



Lucas de Lima Casseres dos Santos ^{1,2}, Jean Bruno Melo Silva ¹, Luisa Soares Neves ¹, Natalia dos Santos Renato ¹, Julia Moltó ³, Juan Antonio Conesa ³ and Alisson Carraro Borges ^{1,*}

- ¹ Federal University of Viçosa, Viçosa 36570-900, Brazil; lds5498@psu.edu (L.d.L.C.d.S.);
- jean.bruno@ufv.br (J.B.M.S.); luisa.neves@ufv.br (L.S.N.); natalia.renato@ufv.br (N.d.S.R.)
 - The Pennsylvania State University, State College, PA 16802, USA
- ³ University of Alicante, 03690 Alicante, Spain; julia.molto@ua.es (J.M.); ja.conesa@ua.es (J.A.C.)
- * Correspondence: borges@ufv.br

Abstract: The scarcity of natural resources makes it essential to develop products that meet environmental requirements. This is also true for the water and wastewater treatment business, where even consolidated processes, such as coagulation and flocculation, must be improved, opening opportunities for searching for alternative options to conventional processes. Among the existing options, tannin-based agents (TBAs) have been highlighted in recent years due to their biodegradability and proven efficiency. However, little is known about the impacts of the production process of these agents on an operational/industrial scale. In this study, an examination of the environmental impacts of the full-scale production (more than 500 tons yearly) of a TBA from Acacia spp. (known as black acacia or mimosa) was carried out. To accomplish this, a life cycle assessment (LCA) was developed using openLCA version 2.0.0 to assess a cradle-to-gate system of 1 kg of packed TBA produced. Additionally, a comparison was made between the impacts of the production of TBA and a conventional water treatment agent, aluminum sulfate, to verify the benefits of producing the former. The most relevant impacts resulting from the production of 1 kg of TBA are observed in the following categories: global warming (1.52 kg_{CO2-eq}); terrestrial (7.67 kg_{1.4-DCB-eq}), freshwater (0.06 kg_{1.4-DCB-eq}), and marine (0.08 kg_{1.4-DCB-eq}) ecotoxicities; carcinogenic (0.10 kg_{1.4-DCB-eq}) and non-carcinogenic (1.36 kg_{1.4-DCB-eq}) human toxicities; and water use (0.02 m^3). The main contributors to the impacts were the chemicals ammonium chloride and formaldehyde used, the transport of inputs, and the energy used. The aluminum sulfate showed better performance than the TBA for a greater number of categories; however, the normalization of the impacts showed the TBA as a very interesting option. The results obtained here can be used by TBA producers to act on the most impactful categories so that the production process becomes increasingly sustainable.

Keywords: LCA; coagulation/flocculation; green chemistry; circular economy; acacia

1. Introduction

Industrial development is directly related to water resource availability since these are essential to most production processes. Thus, the increased demand for water in our society emphasizes the need for development and improvement in its treatment processes. The search for these new technologies is highly linked to maintaining the technical viability of industrial processes and is increasingly a requirement due to the increased rigor of environmental standards [1].

Given the justified relevance attributed to water treatment, the importance of the coagulation/flocculation stages in this process stands out. Traditionally, inorganic metallic coagulant agents, such as iron chloride and especially aluminum sulfate, have emerged as the main choices for application in water and wastewater treatment, generally based on the cost–benefit evaluation of treatments. However, these coagulants have limited



Citation: Santos, L.d.L.C.d.; Silva, J.B.M.; Neves, L.S.; Renato, N.d.S.; Moltó, J.; Conesa, J.A.; Borges, A.C. Life Cycle Assessment of a Vegetable Tannin-Based Agent Production for Waters Treatment. *Water* **2024**, *16*, 1007. https://doi.org/10.3390/ w16071007

Academic Editors: Anastasios Zouboulis, Konstantinos Simeonidis, Andrea G. Capodaglio and Evgenios Kokkinos

Received: 25 January 2024 Revised: 25 March 2024 Accepted: 25 March 2024 Published: 29 March 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). pH applications and residual metals from these products have been recently pointed out as harmful to human health and related to several diseases [2,3]. Moreover, the sludge generated in large volumes by treatment with these agents presents difficulties regarding the destination in landfills or agricultural lands, generating environmental problems [4,5].

Consequently, there are increasing studies regarding applying organic agents, usually polymers, during treatment processes. These polymers, including tannin-based ones, aim to mitigate the problems related to the bioaccumulation of metals and pH restrictions [4,6]. The application of these organic agents, compared to metallic products, presents several benefits related to the biodegradability of the sludge formed in a possible smaller volume, associated with an efficiency compatible with that of traditional alternatives [3,4]. However, little is known about the comparative relationship between the impacts of the production process of these, for which industrial implementation is recent, and the consistent manufacturing process of metallic coagulants, such as aluminum sulfate, which is globally structured through bauxite extraction and reaction with sulfuric acid.

