

# A Bibliometric Study of the Unhairing and Liming of the Leather Tanning Process

by

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## Abstract

Unhairing and liming are the most polluting operations of the leather tanning process. Over the years, this sector has been investigated increasingly. Hence, this paper aims to explore and analyze the scientific activity of this field of research with a new view, applying bibliometrics techniques. The method of the study is based on a search and collection of publications indexed in Scopus. Subsequently, bibliometric data were extracted from the corresponding publications. Graphics and bibliometric maps were made to obtain quantitative results and the relationships between countries, authors, journals, and keywords. The results show an upward trend over the last 100 years or so, where the topic of most of the publications has reversed from being purely about engineering and process to focus on the big environmental issue generated by traditional unhairing. At the same time, research in this field has shifted to countries with the biggest tanning industry, such as China and India. In conclusion, bibliometrics has been a good method to know the current state of scientific literature and the timeline of this field of research, which will allow for a deepening in alternative methods to traditional unhairing and advance of the environmental concern caused by these polluting operations.

## Introduction

Leather tanning can be divided into three different stages. The first one is called Wet or Beamhouse stage due to a large amount of water present and used in each of the included operations, such as soaking, unhairing, delimiting, pickling, etc.

Unhairing and liming have always been treated as a single process. Due to their compatibility, both operations can be performed together in the same float, although each one has specific objectives.<sup>1</sup> On the one hand, unhairing consists of removing from the soaked skin the hair or wool, and the epidermis, to hydrolyze keratin (the hair protein). On the other hand, liming has the objective to hydrolyze collagen, causing a loosening of its fibrous structure. Traditional unhairing and liming are achieved using sodium sulfide ( $\text{Na}_2\text{S}$ ), sodium hydrosulfide ( $\text{NaHS}$ ) and calcium hydroxide. Due to its reductive nature, unhairing with sulfides helps to break disulfide bonds of cysteine, leading to the subsequent hydrolysis of

keratin. That occurs due to the combination of hydrosulfide ( $\text{HS}^-$ ) and hydroxyl ( $\text{OH}^-$ ) ions, resulting from the reduction of sodium sulfide in an aqueous solution.<sup>2</sup> Together with calcium hydroxide, the hydrogen bonds between the collagen fibers get broken. The skin swells, the fibers loosen, and the chemical reactivity points increase, making the products added in later stages penetrate the skin correctly. This effect is called lyotropic swelling.<sup>3</sup> Unhairing and liming are easy to control, and it is an inexpensive process.<sup>4</sup>

One of the challenges that tanners face is to reduce the environmental impact generated by the tanning process. Concretely by reducing the high-water consumption produced by the Beamhouse process, and particularly unhairing and liming operations. Reductive unhairing (with sulfides) is the most effective and traditional, but it is the most polluting. Not only does it entail an extremely high consumption of water and chemical products. It also generates highly polluting and waste of water due to the hair and other dirt and fats present in the water, which contributes to the increase of polluting parameters such as Chemical Oxygen Demand (the amount of dissolved oxygen that must be present in water to oxidize chemical organic materials), Biochemical Oxygen Demand (the amount of oxygen required to breakdown organic pollutants biologically with microorganisms),<sup>5</sup> Total Suspended Solids (organic and inorganic particles larger than 2 microns found in water), sulphides ( $\text{S}^{2-}$ ), and so on.<sup>6,7</sup> Moreover, the use of sodium sulfide in this type of unhairing does not only affect the wastewater. When working at pH values below 10, sodium sulfide is released in the form of hydrogen sulfide ( $\text{H}_2\text{S}$ ), causing a stink, and in sufficient quantities, severe respiratory problems, or even death.<sup>8,9</sup>

Therefore, due to this enormous environmental problem caused by traditional unhairing, this sector has evolved over the years, looking for less polluting and alternative methods to traditional unhairing.<sup>9</sup> Oxidative unhairing uses hydrogen peroxide as an oxidative agent and sodium hydroxide as a source of alkali in the same float to hydrolyze the hair, with the advantage of working with less water and reducing the polluting parameters of the wastewater.<sup>10</sup> In addition, research in recent years focused on a type of enzyme that allows the replacement of sodium sulfide as an unhairing agent. Although enzymatic unhairing is a suitable alternative because of its advantages (diminution of sulfides in water and the amount of water used, recovery of good quality hair), enzymes, in general, are

