contaminated sites. These include soil washing using particle size separation and chemical extraction with aqueous solutions of surfactants and mineral acids and/or chelating compounds. Synthetic surfactants are very effective agents for this purpose, e.g. sodium dodecyl sulphate (SDS), ethylenediaminetetraacetic acid (EDTA), and diethylenetriaminepentaacetic acid (DTPA). Unfortunately, at the end of the treatment they remain as exogenous substances in the treated soil. Depending on toxicity and recalcitrance to biodegradability, they may end up causing a secondary environmental impact (Chaturvedi and Kumar, 2010). Humic substances (HS), naturally occurring in soils, sediments, waters and fossils), have also been considered for use in soil remediation (Perminova and Hatfield, 2005). They are soil endogenous compounds and capable to bind metal ions by the presence of carboxylic and phenolic 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 large scale remediation of contaminated sites is not economically viable due to the low concentration in soil or not environmentally sustainable due to the consequent depletion of fossil sources (Montoneri, 2017). Humic-like substances are present in composts. These materials may be produced in large quantities as a mean to handle the increasing amount of bio-waste from anthropogenic source. Composts may produce multiple environmental benefits. They have been much investigated as auxiliaries for soil remediation. Added to contaminated soil, they can bind metal pollutants. They have great potential to reduce mobility, bioavailability and toxicity of trace elements (Smith, 2009). They are used as fertilizers. They may give benefits in the sectors of bio-waste managements, soil fertilization and remediation (Nwachukwu and Pulford, 2008). 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 elements, in particular Cu, which are associated to the dissolved organic matter, may be mobilised (Zhou and Wong, 2001). The same may occur after compost organic matter mineralisation.

The 2004 started research program (Montoneri, 2017) has demonstrated that compost may be valorized more as feedstock for the production of BPS. These are obtained by alkaline hydrolysis of composts from different of urban kitchen, gardening and sewage sludge wastes. They contain organic and mineral matter representing the memory of the pristine bio-waste 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 kg/mol molecular weight. These contain a wide variety of aliphatic and aromatic C chains, substituted by several acid and basic functional groups 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 are good surfactants. 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. BPS have been demonstrated to comply with Italian regulation on fertilizers. In vivo pig (Morlacchini et al., 2017) and rabbit (Biagini et al., 2016) studies, using BPS as animal feed supplement, demonstrate the lack of BPS toxicity for animals. The investigation of BPS for remediation of soil contaminated by heavy metals has not been carried out so far.

1.4. The research model/framework and the variables at play

The present work reports the performance of three different MBW sourced BPS in the remediation of a heavily contaminated dismissed italian industrial site. In addition to the capacity of chelating metals, which was expected on basis of the content of 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 diameter in solution, and the insolubility at acid pH. These properties allowed developing a new two-step process comprising washing the soil at pH > 4 and cleaning up the recovered washing solution by separating the pollutants' concentrate from clean water for further re-use. Such process could not be carried out with the sourcing compost and digestate of the BPS, due to their insolubility in the whole pH range.

Previous work (Montoneri, 2017) reports that the three BPS have significantly different chemical composition, surface tension activity and solution behavior, one from the other. This is the result of the different nature and composition of the sourcing MBW. The main variable at play in the present work was therefore the difference of the chemical nature of the BPS. As in the other tested BPS applications, a different performance in soil remediation was expected for the three BPS reported here.

As consequence of the biological nature of the sourcing MBW, characterizing the chemical nature of BPS is not possible as well as for synthetic materials. At the current state of knowledge, the only way of doing it is by their content of functional groups, molecular weight and solution behavior. These features allow assessing at least empirical relationships between products' chemical and operational features in the intended application. This situation poses also the problem of standardization. The EU Commission emphasizes the need to develop standards for products and processes to support market competitiveness, particularly in view of the developing bio based industry. So far, no standards are available for products employed in soil remediation. On the other hand, since BPS are only research products, comparing BPS with each other would not allow prospecting their potential marketability. The only way of doing it is assuming current major commercial surfactants as standards to which compare the BPS. The soil washing performance of BPS was therefore assessed by comparison with the conventional SDS, EDTA and DTPA commercial compounds.

Due to the strong dependence of BPS composition and properties on the sourcing MBW, and on the MBW variability depending on geographical, climate, consumers' habits, and seasonal changes, the authors recognize that the results of the BPS comparison with the above commercial surfactants may not be replicable in environments different from that where the investigated BPS have been obtained and used to carry on the present work. However, this is unavoidable challenge that research on renewable feedstock must face. Solving this issue requires numerous efforts over long time as the present work.