In parallel, the production of tannin-based agents (TBAs) considers the extraction of tannin from trees. After that, the solution is exposed to an organic synthesis reaction called the Mannich reaction [7,8]. Unlike aluminum sulfate's primary source, tannins are bioproducts (phenolic compounds) present in plants resulting from their secondary metabolism [9]. In complement to that, there is a scarcity of studies that use life cycle assessment to evaluate the impact of TBAs production. One can cite the study by Carlqvist et al. [10], whose objective was to assess the environmental effects of the production of grafted tannin-based agents. However, no data from the manufacturing process already implemented on an industrial scale were used. Thus, the development of this evaluation on a manufacturing scale, which has not yet been performed, would allow for a more consistent verification of the environmental performance of TBAs, providing knowledge about the extent or otherwise of the beneficial effects of its application, as previously indicated, also for its industrial production. Given this scenario, the present work aimed to evaluate the environmental impacts arising from the production of a TBA through a life cycle assessment.

2. Materials and Methods

This work was developed using the LCA methodology, standardized in ISO 14040 and ISO 14044 [11,12], to evaluate the environmental impacts arising from the production of a coagulant/flocculant based on tannins.

2.1. Definition of the Goal and Scope of the Life Cycle Assessment

The goal of the LCA was to assess the environmental impacts of TBA production in in the Brazilian industry and compare it to aluminum sulfate. The reason for conducting this analysis is to understand the hotspots in the production of TBAs at an industrial scale, which is not available in the literature yet, and investigate the advantages and disadvantages of this organic agent compared to an ordinary inorganic/metallic coagulant used in water and wastewater treatment.

The production system under study is TBA production, which generates the product to be transported to retail application settings. To calculate the flows related to the production system, we considered the production of 565,250 kg of the packaged product, referring to the yearly total produced by the Brazilian manufacturer. However, the functional unit used for the impact assessment was 1 kg of packaged TBA produced, for which each of the inputs and outputs was weighed by the openLCA version 2.0.0 software used for the analyses.

The system boundary of the assessment was cradle to gate for the TBA production process. This means that all stages of obtaining raw materials, such as planting trees, were considered in the impact assessments. However, the destination of the product after the factory, as well as the solid waste disposal from the production process, were not included in this analysis. Internal shifts in the factory were also not considered due to their relatively low impact.

Furthermore, no divisions were made between production steps. That is, the entire production process up to the packaging/bagging stage is treated as a single block in the system, as shown in Figure 1. The inputs are all of the entries that are necessary to produce the TBA, including energy, and the outputs are, in addition to the final packaged product, the wastes from the entire process. The production block included the reception of the black acacia bark in natura, the step of processing and extracting the tannin, the evaporation stage, subsequent chemical reactions, and, finally, the atomization and bagging/palletization.



Figure 1. Tannin-based agent (TBA) production system.

The transportation of each of the inputs to the main city of the factory was included in the analysis. Although the use of electricity is dominant in Brazil, in the case of transport, the use of liquid fossil fuels persists, and these differences regarding energy sources are considered in the allocations. It is also noteworthy that the internal treatment of production effluents, from which water is reused in production, was included in the analysis.

2.2. Allocation, Limitations, and Life Cycle Inventory

The TBA manufacturer works in a plant which is divided into three production units, with TBA belonging to one unit. At the time of this study, the company lacked a tracking mechanism for certain shared flows among the three systems. This absence of data makes it challenging to precisely ascertain the exact amounts of these inputs and outputs of the TBA system. Considering this, to build the life cycle inventory, it was necessary to allocate data whose values provided did not refer only to the production of the TBA and for which values were not possible to obtain in a more specific way. Based on ISO 14044, since the allocation could not be avoided through the expansion of the system, the physical mass allocation was used for its execution, since this is preferable when compared to economic allocations [13].

The allocation was used for these specific flows: water consumption, steam, wastewater treatment, and outputs (wood ashes, wastewater sludge, wood sawdust, wood waste, packaging waste, and plastic). This allocation factor is 3% and comes from the division of the total 565,250 kg of the TBA by 18,588,000 kg of the other products produced in the factory. For electricity, the allocation was not used; instead, it was calculated based on the time of use of machines used in the process, multiplied by their power, and the days of operation on a yearly basis. According to the system boundaries (Figure 1), the study carried out did not include the treatment and disposal of production waste since its focus is on the production plant of the tannin-based agent. Furthermore, the analysis was limited to a single "production block" without specifying each of the production stages with their respective inputs and outputs.

