Resources, Conservation & Recycling Advances 18 (2023) 200153

Contents lists available at ScienceDirect

Resources, Conservation & Recycling Advances

journal homepage: www.sciencedirect.com/journal/Resources-Conservation-and-Recycling-Advances

Leather-based fertilizers from Personal Protective Equipment (PPE) reverse logistics: Technical efficiency and environmental safety

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ARTICLE INFO

Keywords:
Chrome-tanned leather residues
Circular economy
Chromium removal
Agronomic efficiency

ABSTRACT

Agriculture and industry are seeking healthy food and enough goods to meet the global demand without causing environmental impacts, which motivates the search for sustainable and eco-efficient technologies. This study focuses on reverse logistics in the Personal Protective Equipment (PPE) industry. Chrome-tanned leather shavings from the manufacture of PPE and post-use leather PPE were used to produce leather-based fertilizers (LBFs), which were evaluated for their agronomic efficiency and food safety. N-rich liquid LBFs were successfully produced through hydrolysis, either with or without previous chromium extraction. At the dose of maximum technical efficiency, LBFs are safe, with acceptable levels of Cr in the plant biomass and the soil compartments. However, LBF overdoses promote Cr accumulation in plants and soils, which demonstrates the need for a rigorous control over the fertilization management to ensure successful PPE reverse logistics.

1. Introduction

With the mission to guarantee healthy food and enough goods to meet the growing global demand with minimal impacts on the environment, the agricultural and industrial sectors are in the spotlight of the modern society. This, along with the scarcity and high costs of raw materials, has prompted the search for sustainable and eco-efficient technologies in line with the Sustainable Development Goals, such as zero waste, waste reduction and reuse of raw materials, with a special appeal to the bioeconomy and circular economy.

Environmental concerns and escalating landfill costs have driven the research and technological sector towards innovative ways of waste decontamination and transformation of solid residues and byproducts into valuable materials (Chojnacka et al., 2021; Li et al., 2019; Majee et al., 2021). In this sense, tanning industry wastes could be used to compose a set of value-added products such as keratin, collagen, gelatin, adsorbents and fertilizers (Chojnacka et al., 2021; Li et al., 2019). Organic fertilizers produced from hydrolyzed leather waste (leather-based fertilizer - LBF) have been used as a nitrogen (N) source for crops in Italy, United States, Korea and Poland (Abichequer et al., 2011; Ciavatta and Sequi, 1989; Dell'Abate et al., 2003) and are a subject of research in China (Dang et al., 2019), India (Majee et al., 2019), Slovenia (Vončina and Mihelič, 2013), Brazil (Abichequer et al., 2011; Bavaresco et al., 2019; Coelho et al., 2015; Nogueira et al., 2011), among others. In Brazil, despite the significant availability of leather residues and the promising results of the use of the residues as a nitrogen source due to the collagen structure of leather, only a few initiatives have taken place in the industry for the use on a large-scale. Isolated initiatives have been launched in the Brazilian industrial sector, especially since the promulgation of the National Policy on Solid Waste, with the objective to reduce the volume of solid waste from the manufacturing process. A successful example is the use of leather residues from tanneries in the production of agricultural inputs by some Brazilian fertilizer companies. However, the use of products at the end of their life cycle in the production of valuable new products is still incipient in Brazil, despite some practice of isolated sustainable actions (Schreiber et al. (2023). Furthermore, to the best of our knowledge, there are no reports on using post-use PPE in the production of organic

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https://doi.org/10.1016/j.rcradv.2023.200153

Available online 28 April 2023

liquid fertilizer for the purpose of reverse logistics.

Brazil has the largest commercial cattle herd, is the second largest leather producer worldwide (CICB, 2019; Countries Today, 2019) and one of the countries with the largest fertilizer consumption, with production far below demand (ANDA, 2020; IFA, 2019). Additionally, it is estimated that the annual generation of shavings in the national leather production is around 183,212 ton, since the national production of finished bovine leather was 91,606 thousand m^2 in 2021 (CICB, 2022). According to Lawinska et al. (2019), it is estimated that 1 ton of waste tanning shavings is produced for each 4 tons of raw leather undergoing tanning, which gives more than 2 kg of waste for each square meter of finished leather.

Despite this, there are only a few organic LBFs available as registered products for the agricultural sector. Limitations posed by the legislation partially explain the scarcity of LBFs in Brazil. Regarding organic fertilizers, until 2016, chromium (Cr) was regulated only as total Cr, and the threshold value of the total Cr content (200 mg kg^{-1}) was considered restrictive for products based on chrome-tanned leather. Since the Normative Instruction No. 27/2016 (Brasil, 2016), only the hexavalent form of Cr (Cr (VI)) has a maximum permissible limit established (2 mg kg^{-1}), allowing the development of a new set of LBFs. The European Union, United States and Italian legislation also allow the use of Cr-containing fertilizers (Ciavatta et al., 2012). Although the trivalent form of Cr (Cr (III)) is considered an essential nutrient for animals and humans (Pechova and Pavlata, 2007), it can be toxic for plants, even at very low concentrations (Alloway, 1993; Macnicol and Beckett, 1985). In specific situations, Cr (III) can be converted into Cr (VI) (Shadreck and Mugadza, 2013). Therefore, efficient and low-cost Cr removal processes are desired. At the same time, setting adequate doses of LBF is imperative for the agronomic efficiency of the developed products, in order to avoid negative impacts of Cr on the crop yield and the environment.

Although the literature indicates potential directions for the valorization of leather waste (Chojnacka et al., 2021), few initiatives support the use of leather byproducts on a large scale. Furthermore, to the best of our knowledge, there are no reports or patents using post-use PPE in the production of organic liquid fertilizer for the purpose of reverse logistics. The lack of feasible and low-cost technologies limits the economic viability of LBFs, despite concerns related to the increasing amount of waste and the growing demand of raw materials. According to Chojnacka et al. (2021), the challenge is to reconcile the needs of consumers with responsible waste management to effectively bring the recycled waste as efficient and safe products to the market.

This paper focuses on an alternative solution for chrome-tanned leather waste, aiming to provide technical-scientific support to an initiative to implement reverse logistics for the Brazilian Personal Protective Equipment (PPE) industry. Two types of wastes – chrome-tanned leather shavings from the manufacture of leather PPE and post-use leather PPE (gloves, leg cover, apron) – were used for the synthesis of organic liquid fertilizers, with or without a partial Cr removal, in an environmentally friendly semi-industrial process. The process was developed as part of an Innovation Project for Industry, involving a PPE producer company and a steel producer.

The LBFs were produced by hydrolysis on a pilot scale. Subsequently, the agronomic efficiency and the safety of the products were evaluated in the growth of arugula (immediate effect) and ryegrass (residual effect) crops under two contrasting soil types.