2. Methods

2.1. BPS and other reagents

The BPS were available from previous work (Montoneri, 2017). They were sourced from MBW sampled from the process lines of ACEA Pinerolese Industriale waste treatment plant in Pinerolo, Italy. These were the anaerobic digestate of food kitchen waste (FORSUD), the compost CV of gardening residues and the compost CVDF made from a mix of gardening residues, FORSUD and sewage sludge. These materials were hydrolysed at pH 13 and 60 °C to yield the BPS. Solutions of BPS at different concentrations were obtained by dissolving BPS in water. All solutions were stored at 4 °C before use. They were analyzed for metal content by Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-OES) Liberty series II Varian®. The analyzed elements and selected emission wavelengths were Cr 267.716 nm, Ni 231.604 nm, Cu 327.393 nm, Zn 206.200 nm, Cd

228.802 nm, Pb 220.353 nm, Mn 257.610 nm, Na 589.592 nm, K 766.490 nm, Ca 317.933 nm, Mg 285.213 nm, Al 396.253 nm, Fe 238.204 nm. Ten standard solutions were prepared by successive dilutions (from 25 mg L^{-1} to 30,000 mg L^{-1}) of a multi elemental solution (1000 mg L^{-1}). The concentration of the trace elements (Cr, Ni, Cu, Zn, Cd, Pb) was registered in mg L^{-1}. Hereinafter, the raw BPS are identified by the acronym of the sourcing material, i.e. CV, CVDF and FORSUD.

2.2. *Soil treatment and characterization*

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

2.3. *Equilibrium partition time measurement*

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, 31, 36, or 48 h, in an end-over-end shaker. They were then centrifuged (15 min, 3000 rpm), filtered using a 2.5 mm 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 contributed by the neat BPS in the solution. The calculated net amount of metal extracted from the soil by the BPS solution was used to calculate the % metal recovery (MR, % w/w) in solution referred to the starting amount of metal in soil (W) before washing, according to the following equation:

$MR = 100\ (X-Y)/W$ (I)

where X is the total metal content found in the washing solution and Y is metal content contributed by the total amount of BPS in the washing solution. Total organic C, in after use recovered washing solutions, was measured according to according Italian official methods of analysis (Ministero per le Politiche Agricole, 1999).

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/$CaCl_2$ 5 mM/0.01M, SDS (5 g L^{-1}). These washing solutions were analyzed following the same procedure reported in the above section.

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, 4000 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 kg/mol cut-off. The permeate was analyzed for heavy metal as described above.

2.6. *Statistical analyses*

Five replicates consecutive washing trials were run on each soil sample, each trial performed in triplicates with fresh surfactant solution on the soil recovered from the previous washing run. Unless otherwise stated, all data are expressed as mean ± standard deviations calculated over 15 samples, i.e. the three replicates performed on three different soil samples taken after the five consecutive washing runs performed on the same starting soil sample. The means of all the parameters were examined for significance by factorial Analysis of Variance (ANOVA) using the software JMP version 9 (SAS Institute Inc., Cary, North Carolina, USA).

When F values showed significance, individual means were compared using Tukey’s honest significant difference at $P \leq 0.05$.

3. Results

3.1. BPS characterization

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

Data for FORSUD, CV and CVDF BPS have already been published (Montoneri, 2017). Table 1 lists selected data, which are relevant to understand the different chemical composition, properties and performance in the intended application of the investigated BPS. The aliphatic to aromatic C ratio (Af/Ar) indicates the type of lipophilicity (mostly aliphatic or mainly aromatic) of the BPS. The amine (NR), phenol (PhOH) and carboxylic (COOH) groups are relevant for their property to chelate metal ions. The surface tension data provide hints on the solution conformation of the BPS. The data show that the FORSUD and CV BPS exhibit the largest differences. The former has the lowest values for the ash content and for the content of COOH acid groups, while exhibiting the highest values for the Af/Ar 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.

Montoneri (2017) reports also other data on the hydrolysis of MBW, which are particularly relevant in relation to the objective of the present work. 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 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 the 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, Table 1 data indicate that all three BPS, for 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.

Table 1. Chemical composition and surface tension data[a] for BPS.