In addition, the stages of assembly and future closure of the factory, as well as equipment maintenance, were not considered, since they have little importance given the production volume over the entire useful life of the factory or specific equipment. Internal transportation in the plant was also not incorporated into the model. The generation of waste or rejects arising from human and/or administrative activities not directly related to factory production were not considered as well.

The information collected from the company's employees, referring to the mass and energy flows associated with the process, was organized and analyzed to build the life cycle inventory. In addition to all the inputs (incoming material flows), energy flows (electricity and steam) and external transport were also considered in this LCA. As a product output in the process, a mass of 565,250 kg of the TBA was considered and built into the software.

After consolidating the data related to the total amount of TBA produced, we were able to start building the life cycle inventory for the product system (Table 1). To include the cradle-to-gate perspective in the inventory, process providers from the ecoinvent 3.7.1 database were used for each flow included in the life cycle assessment (Table 2). For cases in which the life cycle inventory of specific inputs used in the production of the TBA were not available in the ecoinvent 3.7.1 database, an appropriate process provider substitute was selected to represent the input. That approach was used for soy lecithin and the anti-foaming agent. For soy lecithin, a process with a similar function was used, namely soybean meal and crude oil production. Lecithin is one of the byproducts produced during the production of soybean oil. For the anti-foaming agent, the criteria used to define the best process provider was the major component in the formula of the product used in the factory, which is ethylene glycol. To assess the influence of the inputs on the overall system impact, a sensitivity analysis was performed to verify the impact of these substitutions on the results. For the evaluation, a cut-off criterion of 1% relevance was defined.

Flow	Unit	Quantity	Transportation *	Transport Type	
Inputs					
Bark chips	kg	1,578,206	246,064	Freight, lorry	
Activated silica	kg	183	3	Freight, lorry	
Anti-foaming	kg	137	201		
Ammonium chloride	kg	147,555	3,014,468 168,877	Freight, sea Freight, lorry	
Formaldehyde **	kg	246,732	(07 00E	Encicht long	
Deionized water **	kg	420,113	687,683	Freight, forry	
Water	kg	22,764			
Soy lecithin	kg	1131	159	Freight, lorry	
Electricity	MWh	140			
Heat	GJ	5860			
Sacks	kg	2261	1826	Freight, lorry	
Pallets	unit	943	2096	Freight, lorry	
Output					
Wastewater	m ³	2322			
Wastewater sludge ***	ton	117			
Boiler ashes ***	ton	22			
Other residues ***	ton	19			
Plastic sacks ***	kg	700			
TBA coagulant/flocculant	kg	565,250			

Table 1. Life cycle inventory for the system of tannin-based agent production.

Notes: * values in ton-km; ** the values used for deionized water and formaldehyde are the same because they were transported as a solution; *** Outputs presented to understand the process but not included in the inventory.

Flow	Ecoinvent Process Providers Used
Inputs	
Bark chips	Bark chips production, hardwood, at sawmill Cutoff, U—RoW
Activated silica	Activated silica production Cutoff, U—GLO
Anti-foaming	Market for ethylene glycol Cutoff, U—GLO
Ammonium chloride	Ammonium chloride production Cutoff, U—GLO
Formaldehyde	Oxidation of methanol Cutoff, U—RoW
Deionized water	Water production, deionized Cutoff, U—RoW
Water	Tap water production, underground water with
	disinfection Cutoff, U—BR
	Soybean meal and crude oil production, mechanical
Soy lecithin	extraction Cutoff, U—RoW
F1	Market for electricity, medium voltage Cutoff, U—BR-Southern
Electricity	grid
TT /	Heat and power co-generation, wood chips, 6667 kW Cutoff,
Heat	U—RoW
Sacks	Textile production, non-woven polypropylene, spun bond Cutoff,
	U—RoW
Pallets	EUR flat pallet production Cutoff, U—RoW
Transport by ground	Market for transport, freight, lorry, unspecified Cutoff, U—RoW
Transport by sea	Market for transport, freight, sea, container ship Cutoff, U—GLO
Output	
T A7	Treatment of wastewater, average, capacity
Wastewater treatment	1E91/year Wastewater, average Cutoff, U—RoW

Table 2. Life cycle inventory flows and their respective process providers obtained from ecoinvent.