2. Material and methods

2.1. Leather waste and post-use leather PPE

The LBF production process was developed as part of an Innovation Project for Industry, carried out by Senai Institute of Technology in Leather and the Environment in partnership with the company JGB Personal Protective Equipment (São Jerônimo, Rio Grande do Sul, Brazil) and its main PPE customer, which is a Brazilian steel producer. PPE is supplied by JGB to the customer, which returns it after use. The post-use PPE were decontaminated before the hydrolysis process, thus avoiding the presence of contaminants from the processes in which they were used. The leather shavings from the manufacture of leather PPE (wet blue leather, semi-finished leather and leather dust) provided by JGB Personal Protective Equipment were mixed with the decontaminated post-use leather PPE and submitted to hydrolysis with or without previous Cr removal.

2.2. Cr removal and development of leather-based fertilizer (LBF)

Prior to the hydrolysis, a part of the mixture of leather shavings and post-use PPE was submitted to a Cr removal process with potassium sodium tartrate tetrahydrate ($KNaC_4H_4O_6 \cdot 4H_2O$) and citric acid anhydrous in a milling drum according to Malek et al. (2009). Subsequently, both batches (with and without previous treatment for Cr removal) were submitted to hydrolysis in an environment with a controlled temperature and pressure. To briefly describe the process, 300 kg of the mixture and an additive to correct the pH (0.1% m/m calcium oxide) were gradually heated in a hydrolyzer until reaching 160 °C under a pressure of 6 kgf cm^{-2} and then kept under these conditions for 60 min. It is important to mention that prior to adding the mixture to the hydrolyzer, the equipment was gradually heated for 6 min at 120 °C. Then, immediately after the period of 60 min in the hydrolyzer and before opening the equipment, a pressure relief and a cooling down to 90 °C were performed. Subsequently, the collagen material was cooled to a temperature of 50 °C by using artificial ventilation for 15 to 20 min and then stabilized by adding 1.4% (m/m) (4.2 kg) of bromelain enzyme under constant stirring until reaching a temperature of 35 °C. This process was described in detail in the patent application entitled – "Process and composition of liquid fertilizer from PPE leather waste" (BR 102,021, 020,470–2).

The developed process resulted in two LBFs, both in liquid form: 1. LBF 67 - hydrolyzed collagen from chromium-tanned leather with a partial extraction of chromium; 2. LBF 64 - hydrolyzed collagen from chromium-tanned leather without chromium extraction. A complete chemical characterization of these products was carried out at Icasa - Instituto Campineiro de Análise de Solo e Adubo Ltda (Campinas, São Paulo, Brazil), according to the methodology for analyses of fertilizers established by the Brazilian Ministry of Agriculture, Livestock and Food Supply (Brasil, 2017).

2.3. Agronomic efficiency and safety of LBF

2.3.1. Experimental setup

To assess the safety and efficacy of the LBF 67 and the LBF 64 as a N source, pot experiments were designed and conducted to evaluate the immediate effects with arugula (*Eruca sativa* cv. Apreciata) and the residual effects with ryegrass (*Lolium multiflorum* cv. BRS Ponteio). The succession system prioritized arugula for two main reasons: (1) to assess the food safety risk, as the above ground parts of the plant are entirely edible, (2) any damage to the leaves caused directly or indirectly by the LBF can reduce the nutritional and commercial value of the product. In turn, ryegrass was selected due to its importance as a grazing crop in livestock systems and as a cover crop in grain and vegetable production systems in Southern Brazil.

The experiments were conducted under environmentally controlled conditions in a greenhouse in Pelotas (31°40′S and 52°26′W), State of Rio Grande do Sul, Brazil. The topsoil (0.00–0.20 m) of two Brazilian agricultural soils with contrasting characteristics were employed: an Ultisol or "Argissolo Vermelho Amarelo" and an Oxisol or "Latossolo Vermelho", according to the FAO classification (IUSS, 2022) and the Brazilian system of soil classification (Embrapa, 2018), respectively. According to the Köppen classification, the climate of the region is humid subtropical (Cfa), with an average annual temperature of 17 °C and an average annual rainfall of 1.400 mm (Alvares et al., 2013).

The soils were chemically characterized and then supplied with dolomitic limestone to achieve a pH of 6.0, which is considered ideal for arugula and ryegrass cultivation (CQFS, 2016). After liming, the soils were mixed, humidified and left to react for 30 days. Thereafter, the soils were analyzed again to allow the determination of fertilizer doses. The Ultisol and the Oxisol present a clay content of 280 and 420 g kg^{-1}, an organic matter content of 10 and 44 g kg^{-1}, a pH of 6.7 and 5.4, and a $CEC_{7.0}$ of 8.3 and 16.6 $cmol_c$ dm^{-3}, respectively (Table A.1, Supplementary Material).

Each experimental unit (plastic pot) was filled with 2 kg (dry basis) of unstructured soil (clods < 4 mm) and a base fertilization was applied according to the requirements of each soil type as follows (CQFS, 2016): 20 kg N ha^{-1}, 240 and 120 kg P_2O_5 ha^{-1}, and 180 kg K_2O ha^{-1}, for the Ultisol and the Oxisol, respectively. The sources of N, P and K were urea, triple superphosphate and potassium chloride, respectively. The soil moisture content was kept at 90% of the water holding capacity of each soil throughout the experimental period.

2.3.2. Experimental design and treatments

Each product (LBF 64 and LBF 67) was considered an individual experiment. The experimental design for each one was a randomized block design with split-plot and four replicates. The factor 'soil type' consisted of two levels (Ultisol and Oxisol) and the factor 'dose of LBF' of five levels (LBF 64: 0, 89.1, 178.1, 356.3, and 712,5 kg N ha^{-1} and LBF 67: 0, 91.9, 183.8, 367.5, 735.0 kg N ha^{-1}) (Table A.2, Supplementary Material). Thus, the treatment design was factorial, with the soil type allocated in the plot and the dose of LBF in the subplot. Application rates were calculated based on the total N content in each LBF and the typical agronomic recommendations for nitrogen (N) fertilization of arugula (180 kg N ha^{-1}) along with under- and overdoses, the latter to simulate application over time.

Each LBF dose was split into thirds and applied in the soil (fertigation) exclusively along the arugula crop cycle, following technical recommendations: 1st application in the seedling transplantation; 2nd application at 14 days after transplantation; 3rd application at 21 days after transplantation. Each LBF dose was diluted with 100 mL of deionized water, and the resulting solution was gently dropped on the soil surface, avoiding runoff and leaching.