		FORSUD	CVDF	CV
Ash[b]	w/w%	15.4±0.1c	27.3±0.2b	27.9±0.1a
C[b]	w/w%	45.1±0.1a	35.5±0.1c	38.3±0.1b
Af/Ar[c]		3.4±0.1a	1.3±0.1c	1.8±0.1b
NR[c]	% of total C	9.9±0.1a	7.8±0.1b	7.2±0.02c
PhOH[c]	% of total C	2.3±0.1c	5.9±0.1a	5.2±0.1b
[C]COOH[C]	% of total C	6.7±0.1c	9.4±0.1b	12.1±0.1a
γ_{CMC}[d]	mN m^{-1}	48.8±1.1b	61.8±2.1a	61.2±2.0a
CMC[d]	g L^{-1}	1.0±0.3c	3.1±0.1a	2.1±0.2b

[a] Values reported as mean and standard deviation calculated over triplicates; within each row, values with no letters in common differ significantly: a>b at $P < 0.05$.

[b] Concentration values referred to dry matter.

[c] Aliphatic (Af)), amine (NR), phenol (PhOH), carboxylic acid (COOH) C content.

[d] Critical micellar concentration (CMC) and surface tension at the CMC (γ_{CMC}).

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 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 reaction and characterized by Table 1 data, and in the de-ashed form containing less than 1% ash (Montoneri et al., 2019). De-ashing BPS by HCl/HF treatment 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 soil. The results (Fig. 1S in the supplementary material SM file) show that, compared to the raw BPS, the de-ashed derivatives exhibit 10-20% higher washing efficiency. In the authors' opinion, the higher performance level of de-ashed BPS does not justify the additional complexity of preparation deriving from using and handling the strong corrosive HCl and HF reagents and the effort to make the process economically and environmentally sustainable. CVDF exhibited higher washing efficiency than CV and FORSUD. Further experiments were carried out only with the raw CVDF containing 27 wt% ash.

Fig. 2 shows the results of the experiments carried with CVDF 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. 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.

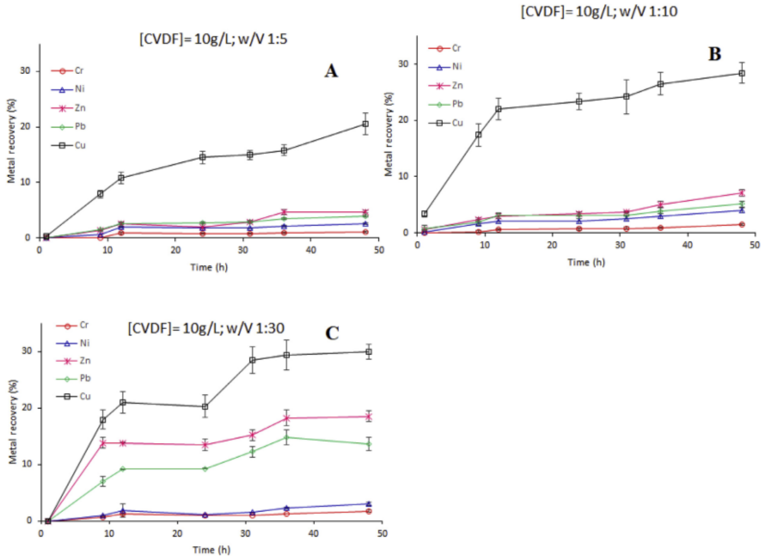

Fig. 2. Metal recovery (%) in 10 g L^{-1} CVDF solution as a function of time (hours) at different w/V soil/solution ratio: 1:5 (A), 1:10 (B), and 1:30 (C). Legend: Cu (black squares), Cr (red circles), Ni (blue up-triangles), Zn (magenta down-triangles), and Pb (green diamonds). Results of statistical analysis comparing metal recovery % values at each contact time for Fig. 2 A, B and C, separately, are given in the SM file, Table 1S.

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), DPTA (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/$CaCl_2$ 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, DPTA and SDS, five consecutive washing trials were performed with 24 h soil/solution contact time for each trial. Usually, a solution of DTPA 5mM is used for washing soils contaminated by heavy metals. Accordingly, in this work, the same concentrationwas 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 5mM DTPA. Plain water was used as control washing solution. Fig. 3 shows 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.