2.3. Performing the Life Cycle Impact Assessment

We used the software openLCA version 2.0.0 to perform the study. The method used was ReCiPe 2016 Midpoint (H) with the following environmental categories: fine particulate matter formation; fossil resource scarcity; freshwater ecotoxicity; freshwater eutrophication; global warming; human carcinogenic toxicity; human non-carcinogenic toxicity; land use; marine ecotoxicity; marine eutrophication; mineral resource scarcity; ozone formation, human health ozone formation, terrestrial ecosystems; stratospheric ozone depletion; terrestrial acidification; terrestrial ecotoxicity; and water consumption. The use of this impact assessment methodology is due to their use in previous works that performed an LCA of tannin-based materials [10,14,15].

2.4. Comparison between TBA and Traditional Coagulant

As part of the goal of the LCA, in this work, we also carry out a comparative assessment of the environmental impacts related to the production of tannin-based agents and traditional coagulants, represented here by aluminum sulfate. For this second LCA model, a new system was defined, in which the study boundary no longer encompassed the product packaging phase. Thus, this evaluation used a perspective from the cradle to the final product, in powder form.

As a functional unit, it was understood that, ideally, the mass values of the two products that result in equivalent treatments should be used, which allow the same final quality for a given volume of treated water/wastewater. However, the recommended dosages of TBAs reported in the literature depend on the water type to be treated (Table 3). Therefore, seeking a broader and more generic analysis, it was decided to use the amount of 1 kg of each of the evaluated products as a functional unit, understanding, however, the need to include this discussion in view of the conclusions obtained. The same approach was performed by Carlqvist et al. [10] who argue that this FU could facilitate the future use of their LCA and comparison with other agents.

Water	TBA Dosage (mg/L)	Turbidity Removal (%)	Source
Surface water (river)	20	90.0	Sanchez-Martin et al. [16]
Surface water (river)	2	50.0~60.0	Sanchez-Martin et al. [17]
Industrial wastewater	375	95.0	Lugo et al. [18]
Landfill leachate	1460	53.5 *	Banch et al. [19]
Domestic wastewater	15	80.0	Singh et al. [20]
Dairy wastewater	200	86.6	Justina et al. [21]

Table 3. Dosages of tannin-based agents for treatment of different types of waters.

Note: * Removal of total suspended solids.

The considerations described previously, as well as the mass allocation procedures for the TBA data provided by the Brazilian manufacturer, were maintained. However, since it was not possible to obtain actual production data for sulfate aluminum, the ecoinvent 3.7.1 database was used to evaluate its production process. Given the available options, we opted to use the process "aluminum sulfate, powder {RoW} | market for aluminum sulfate, powder | APOS, U". This process, for instance, does not take into account waste transport and water and waste treatment. Therefore, the relevant limitation is highlighted in that the data referring to aluminum sulfate were based on a global average, while the actual TBA data considered a perspective from a Brazilian region.

3. Results and Discussion

3.1. Life Cycle Impact Assessment of TBA Production

Table 4 shows the environmental impact results of the TBA production. In complement to that, Figures 2 and 3 illustrate the relevance of each process to all impact categories. Ammonium chloride production was the process that had the greatest effect on the different impact categories, followed by the oxidation of methanol to produce formaldehyde, the transportation of inputs, and the energy supply chain.

Table 4. Life cycle impact assessment of a tannin-based agent.

Impact Category		
Fine particulate matter formation	$2.7 imes10^{-3}$	kg _{PM2.5-eq}
Fossil resource scarcity	$673.1 imes 10^{-3}$	kg _{oil-eq}
Global warming	$1518.6 imes 10^{-3}$	kg _{CO2-eq}
Ozone formation, Human health	$6.2 imes 10^{-3}$	kg _{NOx-eq}
Mineral resource scarcity	$4.5 imes 10^{-3}$	kg _{Cu-eq}
Land use	1.0	m ² a _{crop-eq}
Water consumption	18.9×10^{-3}	m ³
Human carcinogenic toxicity	104.8×10^{-3}	kg _{1,4-DCB-eq}
Terrestrial ecotoxicity	7673.8×10^{-3}	kg _{1,4-DCB-eq}
Terrestrial acidification	$6.3 imes 10^{-3}$	kg _{SO2-eq}
Ozone formation, Terrestrial ecosystems	$6.3 imes 10^{-3}$	kg _{Nox-eq}
Freshwater eutrophication	$0.3 imes 10^{-3}$	kg _{P-eq}
Marine ecotoxicity	83.6×10^{-3}	kg _{1,4} -DCB-eq
Marine eutrophication	1.10×10^{-3}	kg _{N-eq}
Ionizing radiation	50.4×10^{-3}	kBq _{Co-60-eq}
Human non-carcinogenic toxicity	1364.3×10^{-3}	kg _{1,4-DCB-eq}
Stratospheric ozone depletion	92.9×10^{-6}	kg _{CFC11-eq}
Freshwater ecotoxicity	61.8×10^{-3}	kg _{1,4-DCB-eq}



Figure 2. Relative contributions of the processes involved in the TBA production.