2.3.3. Plant harvesting and soil sampling

The arugula plants were harvested 29 days after seedling transplantation and immediately weighed to determine the shoot fresh mass. Subsequently, the harvested aerial part of the plants in each pot was dried in a forced-air drying oven at 60±2 °C to a constant weight to obtain the shoot dry mass (DM). Finally, representative samples were taken after finely grinding the dried biomass (IKA A 11 basic Analytical mill) for a quantification of nitrogen, phosphorus, potassium, calcium, magnesium, manganese, copper, zinc, boron, sodium, hexavalent and total chromium. The quantification of macro and micronutrients was performed according to Teixeira et al. (2017) and the chromium analysis, performed by ICASA (Campinas Institute of Soil and Fertilizer Analysis), according to the methodology of EPA-SW 846–3051a, Rev.1, 2007 (U.S. EPA 2007); EPA-SW 846–6010d, Rev.4, 2014 (U.S. EPA 2014.

For ryegrass, two shoot cuts were performed, the first at 10 cm above the ground and the second at the ground level, at 48 and 68 days after sowing, respectively, aiming to simulate animals grazing. The samples were submitted to the same procedure mentioned above for the determination of shoot fresh and dry mass and quantification of nutrients.

Soil samples were collected after ryegrass harvest, 110 days after the first application of treatments, and submitted to IBRA (Brazilian Institute of Analysis) for analyses of trace elements by microwave digestion (Cd, Pb, Cr, As, Hg) or alkaline digestion (Cr (VI)), according to the EPA 3051A and the EPA 3060A method, respectively (U.S. EPA 2007; U.S. EPA, 1996). Quantification was performed by graphite furnace and hydride generation atomic absorption spectrometry and, in the case of Cr (VI), by colorimetry, according to the EPA 7196A method (U.S. EPA, 1992). Analyses of available nutrients (N, P, K, Ca, Mg, Mn, Cu, Zn, B and Na) were performed by the Soil Analysis Laboratory at the Federal University of Santa Maria as described in Tedesco et al. (1995).

2.4. Statistical data analysis

The dataset of each response variable was submitted to a verification of discrepant values and residual normality tests to verify if they follow the normal probability distribution. An analysis of variance ANOVA (F test, $p < 0.05$) was then performed considering the interaction between the LBF doses and the soil types. When significant, a Tukey test ($p<0.05$) was performed for the soil type factor and, if there was an interaction effect, the degrees of freedom were unfolded, the effects of the LBF doses were compared within each soil type and a polynomial regression was performed. All data analyses were performed using the statistical software WinStat.

3. Results and discussion

3.1. LBF characterization

The leather residues with or without Cr removal were submitted to an enzymatic hydrolysis, which significantly affected the chemical composition of the LBF 64 and the LBF 67. The LBF 67 and the LBF 64 show a pH of around 5.7 and contain 21.6 and 42.0% total amino acids, 4.9 and 9.5% N, 1.04 and 0.75% Na, 25.4 and 29.7% C, 0.17 and 0.68% S, 0.06 and 0.15% P, and 0.09 and 0.04% K, respectively. Complete characterization is available in Table A.3, Supplementary Material.

The N content reached slightly lower values than similar products described in the literature (Casadesús et al., 2019; Majee et al., 2021; Polo et al., 2006). Conversely, the other nutrients occur in the LBFs at low concentrations, which means that these fertilizers must be used as a nitrogen source in association with other products to supply plant requirements. Studies aiming to prospect new organic raw materials are in progress to formulate an NPK LBF, since nitrogenous LBF, when accompanied with phosphorus and potassium, is usually more effective for promising agronomic results, as showed by Nogueira et al. (2010).

Concerning the total Cr content, the LBF 64 contains 0.81%, while the LBF 67 showed 0.49% after the removal with $KNaC_4H_4O_6{\cdot}4H_2O$ and $C_6H_8O_7$ (removal rate of 39.3%, or 3176 mg of chromium per kg of leather-based raw material) (Table A.3, Supplementary Material). The probable reaction occurred in the removal is that the Cr present in the leather residues combines with the ionized carboxylic group of tartrate, as described by Malek et al. (2009). According to these authors, during the tanning process, Cr fixation into leather is obtained through several simultaneous chemical reactions, stabilizing the chemical bonds between the Cr atoms through oxygen bridges, and stable chemical bonds between the Cr atom and the carboxylic groups of collagen. The authors mention that these two kinds of bonds must be destabilized in the Cr removal process through successive chemical reactions that cause their breaking (rupture of Cr–Cr and Cr–collagen bonds).

One could consider this a satisfactory rate of Cr removal, making the removal a valid process for the industry, especially when the post-use PPE presents Cr contamination from the segment in which it was used. However, the Cr removal process also reduced the N content approximately by half (LBF 64 versus LBF 67). Therefore, agronomically, the process would only be justified if the efficiency of the LBF 67 was significantly higher than that of the LBF 64, which was not observed, as will be discussed further. In addition, the process increased the Na concentration of the LBF 67 (Table A.3, Supplementary Material), which was also reflected in the crop tissue (Tables 1 and 2). Despite this increase, the crops did not show visible symptoms of Na toxicity. However, high doses of this product should be avoided in Na-sensitive species and sodic soils.

Considering these results, the LBF 67 may need methodological

Table 1
Nutrient and trace element content in shoot dry mass of arugula and ryegrass cultivated in an Ultisol and an Oxisol with application of increasing doses of LBF 64 (hydrolyzed collagen from chromium-tanned leather without chromium extraction).