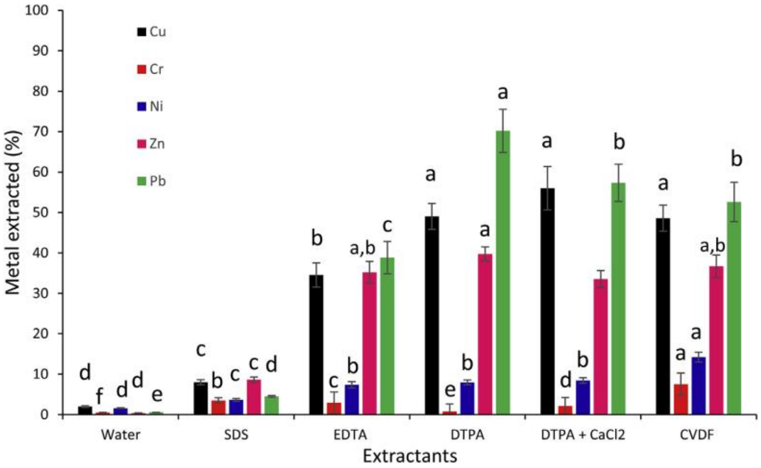

Fig. 3. Effect of different extractants in multiple extraction processes (solution/soil 10 w/V ratio and 24 h contact time) for the heavy metals analyzed. Extractants: bare H_2O, SDS 5 g L^{-1}, EDTA 2 g L^{-1}, DTPA 2 g L^{-1}, DPTA/$CaCl_2$ 2 g L^{-1}/0.01M, and CVDF 10 g L^{-1}. Legend: Cu (black), Cr (red), Ni (blue), Zn (magenta), and Pb (green). Columns with no letters in common indicate significantly different values: a>b at $P< 0.05$.

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 2S 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.

The data in Fig. 2S evidence a definite trend for the specific absorption of metals to increase upon decreasing 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. The only exception to this trend is the specific absorption of Cr reaching the maximum value at Cs 1 g 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 configuration from large aggregates of macromolecules to smaller micelles where the complexing functional groups are more accessible by the metal ions. There seems to be also a trend for the specific absorption to increase upon decreasing the volume/solid ratio at constant Cs value. This implies 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 among the BPS macromolecules in solution, is likely to affect the BPS molecular conformation and accessibility of its complexing functional groups by the soil metal ions. The available data do not allow rationalizing definitely the contribution of the CVDF concentration in solution and the solution/soil ratio to the CVDF soil washing performance. Given the complexity of the BPS molecular pool, it is unlikely that this could be ever established by identifying the active complexing molecules, and their chemical composition, solution behaviour and role in sequestering metal ions. Nevertheless, further experimental work could assess empirical relationships between the types of BPS and soils, and the soil washing parameters, in order to optimize the process for large scale application in real operational environment.

3.3. Secondary treatment of after use washing solutions

The scope of the secondary treatment was to dewater the recovered washing solution by separating a BPS-metal concentrate from clean water. Two processes were investigated by exploiting the BPS macro molecularity and insolubility at acid pH. The solutions recovered after 24 h soil washing with 100 g L^{-1} CV and

CVDF, and 50 g L^{-1} FORSUD (Fig. 1S) were treated by vertical flow membrane filtration under 5 bar pressure, and alternatively by precipitation at acid pH. The two processes allowed obtaining 95% of the starting aqueous solution in the permeate or chloride phase, and a residual 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 the permeate or chloride liquid phase, relative to its content in the solution recovered from the primary soil washing treatment. Contrary to the case of the primary soil washing treatment, in the secondary treatment of the after use washing solution, the lower is the % recovery of the metal in the liquid (permeate or chloride) phase, the better is the process.

Table 2. Results[a] 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[b]	42±2.0b	43±2.0a	51±3.2b	37±1.8b	37±1.7b
CVDF Chloride[c]	33±1.6c	13±0.5d	61±3.4a	59±3.1a	51±2.6a
CV Permeate[b]	23±1.1d	19±0.8c	14±0.8d	30±2.9c	22±1.6c
CV Chloride[c]	44±1.5b	3.0±0.02f	42±3.6c	65±5.5a	55±4.6a
FORSUD Permeate[b]	23±2.4d	6.0±0.3e	6.0±0.4e	12±1.3d	12±0.9d
FORSUD Chloride[C]	62±3.3a	31±1.2b	46±3.8b,c	57±4.8a	54±4.4a

[a]Values reported as mean and standard deviation calculated over triplicates (N = 3); within each column, values with no letters in common differ significantly: a>b at $P< 0.05$.

[b]Permeate after ultrafiltration through a membrane with 5 kg/mol cut-off.

[c]Solution obtained after precipitation with concentrated HCl.

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

4. Discussion

In this study, three MBW, sampled from different sections of an urban waste treatment plant, were used as sourcing materials of humic-like polymeric bio surfactants (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, 2017) 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 with formation of pseudo micelles. At higher concentration, intermolecular interactions take place and yield large aggregates of pseudo micelles. 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 micellise and solution conformation of the resulting molecular aggregates of typical conventional commercial surfactants, e.g., SDS 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. 2 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. 3), 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. 3) 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. 2. 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. 2. 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. 3 show that five sequential extractions, carried out with the CVDF solution, allowwashing 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

soil-M_t + ‘BPS(COOM)aq’ $\leftrightarrow$ soil + ‘M_t-BPS(COOM)aq’ (1)

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. The soil-M_t substrate is the soil containing the M_t trace metals. The water soluble BPS carboxylate, by its complexing/chelating capacity extracts the heavy metal contaminants (M_t) from soil to yield the 'M_t-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_t-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_t-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.