Two-thirds of the impact's attributed to the TBA for global warming are linked to processes related to the chemicals used in the production. Ammonium chloride represented 40% of the total global warming impact, whereas methanol oxidation to produce formalde-hyde offered 28% of the impact. Transportation was the third process with substantial influence (21%). In a previous ex ante LCA work, Carlqvist et al. [10] showed that chemical processes can have a great influence on the global warming impact category. These authors highlight the fact that a great part of these chemicals' impacts come from fossil fuel consumption, which influences the overall impact. These statements were confirmed in our analysis of TBA production at the industrial operation level.

The energy supply (Figure 3) was the fourth impact. Radovic et al. [22], in Serbia, reported that the greatest impact of the production of coagulants from common bean seeds originated from electricity consumption, mostly within the spray drying phase. It is important to mention that the European electricity grid is different from the renewable hydropower-dominated Brazilian grid. Moreover, the processes for producing agents from acacia and bean seeds are reasonably different.



Figure 3. Boxplot of the contribution of each process to the production of TBA for all the environmental impact categories.

Analyzing the human carcinogenic toxicity category, based on Figure 2, it can be observed that the inputs that contribute most to the associated impacts are ammonium chloride (38%) and formaldehyde production (26%), followed by transportation (18%) and energy production (8%). Since the former are essential for obtaining the desired TBA, as they are the essential reagents for the Mannich reaction, the simple substitution of these components aiming at reducing their potential associated impacts does not prove to be a viable alternative, and in-depth studies of the chemical reactions involved are necessary. For human non-carcinogenic toxicity, similar behavior was observed. Ammonium chloride (45%) and formaldehyde (22%) again stand out among the inputs that contribute the most to the impacts associated with this category, and the strategies to minimize such impacts are analogous to those associated with human carcinogenic toxicity.

Ecotoxicity refers to the emission of toxic substances to the ecosystem, be it terrestrial or aquatic. For the freshwater and marine aspects of ecotoxicity, the main impacts can be identified, in descending order, for formaldehyde and ammonium chloride, which together account for 82% and 79% of the impacts for the respective areas, with small variations in the individual proportions. It is understood that the reduction in impacts for the two chemical inputs (ammonium chloride and formaldehyde) in aquatic aspects would be of greater complexity since it would require product reformulation or investment in optimization studies of the chemical reactions arising from the process. However, it is worth noting that if faced with other coagulant options, the impact of these inputs for the tannin-based product still stands out.

For terrestrial ecotoxicity, the main contributors are transportation (66%), ammonium chloride (13%), and energy (12%), which together correspond to more than 90% of the impacts inherent in the production for this category. Most of the impacts of transportation (in ton-km) come from the terrestrial logistics of formaldehyde (62%), bark (22%), and ammonium chloride (15%). Thus, it can be said that the search for formaldehyde suppliers closer to the factory location would represent an impactful environmental improvement for the product.

Considering water consumption, four processes were important to defining the results: ammonium chloride (64%), energy production (31%), formaldehyde production (14%), and wastewater treatment (-20%). One way to improve this system's environmental performance is to utilize less water within these steps. Since TBA production utilizes a lot of energy, decreasing water consumption can also be achieved through reducing energy demand [23]. A negative contribution from wastewater treatment occurs because it is the only process that considers not only the consumption of water but also the return of water outside of the system boundary.

For land use and ozone formation impacts, a different pattern is present, where the chemicals were not the main contributors. For land use, energy production (48%) and bark production (41%) stood out. This is a result of land-producing biomass that is an important input of these processes. Meanwhile, for ozone formation, both for human health and for terrestrial ecosystems, transportation (40%) and energy production (~22.5%) were the factors with a greater contribution of nitrous oxide emissions. The energy is mainly composed of heat production in the factory, in this case.

Other processes such as silica production, pallet production, tap water production, textile production, and deionized water production did not have a greater impact in the analysis of the 18 categories. For the soybean meal and crude oil production and ethylene glycol processes, the impact in the categories will be discussed in the following section.

3.2. Sensitivity Analysis for Soy Lecithin and Anti-Foaming Agent

As stated previously, our study found limitations related to the availability of some life cycle inventories in the database. Considering this, we conducted a sensitivity analysis on the processes that we selected as being the most appropriate process provider substitutes for the cases where the specific process flows were not available. Based on the relative contribution of the processes for the product system, the influences of the processes related to soybean lecithin and the anti-foaming agent in the different impact categories were verified. These two processes can be identified in Figure 2 as the crude soybean meal and crude oil production process and the market for ethylene glycol process, respectively.