Soil	Treatment	N	P	K	Ca	Mg	Mn	Cu	Zn	B	Na	Cr	Cr (VI)
		%	g kg^{-1}				mg kg^{-1}						
							Arugula						
Ultisol	Control	5.1	4.6	61.8	21.4	7.5	131.6	10.1	29.3	28.0	867.0	1.3	<0.10
	LBF 64 – D1	5.9	4.2	67.5	19.5	6.4	107.1	6.9	32.6	41.1	1212.9	4.0	<0.10
	LBF 64 – D2	6.5	4.9	62.2	20.7	6.3	103.4	8.6	28.9	30.1	1443.8	6.1	<0.10
	LBF 64 – D3	6.9	5.0	54.5	19.1	6.0	120.3	8.0	34.2	34.0	1594.3	8.6	<0.10
	LBF 64 – D4	7.7	4.2	51.7	19.4	6.9	161.0	10.1	35.5	29.1	2297.3	28.3	<0.10
Oxisol	Control	5.1	3.9	49.0	25.4	10.1	76.7	7.6	27.9	26.1	1029.7	1.1	<0.10
	LBF 64 – D1	5.7	3.2	41.7	24.2	9.0	56.4	6.7	27.6	22.4	1071.0	5.2	<0.10
	LBF 64 – D2	6.2	2.5	42.8	25.5	9.3	82.9	8.7	41.1	28.7	1309.6	4.1	<0.10
	LBF 64 – D3	6.3	2.9	49.4	17.2	7.4	54.3	5.7	24.0	17.9	1971.3	6.6	<0.10
	LBF 64 – D4	6.7	3.7	50.1	22.3	8.3	66.4	9.1	34.9	30.9	2173.7	18.0	<0.10
							Ryegrass						
Ultisol	Control	2.0	5.8	39.8	8.5	4.3	121.2	11.3	29.6	36.9	850.2	n.a.	n.a.
	LBF 64 – D1	3.3	4.7	41.8	8.8	4.6	71.2	18.7	28.1	29.9	2067.4	n.a.	n.a.
	LBF 64 – D2	5.0	4.5	41.4	8.8	5.1	64.3	15.4	28.7	36.7	2566.4	n.a.	n.a.
	LBF 64 – D3	4.8	4.9	41.1	10.4	5.7	84.4	30.7	30.3	32.1	4359.8	n.a.	n.a.
	LBF 64 – D4	5.0	4.9	35.8	11.8	5.8	163.8	28.5	38.6	37.8	2126.1	n.a.	n.a.
Oxisol	Control	2.6	2.4	50.0	10.1	6.3	50.3	12.9	26.3	30.7	1167.6	n.a.	n.a.
	LBF 64 – D1	4.4	2.3	48.9	11.3	7.1	71.6	15.9	26.5	28.3	3537.5	n.a.	n.a.
	LBF 64 – D2	5.2	2.5	53.8	11.3	7.2	90.1	15.9	30.0	28.8	4988.5	n.a.	n.a.
	LBF 64 – D3	4.9	2.6	56.8	11.2	7.6	122.4	15.6	35.4	24.3	4079.2	n.a.	n.a.
	LBF 64 – D4	5.4	2.3	48.6	9.9	6.0	115.4	15.3	39.5	31.0	3279.5	n.a.	n.a.

n.a.: not analysed.

Table 2
Nutrient and trace element content in shoot dry mass of arugula and ryegrass cultivated in an Ultisol and an Oxisol with application of increasing doses of LBF 67 (hydrolyzed collagen from chromium-tanned leather with partial chromium extraction).

Soil	Treatment	N	P	K	Ca	Mg	Mn	Cu	Zn	B	Na	Cr	Cr (VI)
		%	g kg^{-1}				mg kg^{-1}						
							Arugula						
Ultisol	Control	5.1	4.6	61.8	21.4	7.5	131.6	10.1	29.3	28.0	867.0	1.3	<0.10
	LBF 67 – D1	6.0	4.1	66.5	18.2	6.1	80.6	14.2	28.7	21.4	1489.8	4.9	<0.10
	LBF 67 – D2	6.5	5.3	59.7	18.5	6.9	93.4	8.2	28.8	26.3	2516.9	5.8	<0.10
	LBF 67 – D3	6.9	4.2	63.0	17.5	5.9	108.7	9.2	28.2	27.9	2695.7	18.9	<0.10
	LBF 67 – D4	7.1	ISQ	ISQ	ISQ	ISQ	ISQ	ISQ	ISQ	ISQ	ISQ	35.0	<0.10
Oxisol	Control	5.1	3.9	49.0	25.4	10.1	76.7	7.6	27.9	26.1	1029.7	1.1	<0.10
	LBF 67 – D1	5.5	3.8	51.3	22.3	8.2	78.6	7.4	31.4	17.4	1583.9	1.9	<0.10
	LBF 67 – D2	6.3	3.1	50.0	28.6	9.4	78.9	6.9	29.9	28.4	1316.7	3.7	<0.10
	LBF 67 – D3	6.2	3.0	54.9	29.7	10.0	74.6	14.8	36.4	21.4	2313.5	31.5	<0.10
	LBF 67 – D4	6.9	3.2	58.3	23.6	8.4	63.7	12.9	31.1	18.7	3247.2	36.3	<0.10
							Ryegrass						
Ultisol	Control	2.0	5.8	39.8	8.5	4.3	121.2	11.3	29.6	36.9	850.2	n.a.	n.a.
	LBF 67 – D1	3.0	4.5	41.4	8.8	5.1	99.2	13.6	25.6	26.5	2388.5	n.a.	n.a.
	LBF 67 – D2	4.8	4.9	41.1	10.4	5.7	83.0	15.5	27.9	36.5	4509.6	n.a.	n.a.
	LBF 67 – D3	5.1	4.9	35.8	11.8	5.8	84.6	14.8	24.7	41.4	6728.2	n.a.	n.a.
	LBF 67 – D4	4.7	5.1	38.1	11.5	5.3	190.8	17.0	35.3	46.0	5426.2	n.a.	n.a.
Oxisol	Control	2.6	2.4	50.0	10.1	6.3	50.3	12.9	26.3	30.7	1167.6	n.a.	n.a.
	LBF 67 – D1	4.2	2.4	41.6	9.3	6.4	51.4	13.7	30.5	43.7	5220.1	n.a.	n.a.
	LBF 67 – D2	5.1	2.8	54.1	11.5	8.5	107.4	17.3	36.2	36.5	5245.6	n.a.	n.a.
	LBF 67 – D3	5.1	2.8	58.1	10.8	8.2	103.2	16.9	35.8	41.4	4261.1	n.a.	n.a.
	LBF 67 – D4	5.2	2.6	44.1	7.7	6.0	109.4	16.5	35.6	41.9	5432.4	n.a.	n.a.

ISQ: insufficient sample quantity, n.a.: not analysed.

adjustments to be a viable solution, since the Cr removal is a unique and costly step in the process, resulting in an increase in the production cost. In addition, its application also has limitations, as the dose required to supply the same amount of N as the LBF 64 is double (Table A.2, Supplementary Material) and, finally, the products' total input of Cr into the soil will end up being similar.

3.2. Plant growth study

A significant interaction between the soil type and the doses of LBF was observed (Table A.4, Supplementary material). Of the evaluated LBFs, the LBF 64 showed the most promising effects, for an upward trend was observed until the dose D3 in both soils, with yield increments up to 20 and 44% in arugula shoot dry mass and up to 67% and 64% in ryegrass dry mass in the Ultisol and the Oxisol, respectively (Fig. 1). The LBF 67 demonstrated similar behavior in the Ultisol, with an increase of up to 19% in arugula and 86% in ryegrass dry mass yield. However, no significant differences between the doses were observed in the Oxisol (Fig. 2).