'M_t-BPS(COOM)aq' + 'HClaq' $\leftrightarrow$ 'M_t-BPS(COOH)solid' + 'MClaq' (2)

Alternatively, due its macromolecular nature, the 'M_t-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.

'M_t-BPS(COOM)aq' membrane filtration $\rightarrow$ 'M_t-BPS(COOM)retentate' + permeate (3)

Ultrafiltration of BPS has been proven to remove 94% of the water contained in the pristine BPS 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 chloride and permeate phases contain trace metals. The metals in both phases are likely bonded to BPS molecules with molecular weight lower than the membrane molecular cut off. These are water soluble at acid pH and permeate through the membrane. The permeate phase recovered from step (3) contains significantly less metals than the chloride phase recovered from reaction (2), with few exceptions for Cu in the CVDF and CV permeate and Cr in CVDF permeate. In the present work, step (3) has been carried out with membranes with 5 kg/mol molecular cut-off. Upon using membranes with lower molecular cut-off, it is more likely to obtain permeates with reduced metal-content through step (3) than trace metal-free chloride solution by reaction (2). Moreover, the reaction (2) yields a salt solution which requires further desalting treatment. Both treatments (2) and (3) yield a trace metal concentrate in the 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 industry or landfill. However, reaction (3) should allow obtaining cleaner water for further use.

4.1. Comparison of results with similar studies and perspectives of further improvement

Liu et al. (2018) report that the global land contaminated by heavy metals is over 20 million ha. The European Pollutant Release and Transfer Register (European Environmental Agency, 2018) includes information on pollutant releases to the environment from some 33000 industrial facilities in Europe for the period 2007-2016. Major released pollutants are Cu, Pb, Ni and Zn. The same are present also in the dismissed industrial site investigated in the present work by BPS soil washing.

A wide number of different techniques (Liu et al., 2018) are reported in literature to remediate metal contaminated soil. The cost and duration of soil remediation are technique-dependent and site-specific, up to \$500 ton^{-1} soil and 15 years. A thorough review of and comparison of the BPS soil washing performance with the known soil remediation techniques was not in the scope of the present work. Considering the wide variability of techniques and operating environments, it was unfeasible or not meaningful. Yet, a comparison/discussion of the findings in the present work and in previous similar work was proper to identify differences and perspectives of improvement.

To the above scope, a literature research was performed. It was restricted to case-studies where commercial surfactant had been used to wash soils containing the same trace metals as in the soil investigated in the present work. Most surfactant assisted soil washing on field tests have been performed for the removal of hydrocarbons from oil-contaminated sites. The literature reports a limited number of studies on soil washing for metal removal.

Wuana et al. (2010) tested EDTA, citric acid and tartaric acid as chelating agents to wash a type of sandy soil with texture close to the soil investigated in the present work. They spiked the soil with a mixture of Ni, Cu, Zn, Cd and Pb nitrates, and then washed it for 6 h with a 0.05M solution of the chelating agent at 1:25 solid/liquid ratio. They report EDTA being the most efficient extractant and the following extraction yields: Cu 70.3% > Ni 62.5% > Zn 60.4% > Cd 58% > Pb 56.7%. These yields are higher than achieved with BPS 10 g L^{-1} and EDTA 2 g L^{-1} (0.007 M) solutions, even after multiple extractions, each carried out for 24 h (Fig. 3). However, 24 h single extraction with 100 g L^{-1} solution (Fig. 1S) extracted 82% Cu. Also, the order of decreasing extraction yield of the different metals reported by Wuana et al. (2010) is much different than in Fig. 3. In the former case, Pb shows the least extraction yield. On the contrary, Fig. 3 shows higher extraction yield for Pb than for the other metals, both in the BPS and EDTA trials. This proves how results by the same extractant may change from case-to-case.

Particularly relevant for the present BPS case is the literature on the use of microbial surfactants (sophorolipids and rhamnolipids) for metal contaminated soil. These products have all desirable features for soil remediation. They are capable to lower the surface tension of water to 28 mN m^{-1} at critical micellar concentration of 0.8-2 g L^{-1} (Randhawa and Rahman, 2014). Compared to surfactants obtained from petrochemical raw materials, they offer the advantages of biodegradability, biocompatibility, low toxicity.

Mulligan et al. (1999) report removal of 70 Cu and 100% Zn from oil-contaminated soil by a series of five batch washes performed with 0.1-4% microbial surfactants solutions.