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expensive and need much more accurate control in comparison to other products.<sup>11</sup> Nor a process has been found that can be carried out only with enzymes, giving results comparable to traditional unhairing. Another alternative that many factories have already started to use is hair-save unhairing. It significantly reduces the pollution load of the resulting water, especially in terms of solid waste (hair and sludge generated in the process), even though it uses the same chemicals as the traditional process (sodium sulfide and lime). Recently, recirculation systems for wastewater floats have also started to reduce water consumption. However, there is not yet a satisfactory solution.<sup>12</sup>

Scientific and technological research and the divulgation of the resulting knowledge are fundamental activities to satisfy the growing needs of society, and there is also a need to analyze and evaluate this scientific production. It is at this point that Information Science comes in, developing techniques to measure and value postgraduate scientific activity. Among the different metric disciplines within Information Science is Bibliometrics, which is a part of Scientometrics. Bibliometrics is the science that uses mathematical and statistical methods to study the nature and scientific activity of a specific line of research. This field of Scientometrics aims to investigate and evaluate the quality and quantity of published scientific literature. To know the trend of publications, the most relevant journals where these documents are published, the most active authors in the subject, and the relationship and contribution between countries and institutions in a particular field, and the most used keywords in the publications.<sup>13</sup>

Around the 1960s, the curiosity to understand scientific development led to the first works on Bibliometrics. Price created the concept of "Science of Science", and it was then that the application of scientific methods for the analysis of science began. Due to the digitalization of databases and the great demand to evaluate the effectiveness of the policies of science planning authorities, there was an important boom in bibliometric studies. Bibliometrics took a step forward in 1978, with the foundation of the journal *Scientometrics*, when research articles related to scientometrics, the science of quantitative analysis of scientific research activity, began to be published.<sup>14</sup> However, it was not until two decades ago that J. M. López Piñero and M.L. Terrada introduced bibliometric studies in Spain.<sup>15</sup>

To develop bibliometric research, it is essential to have bibliographic information on scientific publications, such as the author/s, the title of the publication, the year of publication, the journal, etc. To obtain this, bibliographic databases are used, which are formed of an extensive number of registers stored and managed through computer systems. Some of the most used databases are Scopus, Web of Science, Journal Citation Reports, Google Scholar, etc..<sup>16,17</sup> Once the bibliographic information is obtained from the

selected publications, it is extracted and converted into a specific format. To value this information, the application of bibliometric indicators is useful. For years, these numerical parameters have been decisive in analyzing the impact of scientific papers, valuing the research activity of an author, an institution, or a specific country.<sup>18</sup> In general, some of the aspects that can be determined using bibliometric indicators are the chronological evolution of scientific production, the productivity of authors or institutions by measuring the number of their works, the collaboration between scientists and institutions, the analysis of sources that distribute published works and their evolution, etc. There are many distinct categories used to distinguish the bibliometric indicators currently in use. Generally, there is a difference between qualitative indicators, which evaluate the scientific quality of the work, and quantitative indicators. Within this group, a distinction is made between those of scientific activity and those of scientific impact.<sup>19,20</sup> Depending on the purpose of the study, these indicators can be unidimensional or multidimensional. Unidimensional indicators study a single characteristic of publications, such as which journals they have been published in, which authors have produced the papers, etc., while multidimensional indicators investigate the relationships between characteristics, such as co-authorship relationships, co-citation relationships, or keyword co-occurrence relationships.<sup>21</sup> Bibliometric maps are a sort of multidimensional bibliometric indicator that provides a preliminary view of the quality and evolution of a particular line of research through representative diagrams of connected within words, ideas, or concepts.<sup>22-24</sup> For creating bibliometric maps, it is necessary to have software capable of constructing this type of complex graphics, such as VOSviewer. One of the advantages provided by this software is that it allows visualizing the maps created in three different ways, network visualization, density visualization and overlay visualization. That makes it easier to explore the maps in detail, which is especially useful and essential when working with maps containing many elements. Some of the most common maps that could be created are co-citation networks, co-authorship networks, keyword co-occurrence networks, etc..<sup>25-28</sup> One last outcome of using Bibliometrics to analyze a scientific topic is the possibility to find literature gaps, that is, to identify topics or areas of research still to be fully explored.

This science has been applied to research a wide variety of fields of current interest, e.g., Big Data, energy efficiency, and sustainability, biomedicine, mobile technology, etc. To the best knowledge of the authors, there is not any bibliometric analysis or publication on the unhairing and liming of leather tanning. Therefore, this paper aims to apply bibliometric analysis techniques to explore and evaluate the current status of this scientific and industrial process and its evolving trends in recent years. The results should help the research community to accentuate the find new lines of investigation to improve the sustainability of this process.