The calculated maximum technical efficiency (MTE) dose referring to the immediate effect (arugula bioassay) was close to 280 kg ha^{-1} of N equivalent for both LBFs in the Ultisol and 327 kg ha^{-1} of N equivalent for the LBF 64 in the Oxisol. It is important to point out that the MTE doses were similar between the products, meaning that the LBF 67 did not present a greater N use efficiency, which would have allowed a reduction in its application doses. Therefore, the developed process for

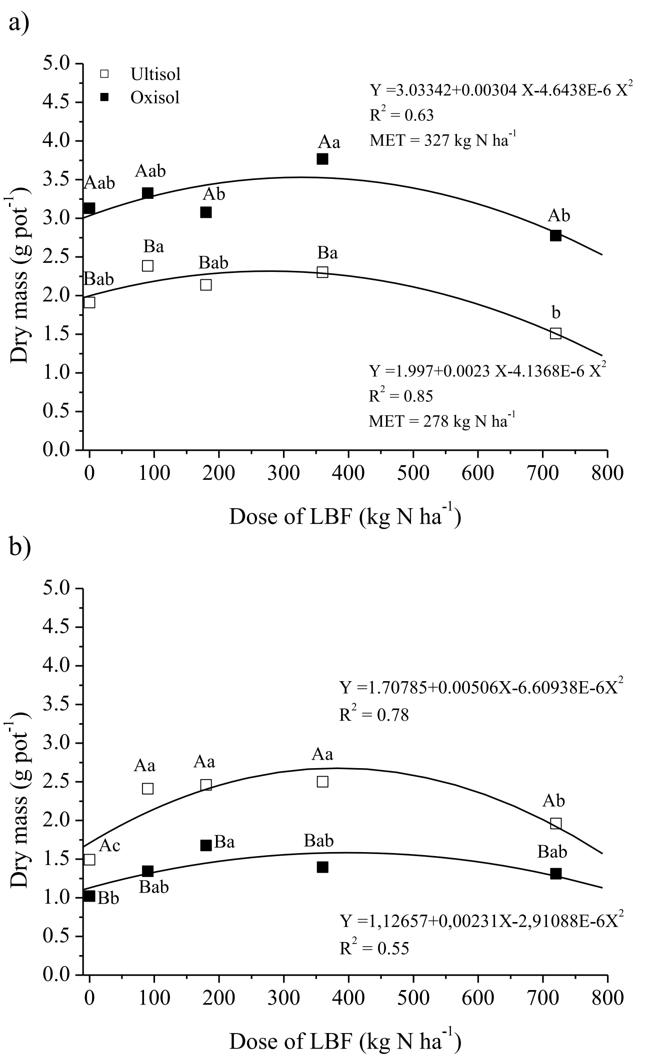

Fig. 1. Shoot dry mass of arugula (a) and ryegrass (b) cultivated in Ultisol (□) and Oxisol (■) with increasing doses of LBF 64. Means followed by the same letter do not differ by Tukey's test ($p \leq 0.05$). Uppercase letters compare soil types within the same dose and lowercase letters compare doses within the same soil. .

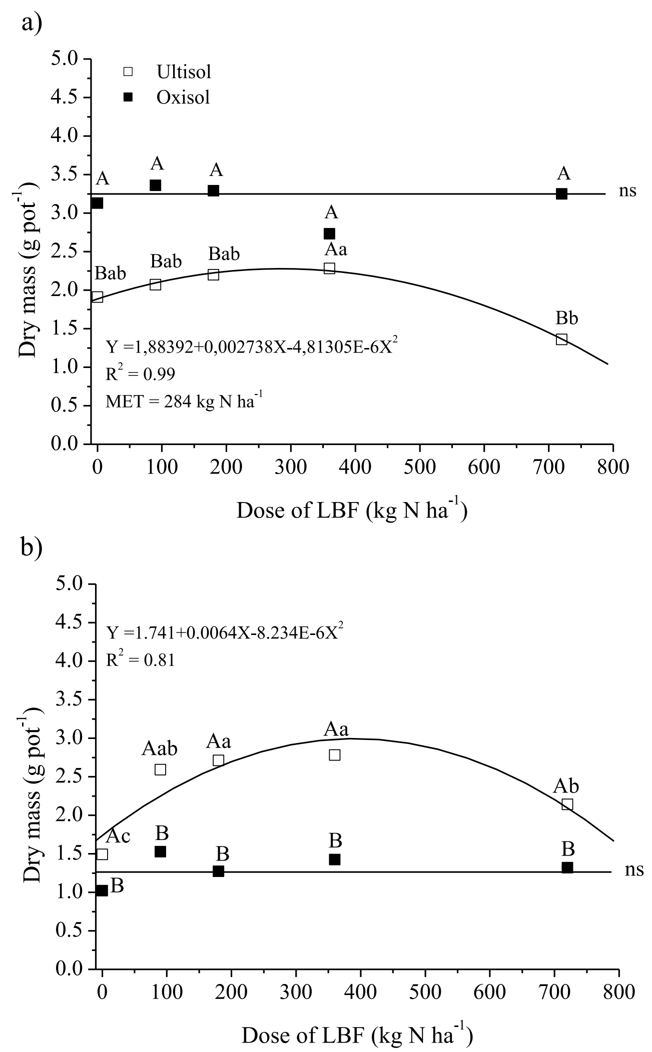

Fig. 2. Shoot dry mass of arugula (a) and ryegrass (b) cultivated in Ultisol (□) and Oxisol (■) with increasing doses of LBF 67. Means followed by the same letter do not differ by Tukey's test ($p \leq 0.05$). Uppercase letters compare soil types within the same dose and lowercase letters compare doses within the same soil. ns: not significant.

Cr removal was not effective from the agronomic perspective and needs adjustments in order to remove Cr without a N reduction. However, it is a clean process that uses environmentally safe reagents and, thus, might be interesting for the industry when the raw material presents a high level of contamination.

The contrasting response between the soil types was somewhat expected since the Oxisol has a higher fertility level than the Ultisol (Table A.1, Supplementary Material), which resulted in a higher arugula dry mass production in this soil than in the Ultisol, regardless of the treatments. However, an opposite behavior was observed when the residual effect of the LBFs was evaluated, with the DM production of ryegrass being lower in the Oxisol than in the Ultisol (Figs. 1b and 2b). The low production of dry mass in the Oxisol may be due to a possible P deficiency in this soil, as shown by the soil analysis results at the end of the experimental period (Table A.5, Supplementary Material), where the soil P levels were in the order of 5 mg of P dm^{-3}, while the levels considered adequate for this type of soil are between 12.0 and 24.0 mg of P dm^{-3} (CQFS, 2016). In addition, the P levels in the shoot dry mass of the plants in the Oxisol were lower than those observed in the Ultisol, especially for ryegrass, where the P levels in the plants grown in the Oxisol were less than half of those observed in the Ultisol (Tables 1 and 2). This was due to the absence of fertilization in the second crop, as well as the low natural availability and high adsorption and fixation of P in the Oxisol, indicating that the residual effect of fertilization was not sufficient to meet the demand of the successor crop in this soil.