Slizovskiy et al. (2011) conducted batch studies on a soil, where a zinc smelting facility had deposited metals for 80 years. They compared a commercial rhamnolipid surfactant with commercial 1-dodecylpyridinium chloride and oleyl dimethyl benzyl ammonium chloride. They found that the rhamnolipid bio surfactant was the most efficient. It removed 39-68% Zn, Cu, Pb, and Cd from the soil, compared to <6% by water alone. Addition of EDTA to the bio-surfactant yielded >90% removal of all metals.

Juwarkar et al. (2007) report similar performance for a rhamnolipid bio surfactant solution, which removed, after 36 h flushing, 88% Pb from a clay soil containing 0.4 organic C %, spiked with Pb acetate to 905 ppm level. Flashing the soil with tap water under the same conditions removed 2.7% Pb.

Qi et al. (2018) collected a surface clay soil sample containing 0.66% organic C, spiked with Pb acetate at 265 mg/kg dry soil level and batch washed it with three types of sophorolipids, namely total SLs, lactonic SLs and acidic SLs, and two types of synthetic surfactants (SDS and Tween-80). Soil washing trials were carried out at 1/10 g/ml soil/surfactant solution for 24 h at room temperature. The removal efficiency of Pb from soil depended upon the type and solution concentration (Cs) of the surfactant. At 8% Cs, it was 30% by total SLs, 20% by SDS, 5% by Tween-80. At 1% Cs, it was 7% by total SLs, 18% by SDS, 2.5% by Tween 80. At 0.5% Cs, it was 2.5% by total SLs, 18% by SDS, 2% by Tween 80. By comparison, Fig. 2 reports 10% Pb removal efficiency by CVDF under similar conditions as total SLs (i.e. 24 h soil-solution contact time and 1% CVDF concentration). Fig. 3 reports 5% Pb removal efficiency from soil by 0.5% SDS. The comparison shows that under similar conditions, total SLs and CVDF BPS achieve close removal efficiencies. For the SLs-SDS trials, the Pb removal efficiency order by SLs and SDS changes upon increasing surfactant concentration. This is due to strongest dependence of the Pb removal efficiency by SLs upon the surfactant concentration.

It is noteworthy in the paper by Qi et al. (2018) to mention that at 24 h contact and 8% surfactant solution concentration, the Pb removal efficiency changes significantly depending on the SLs type, i.e. 30% by total SLs, 45% by acidic SLs, very poor removal efficiency by Tween-80. The reason of the higher Pb removal efficiency by acidic SLs is that they contain more COO^- functional groups and are more water soluble. By this feature, they can complex more metals and increase the metal adsorption to the surface of the surfactant.

By comparison with the SLs results, the multiple extractions by BPS (Fig. 3) achieve 50% Pb removal efficiency. Table 1 shows that BPS have several functional groups, such as amine, phenol and carboxylic, which in principle may play even more efficient metal complexing activity. At this regard, it should be considered that the SLs-washed soil contained 0.66 organic C and the Pb was spiked into the soil. Instead, the BPS washed soil contained one order of magnitude more organic C and Pb aged in it for over 50 years. The BPS therefore faced a stronger competition from the metal sequestering power of the soil organic matter. These considerations offer worthwhile scope to study further the effects of BPS concentration in the soil washing solution on the metal recovery efficiency. Motivation for more investigation of BPS performance in soil remediation comes from a recent paper (Montoneri et al., 2016). This reports that ozonisation of BPS allows increasing the content of acidic functional groups and lowering the product surface tension by 20%. The ozonized BPS and the acidic SLs share common features, such as some functionalized C moieties, surface activity, renewable source, biocompatibility and low/no toxicity. SLs are molecules constituted by long chain aliphatic hydroxyacid bonded to sugar residues. These make up an optimum lipophilic/hydrophilic C balance, which is responsible of the SLs' exceptional surfactant properties. BPS contain aliphatic and sugar residues, but also aromatic C moieties, all being memories of the polysaccharide, fat, protein and lignin proximates in the pristine MBW. Ozonisation of BPS has been found to oxidize mainly the aromatic rings and convert them to aliphatic carboxylic acids. This chemical change is associated with the improved surface tension properties of ozonized BPS, compared to the pristine BPS. Oxidation of MBW to convert the lignin aromatic rings to carboxylic acids seems the route to obtain bio surfactants matching sophorolipids' and rhamnolipids' properties. Ozonolysis is carried out also on SLs to increase their hydrophilic character and make them more efficient in detergency applications (Van Bogaert and Soetaert, 2011).