## Experimental

The function of bibliometric studies is to analyze and evaluate the results of lines of scientific research. For its realization, it is essential to have one or more databases. In this paper, Scopus is used, accepted by the international scientific community as the largest database of citations and abstracts of scientific literature to analyze scientific publications.<sup>29,30</sup> However, like all databases, Scopus presents a limitation, it does not consider national journals as they do not meet some of the requirements to be in the database.<sup>30</sup> The methodology followed to perform this bibliometric analysis in this study is shown schematically in Figure 1. The first step consists of an advanced search and data collection in Scopus. Through the advanced search, one could obtain more technical information about the topic of interest in comparison to a basic search. Like most databases, Scopus works with subfields (title, abstract, keyword, etc.) and Boolean operators (AND, OR, AND NOT, etc.), elements that allow combining and establishing relationships between the keywords chosen to perform the search.<sup>31</sup> Initially, a first advanced search was carried out at the end of 2020, using the following keyword string:

```
TITLE-ABS-KEY (( "unhairing" OR "liming" )
AND ( "hide" OR "skin" OR "leather" )
AND NOT ( "parchment*" OR "clinic*" ))
```

In this initial search, a total of 363 documents resulted, from 1926 to 2020. The keywords "unhairing" and "liming" appeared in the investigation. Additionally, the terms "hide", "skin", and "leather" were key in this study. It was necessary a general reading of each of the publications to get accurate understanding and to keep in the query only those that deal with the topic of interest.<sup>32</sup> Thus, using the AND NOT operator, the keywords "parchment\*" and "clinic\*" were excluded from the search. In March 2021, 22 new documents were added in the same query, a result of a total of 383 papers. Following