By verifying the relative contributions, it is evident that the anti-foaming agent has a small contribution in face of the impact magnitude of the other processes. The maximum influence was 0.047% for the ionizing radiation category, which represents an irrelevant impact according to the 1% cut-off established previously. Differently from the previous process, the process chosen to represent soybean lecithin was relevant for three of the eighteen impact categories assessed: global warming (1.0%), land use (1.4%), and ozone depletion (3.8%). Still, the process that represents soy lecithin is not close in magnitude to the major impact contributors, as can be seen in Figure 3.

3.3. Comparative Life Cycle Assessment: Organic versus Inorganic Products

Comparing the results between TBA coagulant/flocculant and aluminum sulfate, the former has a superior impact in most impact categories for the functional unit chosen in this study (Figure 4 and Table 5). Land use, marine eutrophication, and fossil resource scarcity were the categories in which TBA presented greater relative difference. This is influenced by the agricultural component for land use and by the chemical's components for the two other categories. For marine eutrophication, for instance, 95% of the kg_{N-eq} were from NH_4Cl production.



Figure 4. Comparison between TBA and inorganic metallic coagulant.

Table 5. Absolute and relative results for the comparison between TBA and inorganic metallic coagulant.

		Absolute Results		Relative Results	
Name	Unit	TBA	$Al_2(SO_4)_3$	ТВА	$Al_2(SO_4)_3$
Fine particulate matter formation	kg _{PM2.5-eq}	$2.7 imes10^{-3}$	$2.6 imes10^{-3}$	100%	96%
Fossil resource scarcity	kg _{oil-eq}	673.1×10^{-3}	$218.1 imes 10^{-3}$	100%	32%
Freshwater ecotoxicity	kg _{1,4-DCB-eq}	$61.8 imes10^{-3}$	$133.1 imes 10^{-3}$	46%	100%
Freshwater eutrophication	kg _{P-eq}	$335.1.3 imes 10^{-6}$	$453.9 imes 10^{-6}$	74%	100%
Global warming	kg _{CO2-eq}	1518.6×10^{-3}	$793.9 imes 10^{-3}$	100%	52%
Human carcinogenic toxicity	kg _{1,4-DCB-eq}	104.8×10^{-3}	$358.7 imes 10^{-3}$	29%	100%
Human non-carcinogenic toxicity	kg _{1,4-DCB-eq}	1364.3×10^{-3}	2673.9×10^{-3}	51%	100%
Ionizing radiation	kBq _{Co-60-eq}	$50.4 imes 10^{-3}$	$46.4 imes 10^{-3}$	100%	92%
Land use	m ² a _{crop-eq}	1.0	$20.8 imes 10^{-3}$	100%	2%
Marine ecotoxicity	kg _{1,4-DCB-eq}	$83.6 imes 10^{-3}$	$173.9 imes 10^{-3}$	48%	100%
Marine eutrophication	kg _{N-eq}	$1109.7 imes 10^{-6}$	$23.4 imes 10^{-6}$	100%	2%
Mineral resource scarcity	kg _{Cu-eq}	$4.5 imes 10^{-3}$	$26.3 imes 10^{-3}$	17%	100%
Ozone formation, Human health	kg _{NOx-eq}	$6.2 imes 10^{-3}$	$2.4 imes10^{-3}$	100%	39%
Ozone formation, Terrestrial ecosystems	kg _{NOx-eq}	$6.3 imes10^{-3}$	$2.4 imes10^{-3}$	100%	38%
Stratospheric ozone depletion	kg _{CFC11-eq}	$92.9 imes10^{-6}$	$28.2 imes 10^{-6}$	100%	30%
Terrestrial acidification	kg _{SO2-eq}	$6.3 imes10^{-3}$	$6.4 imes10^{-3}$	98%	100%
Terrestrial ecotoxicity	kg _{1,4-DCB-eq}	$7673.8 imes 10^{-3}$	3333.9×10^{-3}	100%	43%
Water consumption	m ³	$18.9 imes 10^{-3}$	12.4×10^{-3}	100%	66%

Considering the overall impact calculated through World 2010 H normalization, the TBA has a lower environmental impact for the categories defined in this work (Figure 5). The normalized results in the analysis are substantially affected by three impacts: marine ecotoxicity, freshwater ecotoxicity, and human carcinogenic toxicity. Since the aluminum sulfate had higher values for these environmental impacts, it ended up having a greater environmental impact compared to the tannin-based agent.



Figure 5. Normalized results comparison between the two coagulants/flocculants.