Regarding the MTE dose, there is consistency between the recommended dose to supply the plant N requirements (CQFS, 2016) and the N mineralization rate of the LBFs. In an essay carried out over 100 days (data not shown), the LBF 64 mineralized up to 62% and 66% and the LBF 67 up to 65% and 52% of its total N content in the Ultisol and the Oxisol, respectively, on the 29th day, when the arugula was harvested. The results corroborate those of Majee et al. (2021), who developed a product with similar characteristics to the LBFs evaluated in this study and compared it with a chemical fertilizer, stating that a similar growth effect was obtained by increasing the amount of the bio-organic fertilizer to twice that of the chemical fertilizer. However, it is important to avoid higher doses than the MTE, since overdoses might cause negative effects similar to what we observed in the present study for D4 (2.5 times the MTE dose). The effect of an overdose (D4) was visually demonstrated by the dark green color of the leaves and the leathery appearance, with a consequent reduction in arugula and ryegrass dry mass, which might be related to a nutritional imbalance, as further described.

3.3. Nutrient content in plant tissue and soil

Increasing the doses of LBF 64 and LBF 67 improved the N content in the plant tissue (Fig. 3 and 4) and in the soil (Table A.5, Supplementary Material). In arugula, a quadratic effect ($p = 5.9 \times 10^{-5}$ and $p = 7.7 \times 10^{-5}$ for LBF 64 and LBF 67, respectively) was observed (Fig. 3a and 4a), with an increase in the N content from 5.07% in the control to 6.98% and 7.20% with the highest dose (D4) of LBF 67 and LBF 64, respectively, which means an increase of 38–42%.

A similar behavior was observed in ryegrass (Figs. 3b and 4b), with an increase of almost 50% in the N content. Ertani et al. (2009) suggested that amino acids and small peptides of these products based on hydrolyzed proteins have a role in the regulation of the hormone-like activity and N pathway. They observed an increase in the N assimilation through an increase in nitrate reductase and glutamine synthetase activity when protein hydrolyzate–based fertilizers, one from alfalfa and one from meat flour, were applied to roots.

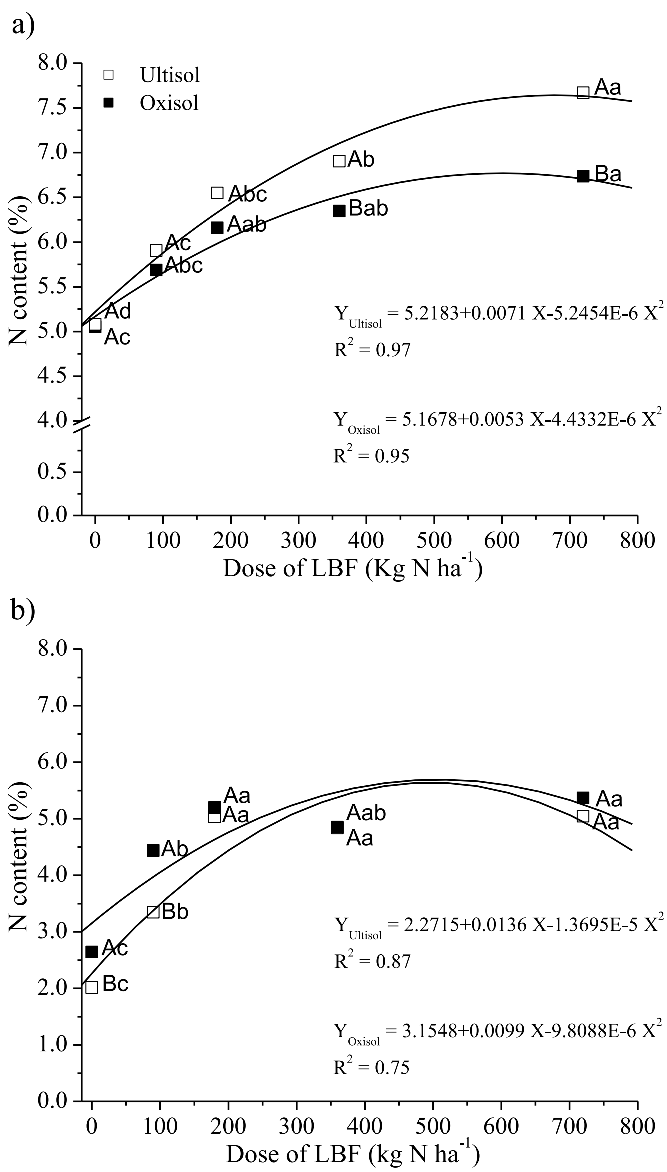

Fig. 3. Nitrogen content in shoot dry mass of arugula (a) and ryegrass (b) cultivated in Ultisol (□) and Oxisol (■) with increasing doses of LBF 64. Means followed by the same letter do not differ by Tukey's test ($p \leq 0.05$). Uppercase letters compare soil types within the same dose and lowercase letters compare doses within the same soil.