One important major difference between the BPS and the bacterial surfactants is that the production cost of BPS is estimated from 0.1 €/kg for the BPS hydrolysates (Montoneri, 2017) to 0.8 €/kg for the ozonized BPS (Montoneri et al., 2016). This is one-two order of magnitudes lower than the 2-5 €/kg production cost reported for SLs (Van Bogaert and Soetaert, 2011) and the 30-150 €/kg market price reported for Rhamnolipids (Connolly et al., 2010). The data in Fig. 1S show that BPS at the maximum solubility concentration (50-100 g L^{-1}) may allow reaching nearly quantitative or competitive metal removal efficiency from contaminated soil. The low cost is a key feature in favour of BPS. Even operating at higher surfactant concentrations to obtain the same metal removal level, the cost of the consumed BPS would be still lower than that of the bacterial surfactants. On this basis, demonstrating equal or higher washing efficiency of BPS, compared to SLs, prospects a real breakthrough in the field of soil remediation technology.

4.2. Limitations of BPS-based technology

In the present work, a full investigation of the operational parameters has not been carried out. The pH, temperature and mixing different surfactants should be further investigated for their effect on the process' metals removal efficiency. One even more important issue is the replicability of the processes in other polluted sites. For implementing the results of the present study to real environment scale, the major uncertainty lies in the replicability of the BPS composition and properties as function the sourcing MBW. This is expected for two main reasons. The MBW chemical composition varies from sourcing site-to-site, because of the differences in climate, seasons and consumers' habits. The nature of the soil to be remediate varies as a function of the type of soil and industrial activities operating on it (Mulligan et al., 2011). Ideally, to achieve the objective of turning MBW into exploitable resource for value added products in every urban settlement in the world, the BPS to remediate a specific soil site should be obtained from the local MBW. Replicability and transferability of the proposed BPS-based production and application technology can only be assessed through a large research program involving different actors located over different regions. This can only be achieved through the cofounding instruments provided by the EU environmental policy.

4.3. The stake in converting EU MBW to value-added chemicals

There are about 2000 MBW treatment plants in EU, with average processing capacity of 17,500MBWt/yr for total 35 Mt/yr treated by fermentation to yield compost (European Compost Network, 2019). Yet, these plants and others based the fermentation-based scheme in Fig. 1 are not cost effective (Montoneri, 2017) and/or cause greenhouse gases (GHG) and fine dust emission (Ellen Macarthur Foundation, 2017). The environmental impact is made worse considering the total EU MBW production (Tsagaraki et al., 2017). Two thirds of this undergo uncontrolled decomposition. They generate 60% of GHG emission, with estimated total 12,000 CH_4 Mm^3/yr emission. The economic burden of this situation is born by tax payers. The problem is addressed by the EU 2011 Roadmap to a Resource Efficient Europe and other directives.

Applying organic chemistry reactions to MBW (chemical route) may allow tailoring the functionalization of the native organic components of biomass to obtain value-added products for specific applications. Implementing this approach to treat the total EU MBW production may yield 56 Mt/yr bio-based products with value of 1500-150,000 €/t, generating a total market impact of 84-8400 billion €/yr. To appreciate the real impact of these figures, it should be considered that EU synthetic chemicals production is 322-330 Mt/yr (Eurostat Statistics Explained, 2017). These have 1037 Mt/yr CO_2 emission potential. The EU current turnover of biobased plastics and chemicals is estimated about 70 billion €/yr (O'Really, 2017), expected to grow at 22% by 2025. Thus, implementing to commercial operational level the MBW-chemical paradigm here proposed may impact the EU market for 17% of its chemicals production and for at least 100% of its bio-based plastics and chemicals turnover value.

Along with the economic impact, the social impact of the implementation of the chemical route may come from creation of jobs and relief of citizens from taxes to cover the tipping fee for waste disposal. Under the above implementation scenario, MBW currently costing EU citizens 9 billion €/yr for disposal would generate a business worth 1-3 order of magnitude more than its cost. The number of processing installations would increase from 2000 to 5000-6000. Based on a recent study (Goldstein, 2014), this may create 254,000 new jobs. Considering that currently 167,000 are employed in the 2000 MBW treatment plants, the job increases by implementing the MBW the organic chemistry approach is estimated being 150% of the current employed labour force. Unanimous social acceptance of this implementation is expected also in view of the 100% reduction of the above GHG emission from uncontrolled waste management and for 17% reduction of the 1037 Mt/yr CO_2 emission from fossil-sourced synthetic chemicals substituted by MBW sourced bio-based chemical products.