As stated previously, the $Al_2(SO_4)_3$ data were based on a global average outside the European perspective, whereas the current TBA data considered a perspective from a Brazilian region. As a suggestion for future studies, a complete LCA (considering the same country's scenario) should be carried out for not only $Al_2(SO_4)_3$ but also for other agents, such as ferric chloride, polyaluminum chloride, and even organic polymers. Furthermore, as stated by Bolton et al. [24] and Niquette et al. [25], the comparison should also consider other criteria, such as cost, corrosiveness, product performance, and others.

4. Conclusions

The relevance of this first evaluation of the environmental impacts of an industrial process to produce tannin-based agents for coagulation/flocculation is highlighted, as well as its comparison with the production process of a traditional product used in the same market. The most relevant impacts resulting from the production of TBA are observed in the following categories: global warming; terrestrial, freshwater, and ecotoxicities; carcinogenic and non-carcinogenic human toxicities; and water use. The use of chemicals (ammonium chloride and formaldehyde) in the process of TBA production is the main source of environmental impact on the system, followed by transport and energy production. The production of bark was not a great burden for most of the categories; however, the normalization of the impacts showed the TBA as a very interesting option. It is recommended that future studies perform an assessment of the use and waste production phases for organic and inorganic agents for clarification. With this information, it will be possible to evaluate whether the organic agent will remain promising compared to the inorganic one.

Author Contributions: Conceptualization, A.C.B.; methodology, L.d.L.C.d.S., J.B.M.S. and L.S.N.; formal analysis, L.d.L.C.d.S., J.B.M.S. and L.S.N.; investigation, L.d.L.C.d.S., J.B.M.S. and L.S.N.; data curation, L.d.L.C.d.S., J.B.M.S., L.S.N. and A.C.B.; writing—original draft preparation, L.d.L.C.d.S., J.B.M.S., and L.S.N.; writing—review and editing, L.d.L.C.d.S., A.C.B., J.A.C., J.M. and N.d.S.R.; supervision, A.C.B., J.A.C., J.M. and N.d.S.R.; project administration, A.C.B.; funding acquisition, A.C.B., J.A.C., J.M. and N.d.S.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Coordination for the Improvement of Higher Education Personnel (CAPES Finance Code 001 and CAPES PRINT 88887.837337/2023-00) and by the National Council for Scientific and Technological Development (CNPq 200945/2022-0 and CNPq 308784/2023-5).