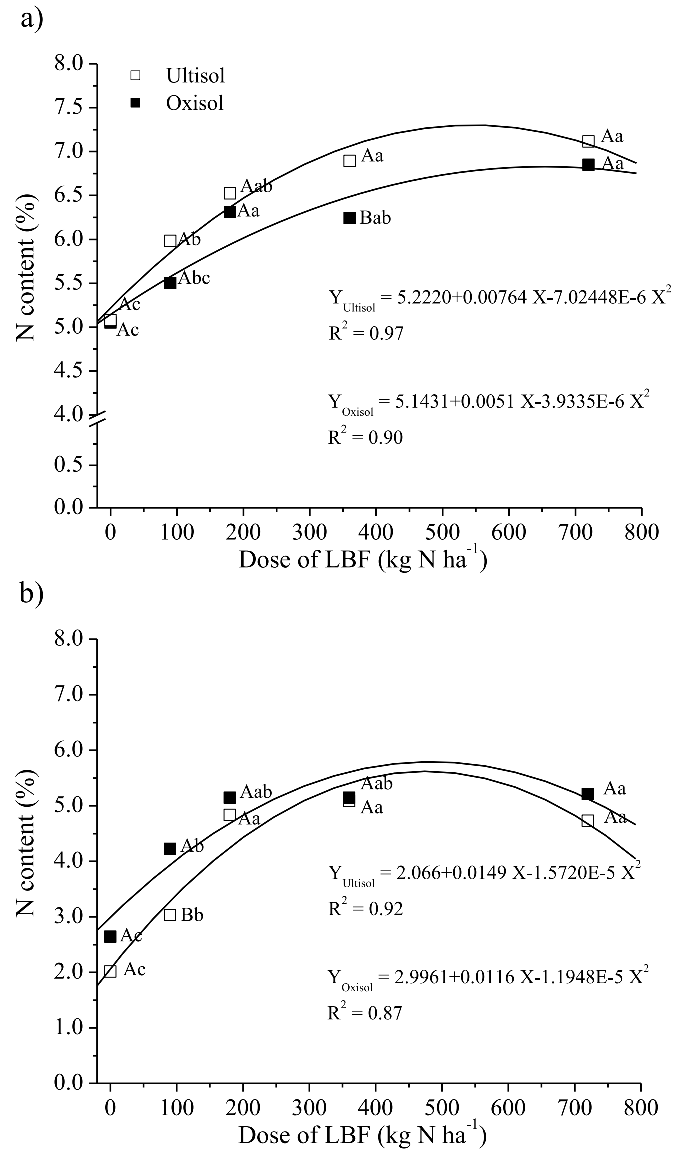

Fig. 4. Nitrogen content in shoot dry mass of arugula (a) and ryegrass (b) cultivated in Ultisol (□) and Oxisol (■) with increasing doses of LBF 67. Means followed by the same letter do not differ by Tukey's test ($p \leq 0.05$). Uppercase letters compare soil types within the same dose and lowercase letters compare doses within the same soil.

Although a maximum N content was observed for an estimated N dose of 585 and 474 kg N ha^{-1} for the LBF 64 on the Oxisol and the Ultisol, respectively, (Fig. 3a) and 648 and 544 kg N ha^{-1} for the LBF 67 on the Oxisol and the Ultisol, respectively (Fig. 4a), the highest dry mass production was obtained with 280 kg N ha^{-1} (Fig. 1 and 2), making it the most agronomically and economically viable dose.

An upward linear trend was observed in the soil samples, and even after the cultivation of arugula and ryegrass, 110 days after the first application of LBFs, the N content in the soil remained high when compared to unamended soil (Table A.5, Supplementary Material). In the Ultisol, the N content was up to 39% higher in the treatments with a LBF addition when compared to the control, while in the Oxisol the maximum increase was around 10%. LBF has a fraction of around 50% fast release occurring within the first 10 days, which is an interesting characteristic from the agronomic point of view, since, unlike most organic fertilizers such as manure and filter cakes, LBFs do not need an early application because they present a fraction of readily available N. At the same time, the remaining slow-release fraction keeps releasing nutrients even after a crop cultivation cycle, if we consider the time scale of the crops evaluated in the present study and other annual agricultural species cultivated in Brazil.

Hartz and Johnstone (2006) also observed a rapid N mineralization of 47–60% organic N within two weeks in a laboratory incubation of four organic fertilizers (seabird guano, hydrolyzed fish powder, feather meal and blood meal). The authors attributed the rapid initial mineralization to the enzymatic hydrolysis of simple compounds such as urea and amino acids (highly labile forms of organic N) and the additional mineralization (after two weeks) to the degradation of more complex organic N forms by microbial processes.

It is important to note that the LBFs evaluated in the present study are liquids; therefore, a greater N availability was somewhat expected. According to Hartz et al. (2010), organic liquid fertilizers can function similarly to conventional N fertilizers. Their rapid N availability is radically different from that of other organic N sources. Usually, far less than half of the N contained in organic sources like chicken manure, cattle manure and cover crops may become plant-available in the growing season after incorporation (CQFS, 2016). N contribution of manure-based compost is even slower, often limited to 10% or less of the N content (Hartz et al., 2000). The rapid N availability of these organic liquid fertilizers provides a viable alternative solution for organic growers who need a readily available source of N.

Apart from N, no significant differences between the LBF doses were observed in the macronutrient and micronutrient content in the plant tissue of arugula and ryegrass (Tables 1 and 2). Na is the only element whose data draws attention. In fact, an expressive increase in the Na levels was observed in the soil and in the plant tissues with increasing doses of LBF (Tables 1 and 2). It was partially expected considering the reagents used in the leather tanning process and, additionally, in the case of the LBF 67, due to the Cr removal process with potassium sodium tartrate. The high levels of Na in the soil resulted in high levels of Na in the dry mass of arugula and ryegrass, being more expressive in the treatments with LBF 67. Despite the high levels of Na in all treatments, no significant correlation was observed between the Na content and the dry mass production or K absorption. A substantial body of studies summarized by Kronzucker et al. (2013) reported beneficial effects of Na on plant growth and, at the same time, problems related to osmotic stress and transport and accumulation of nutrient ions, particularly K^+, due to the presence of high salt concentrations in both the rooting medium and the plant cell walls. The authors emphasize that Na^+ nutrition and toxicity is a complex, multi-faceted trait, and cannot be predicted by simple indicators such as Na^+ accumulation.

Apart from the aforementioned elements, no significant differences were observed in the evaluated indicators between the LBF doses in the soil samples in this experiment (Table A.5, Supplementary Material). However, in the long-term use of these products, possible changes in other soil indicators are expected, especially in their microbiome. Dinca et al. (2022) reported in a literature review that several studies have demonstrated the change in the structure of the soil microbial community (composition, diversity and relative abundance of specific rate) after chemical or organic fertilization. The latter affects microbial growth and competitiveness because different bacterial and microfungal groups can vary in their ability to use the different nutrient forms found in soil. These soil microbiological indicators are the focus of the continuation of the present study, which will be performed in field conditions within a crop rotation system including different species of vegetable crops.

3.4. Heavy metal content in plant tissue and soil

Except for Cr, and Pb in the LBF 64, non-expressive levels of heavy metal were detected in the LBFs (Table A.3, Supplementary Material), meaning that the heavy metals in the LBFs probably come exclusively from leather tanning processes and that the possible contamination of the PPE by the work activities to which it is exposed to was successfully overcome by the process of cleaning the raw material, with the exception of Pb in the LBF 64.

The Pb content in the LBF did not increase the concentration of this heavy metal in the soil (Table A.6, Supplementary material) or in the plant tissue (data not shown). Thus, the discussion in the present report focused on Cr and specifically in the shoot dry mass of arugula, since the trends in Cr availability in leather meal are related to the mineralization of organic N and C (Govi et al., 1996). Therefore, Cr release was expected to occur during the life cycle of arugula. In the case of the LBFs evaluated in this work, 50% of the N mineralization occurred in the first 10 days. Additionally, Govi et al. (1996) reported that the Cr released from leather meal during humification tends to precipitate in insoluble forms over time, decreasing its availability to the soil solution.