To better appreciate the impacts of the above implementation, it should be taken in consideration that the European Commission (2018) reports that current biotechnology based chemicals and biofuels represent approximately 57 billion €/yr revenue and involve 300,000 jobs. The above expected impact from MBW treatment implementation is close to and/or greater than the current EU estimates for the biotechnology/bio-based product sector. Thus, there is enough perspective to allocate bio-based products sourced from MBW in the EU chemical market and double the economic and social impacts deriving from the current biotechnology bio-based industry. Application of the chemical approach to other bio-wastes from agriculture and agro-industrial source would increment the impacts expected from MBW only as feedstock.

4.4. The view points from the authors

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

The hydrolysis of municipal bio-wastes yields polymeric bio surfactants (BPS) with chelating properties, which are particularly suitable for removal of heavy metals from the contaminated soil. The present work proposes a new process comprising washing soil contaminated with metal pollutants 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 in this way, and the residual chloride or permeate liquid phase can be recycled for further uses. The data provide basic data and offer scope for further development/implementation of the proposed process scheme (reactions 1-3) to sustainable operation in real environment in batch or continuous mode.

The results contribute to assessing the hydrolysates of MBW as value-added products for multiple use and the MBW as sustainable feedstock for the production of renewable biobased chemical specialities for use in place of synthetic chemicals from fossil source. The scale up of the proposed BPS technology to operation in real environment must challenge a number of potential criticalities. These are connected with the replicability of the BPS composition and properties as function the sourcing MBW, and the variability of the site to be remediate (see section 4.2).

More ambitiously, the present article has relevance for the sectors of waste management, pollution and chemical industry. So far, except for the production of biogas, MBW are resources not exploited to their full potential as feedstock for the production of biobased chemicals. Thus, mature traditional chemical capabilities of major companies have not been applied for MBW valorization in this direction. At the present time, MBW are resources that major chemical companies do not possess and are not familiar with. On the contrary, they possess chemical processing capabilities, but are not at ease with managing biochemical processes. The present work makes two points. The first is that more chemical processing of MBW, and in general of bio-wastes from any source, should be studied, rather than focusing mainly on biochemical processing. The second is that the two chemical and biochemical processing approaches should be better integrated. The production of BPS by chemical hydrolysis of fermented MBW is a case of this integration. The application of BPS as agents for soil remediation, as proposed in the present work, is an example of product stewardship (Hart and Dowell, 2011). It allows realizing a renewable C cycle based on the use a bio-waste to reduce the pollution impact of the chemical industry. At the same time, it is encompassed in a research framework not merely focused on pollution. Together with previous research on MBW (Montoneri, 2017), it aims to confirm the main thesis of the 2004 original research plan on the sustainability of bio-waste as feedstock and of its processes and products for multipurpose uses in agriculture, animal husbandry, and in the chemical industry. The sustainable development of this strategy is consistent with the proposition (Hart and Dowell, 2011) of the natural-resource-based view (NRBV). At its full development stage, this approach is expected not only to solve the environmental impact of the increasing bio-waste production, but also to develop a biobased industry producing economic and social benefits such as job placement and better life style. These benefits are expected to be realized in all region of the world, rich and poor, due to the shift from a fossil based economy to an economy based on the exploitation of worldwide available bio-waste as feedstock. The authors trust that the reported work can contribute updating the NRBV and helpfully inform actors working for the eco-friendly sustainable exploitation of renewable feedstock and development of a biobased chemical industry.

5. Conclusions

The polymeric biosurfactants (BPS) obtained by alkaline hydrolysis from three different streams of the Acea Pinerolese MBW treatment plant have been demonstrated efficient active principles for soil remediation. Their performance has been shown equal or greater than that of conventional commercial products used for the same purpose. Two alternative secondary treatments of the recovered BPS solution after washing, by precipitation and membrane filtration, have been tested. The latter yields better results. The study confirms the indications of previous findings, i.e. that the BPS are multipurpose products and that MBW is a sustainable efficient feedstock to process in order to obtain valued added products. In line with the Green Supply Chain Management, Sustainable Supply Chain Management and Natural-Resource-Based Views (NRBV), environmental, economic and social benefits for the MBW valorization scenario have been shown. An MBW biorefinery, integrating chemical and biochemical processes, seems feasible.

Declaration of competing interest

None.

Acknowledgement

This work is the result of research carried out at the University of Torino under the Biochemenergy and Agrienergia projects funded by Regione Piemonte and Ministero delle Politiche Agricole, respectively. Polytechnic of Torino is also acknowledged for contribution under project Starting Grant RTD (project number: 54_RSG17NIR01)

Abbreviations

BPS, polymeric bio surfactants; MBW, municipal bio-wastes; 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.

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