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- 1. Bratby, J. Coagulation and Flocculation in Water and Wastewater Treatment, 3rd ed.; IWA Publishing: London, UK, 2016.
- 2. Ritcher, C.A. Água: Métodos e Tecnologia de Tratamento; Blücher: São Paulo, Brazil, 2009.
- 3. Bondy, S.C. Low levels of aluminum can lead to behavioral and morphological changes associated with Alzheimer's disease and age-related neurodegeneration. *Neurotoxicology* **2016**, *52*, 222–229. [CrossRef] [PubMed]
- Kurniawan, S.B.; Abdullah, S.R.S.; Imron, M.F.; Said, N.S.M.; Ismail, N.; Hasan, H.A.; Othman, A.R.; Purwanti, I.F. Challenges and opportunities of biocoagulant/bioflocculant application for drinking water and wastewater treatment and its potential for sludge recovery. *Int. J. Environ. Res. Public Health* 2020, 17, 9312. [CrossRef] [PubMed]
- 5. Hadj Mansour, Y.; Othmani, B.; Ben Rebah, F.; Mnif, W.; Saoudi, M.; Khadhraoui, M. Could plant-based flocculants substitute the conventional synthetic chemicals in the sludge dewatering process? *Water* **2023**, *15*, 2602. [CrossRef]
- Hesse, M.C.S.; Santos, B.; Selesu, N.F.H.; Corrêa, D.O.; Mariano, A.B.; Vargas, J.V.C.; Vieira, R.B. Optimization of flocculation with tannin-based flocculant in the water reuse and lipidic production for the cultivation of Acutodesmus obliquus. *Sep. Sci. Technol.* 2017, 52, 936–942. [CrossRef]
- 7. Klumb, A.K.; Faria, O.L.V. Produção de coagulante vegetal catiônico a partir de cascas de eucalipto (*Eucalyptus tereticornis*). *VETOR-Rev. Ciências Exatas E Eng.* **2012**, *22*, 71–80.
- 8. Tomasi, I.T.; Machado, C.A.; Boaventura, R.A.R.; Botelho, C.M.S.; Santos, S.C.R. Tannin-based coagulants: Current development and prospects on synthesis and uses. *Sci. Total Environ.* **2022**, *822*, 153454. [CrossRef] [PubMed]
- 9. Ding, T.; Bianchi, S.; Ganne-Chédeville, C.; Kilpeläinen, P.; Haapala, A.; Räty, T. Life cycle assessment of tannin extraction from spruce bark. *IForest-Biogeosci. For.* **2017**, *10*, 807. [CrossRef]
- Carlqvist, K.; Arshadi, M.; Mossing, T.; Östman, U.B.; Brännström, H.; Halmemies, E.; Nurmi, J.; Lidén, G.; Börjesson, P. Life-cycle assessment of the production of cationized tannins from Norway spruce bark as flocculants in wastewater treatment. *Biofuels Bioprod. Biorefin.* 2020, 14, 1270–1285. [CrossRef]
- 11. ISO 14040:2006; Environmental Management. Life Cycle Assessment: Principles and Framework. ISO: Geneva, Switzerland, 2006.
- 12. *ISO* 14044:2006; Environmental Management. Life Cycle Assessment. Requirements and Guidelines. ISO: Geneva, Switzerland, 2006.
- 13. Hauschild, M.Z.; Rosenbaum, R.K.; Olsen, S.I. (Eds.) *Life Cycle Assessment: Theory and Practice*; Springer International Publishing: Cham, Switzerland, 2018.
- Arias, A.; González-García, S.; González-Rodríguez, S.; Feijoo, G.; Moreira, M.T. Cradle-to-gate life cycle assessment of bioadhesives for the wood panel industry. A comparison with petrochemical alternatives. *Sci. Total Environ.* 2020, 738, 140357. [CrossRef] [PubMed]
- 15. Carlqvist, K.; Wallberg, O.; Lidén, G.; Börjesson, P. Life cycle assessment for identification of critical aspects in emerging technologies for the extraction of phenolic compounds from spruce bark. *J. Clean. Prod.* **2022**, 333, 130093. [CrossRef]
- 16. Sánchez-Martín, J.; González-Velasco, M.; Beltrán-Heredia, J. Surface water treatment with tannin-based coagulants from Quebracho (*Schinopsis balansae*). *Chem. Eng. J.* **2010**, *165*, 851–858. [CrossRef]
- 17. Sánchez-Martín, J.; Beltrán-Heredia, J.; Solera-Hernández, C. Surface water and wastewater treatment using a new tannin-based coagulant. Pilot plant trials. *J. Environ. Manag.* 2010, *91*, 2051–2058. [CrossRef] [PubMed]
- Lugo, L.; Martin, A.; Diaz, J.; Perez-Florez, A.; Celis, C. Implementation of modified acacia tannin by mannich reaction for removal of heavy metals (Cu, Cr and Hg). *Water* 2020, *12*, 352. [CrossRef]
- 19. Banch, T.J.; Hanafiah, M.M.; Alkarkhi, A.F.; Abu Amr, S.S. Factorial design and optimization of landfill leachate treatment using tannin-based natural coagulant. *Polymers* **2019**, *11*, 1349. [CrossRef] [PubMed]
- Singh, R.; Kumar, S.; Garg, M. Domestic wastewater treatment using Tanfloc: A tannin based coagulant. In *Geostatistical and Geospatial Approaches for the Characterization of Natural Resources in the Environment*; Raju, N., Ed.; Springer: Berlin/Heidelberg, Germany, 2016.
- 21. Justina, M.D.; Muniz, B.R.B.; Bröring, M.M.; Costa, V.J.; Skoronski, E. Using vegetable tannin and polyaluminium chloride as coagulants for dairy wastewater treatment: A comparative study. *J. Water Process Eng.* **2018**, *25*, 173–181. [CrossRef]

- 22. Radovic, S.; Sekulic, M.T.; Agarski, B.; Pap, S.; Vukelic, D.; Budak, I.; Prodanovic, J. Life cycle assessment of new bio-based coagulant production for sustainable wastewater treatment. *Int. J. Environ. Sci. Technol.* **2023**, *20*, 7433–7462. [CrossRef]
- 23. Simões, R.; Simões, C.; Ferreira, R.; Rodrigues, A.C. Life cycle assessment of the extraction of condensed tannins from acacia bark residues. In Proceedings of the Multi Conference on Computer Science and Information Systems, Porto, Portugal, 15 July 2023.
- 24. Bolton, A.; Bouchard, C.; Barbeau, B.; Jedrzejak, S. Comparative life cycle assessment of water treatment plants. *Desalination* **2012**, 284, 42–54. [CrossRef]
- 25. Niquette, P.; Monette, F.; Azzouz, A.; Hausler, R. Impacts of substituting aluminium-based coagulants in drinking water treatment. *Water Qual. Res. J. Can.* 2004, *39*, 303–310. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.