The Cr concentration in the arugula shoot dry mass had a negative correlation with DM ($r = 0.99$ and 0.90 for the LBF 67 and the LBF 64 in the Ultisol, respectively, and $r = 0.82$ for the LBF 64 in the Oxisol), except for the LBF 67 in the Oxisol (data not shown). Negative effects of Cr on the DM yield were evidenced by a maximum concentration in the arugula shoot dry mass, estimated by the correlation equation at 12 and 18 mg Cr kg^{-1} DM for the LBF 67 and the LBF 64, respectively, in the Ultisol and 9 mg Cr kg^{-1} DM for the LBF 64 in the Oxisol. Similarly, Bavaresco et al. (2019) observed the adverse impact of Cr on shoot dry matter (a 41% reduction) and number of nodules (a 49% reduction) in soybeans grown in a soil with a low cation exchange capacity.

There is much variation in the critical levels of Cr for different crops. Critical toxicity levels of less than 1.0 mg Cr kg^{-1} in ryegrass at the five-leaf stage and 10 mg kg^{-1} in barley crop were reported by Macnicol and Beckett (1985). Conversely, McGrath and Fleming, 2006 reported phytotoxicity of Cr on ryegrass at levels above 100 mg kg^{-1} DM. According to Alloway (1993), the Cr content in plants growing in normal conditions ranges between 0.03 and 14.0 mg kg^{-1}, and the critical limit ranges from 5.0 to 30.0 mg kg^{-1}. Ciavatta et al. (2012) emphasize that the toxicity of Cr in plants depends also on its oxidation state, with Cr (VI) being much more toxic than Cr (III). Exposure to excess Cr (III) decreased the chlorophyll concentration and the activities of heme enzymes, catalase and peroxidase, and, thus, its effect resembles Fe deficiency (Pandey and Sharma, 2003). Cr (III) produces reactive oxygen species, being phytotoxic at high concentrations (Ciavatta et al., 2012), and it can indirectly affect the mineral nutrition of the plants (Abreu et al., 2002).

Phytotoxicity is a protection for the food chain, as it occurs at significantly lower concentrations than those harmful to humans or animals. The soil and the plant root system are also efficient barriers to prevent Cr contamination of the food chain due to the strong binding of this trace element to soil components (clay content, organic matter) or root cell walls (Zayed and Terry, 2003). According to Zayed and Terry (2003), only a small fraction of the total Cr concentration is available for plant uptake and, when taken up by plants, more than 90% of the Cr absorbed by plant roots, regardless of the Cr species, is retained in the roots. This was somewhat observed in the present study, as the increase in the Cr content in the arugula's leaves was not proportional to the increase in the Cr levels in the soil, in which an upward linear trend was observed (Table A.6, Supplementary Material).

Furthermore, despite the Cr content being much higher in the Oxisol than in the Ultisol due to the naturally high concentration of Cr in the Oxisol, the Cr concentrations in arugula dry mass were similar in both soils (Tables 1 and 2). Similar behavior was reported by Bavaresco et al. (2019) in soybean plants grown on soils fertilized with hydrolyzed leather, where the Cr concentration in the shoot biomass was not proportional to the Cr content in the soils as a result of the different Cr adsorption potentials in the soils. It is also important to note that, independently of the treatment, hexavalent Cr was not detected in the arugula shoot in either of the soil samples, except in the highest dose of LBF 64 (Table A.6, Supplementary Material).

Despite the protection of this 'soil-plant barrier', the application rates of LBF should not exceed the MTE dose that is here considered agronomically efficient and environmentally safe, as it resulted in a higher DM production (Figs. 1 and 2), acceptable levels of Cr in the plants (Tables 1 and 2) and did not exceed the limits established by the environmental legislation for Cr in soil (Table A.6, Supplementary Material). Generally, the maximum acceptable Cr concentration for agricultural soils in many different European countries was reported to be in the range of 50 – 200 mg kg^{-1} (Kabata-Pendias and Adriano, 1995), although concentrations of up to 250 mg kg^{-1} were found in Irish non-polluted agricultural soils (McGrath and Fleming, 2006). In Brazil, the guiding values of prevention and intervention are 75 and 150 mg kg^{-1}, respectively (Conama, 2009). The risk associated with high levels of Cr in soils is the contamination of the food chain. Plants grown on polluted soils become potential threats to human and animal health. Furthermore, a decrease in crop yields, like observed in the present study, and the consequent economic losses are expected for crops grown on farmland with high levels of Cr.

Nevertheless, the impact of successive and long-term LBF applications in the Brazilian edaphoclimatic conditions still needs to be thoroughly evaluated. The significant and robust literature highlighting the efficiency and low risk of leather meal along with the successful LBF use in several other countries corroborate the results obtained in the present study and reduce uncertainties around the use of leather-based fertilizers in agriculture. The results of the present study facilitate the implementation of reverse logistics for the Brazilian leather industry and could, at the same time, favor the country's agricultural sector by providing new organic N fertilizers, whose production is far below demand.

4. Conclusions

The use of residues from the manufacture of leather Personal Protective Equipment (PPE) and post-use PPE to produce LBFs is feasible, facilitating the implementation of reverse logistics for the PPE industry.

LBFs are an efficient source of N and promote arugula and ryegrass growth in soils with contrasting characteristics. They can be an interesting option for system fertilization due to presenting a fraction of rapid initial N mineralization and another of slow release with a residual effect for the successor crop.

Overdoses of LBF can lead to the accumulation of Cr in the plant biomass and the soil. However, the dose that achieved maximum technical efficiency is agronomically efficient and environmentally safe, as it resulted in a satisfactory dry mass yield, acceptable levels of Cr in the plant biomass and did not exceed the acceptable limits for Cr in soil established by the environmental legislation.

Funding

This work was supported by the National Service for Industrial Training and JGB Personal Protective Equipment.

Supplementary Material

Appendix. Supplementary data

CRediT authorship contribution statement

Rosane Martinazzo: Supervision, Conceptualization, Methodology, Writing – original draft. **Camila Ariana Muller:** Methodology, Formal analysis. **Luciana Costa Teixeira:** Supervision, Conceptualization, Methodology. **Lizete Stumpf:** Investigation, Data curation, Writing – review & editing. **William Rodrigues Antunes:** Investigation, Data curation. **Lisiane Emilia Grams Metz:** Project administration, Resources. **Ricardo Alexandre Valgas:** Formal analysis. **Adilson Luís Bamberg:** Methodology, Writing – review & editing. **Carlos Augusto Posser Silveira:** Methodology, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

Acknowledgments

We gratefully acknowledge the technical assistance and supporting information from Simoni Becker, Mariana da Luz Potes, and Silvia Rudek Wathier.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.rcradv.2023.200153.

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