the same method as with the initial query, the abstracts of the new documents and those already included in the query were reviewed. Finally, after excluding some unwanted terms, the final query is of a total of 291 documents from 1927 to 2021:

```
TITLE-ABS-KEY (( "unhairing" OR "liming" )
AND ( "hide" OR "skin" OR "leather" )
AND NOT ( "parchment*" OR "clinic*" OR "fisheries" OR
"rat" OR "pear*" OR "sanitary" OR "demod*" OR
"leather shavings" OR "coriagen" OR "preparation of
gelatin" OR "nose" OR "liritan" OR "hysteresis" OR
"genotoxicity" OR "bacterial sp*" OR "fatliquoring
agent*" OR "ammonia removal" OR "waterproofing"
OR "organic nanofiltration" OR "anionic
polyelectrolyte" OR "glutaraldehyde" OR "skate" OR
"reverse tanning process" OR "decorin content" OR
"alkaline lipase" OR "fungus growth" OR "growth
factor" OR "fish skin" OR "growth performance"
OR "slaughtering industry" OR "alkylphenol"
OR "bone" OR "air filter" OR "plasma" OR "fruit
quality" OR "bullfrog" OR "red mud" OR "short
term" OR "agroecology" OR "resilient" OR "shaving
operations" OR "interweaving" OR "climate" OR
"biodiesel" OR "adsorption" OR "cowhide fleshings"
OR "proteobacteria" OR "the linear" OR "detergent
tolerance" OR "laboratories*" OR "wet blue leather
manufacture" OR "limed fleshing" OR "relative
elongations" OR "cattle breedings" OR "papermaking"
OR "green productivity" OR "expansive soil"
OR "rabbit skins*" OR "keratose" OR "brines*"
OR "substrate concentration" OR "infusion" OR
"furniture" OR "deamination" ))
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The next step was to extract and convert bibliometric information of the 291 publications, such as the year of publication, author/s, journal,

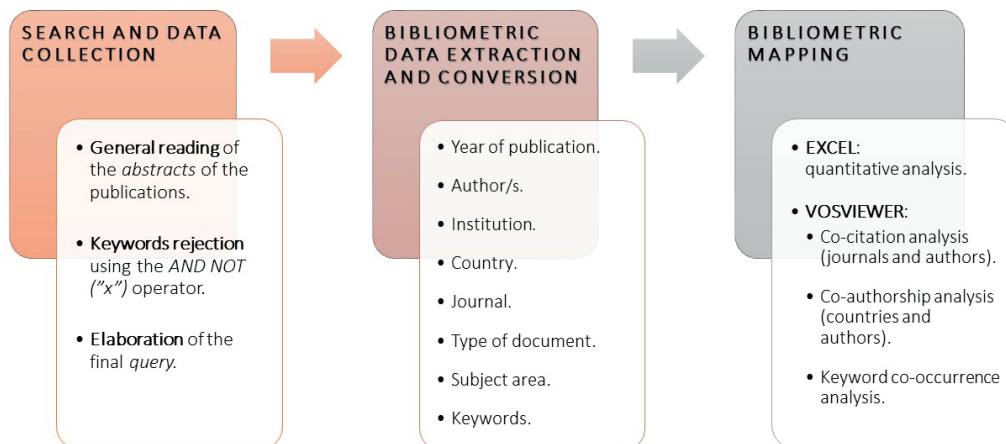


Figure 1. Methodology used for the bibliometric analysis.

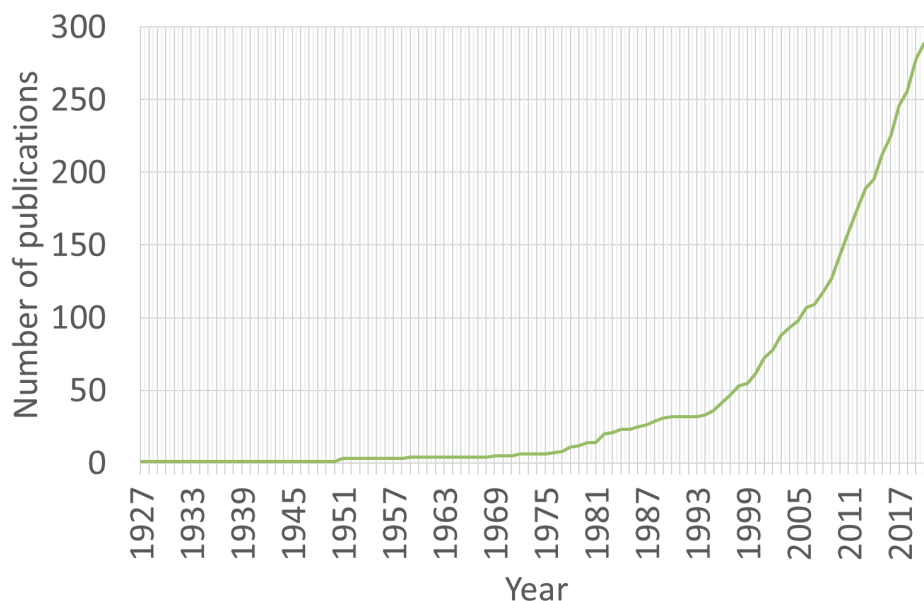


Figure 2. Accumulated annual trend of publications.

country, keywords, etc. Scopus has the advantage of exporting these data in different formats, either through Mendeley, RIS format, CSV, BibTeX, etc. With all the information obtained various graphs and bibliometric maps were elaborated. The spreadsheet Excel was used to perform a quantitative analysis. That is to study the trend, distribution, and quantity of publications according to the year, journal, type of document, subject area, institution, country, and author/s. The software VOSviewer was used to study the diverse relationships and connections between authors, countries, journals, and keywords.

## Results and Discussion

This section shows the results of the bibliometric analysis of the 291 publications selected in the Scopus database, from 1927 to 2021, following the methodology described previously. This bibliometric study is divided into 4 large parts. The first part shows the results of quantitative analysis on the trends and distribution of publications. The second section presents the co-authorship analysis. The analysis of co-citation and co-occurrence of keywords are shown in the third and fourth sections, respectively. The results of these last three sections were obtained with VOSviewer.

### Quantitative analysis. Trends and distribution of publications

In this first analysis, the trend and distribution of publications were studied, according to the year of publication, the journal, type of document, thematic area, institution, country, and author.

Figure 2 shows the cumulative annual trend of publications extracted from Scopus. According to this database, Henry Baldwin

Merrill was the first author who published the first document about unhairing and liming of skins, in 1927.<sup>33</sup> As it can be seen, only 10 documents were published in the early 1980s. From then on, the trend began to increase. By the late 1990s, more than 50 documents had already been published, which some of them began to deal with alternative methods to traditional unhairing and liming operations, emphasizing enzymatic unhairing. Specifically, in 1996, a total of 6 documents were published, of which 4 dealt with the action of enzymes as an alternative to the use of traditional chemical products. Then, the trend is increasing, reaching a total of more than 140 Publications in 10 years elapsed.

Figure 3 shows the annual trends of published documents in different journals, congresses, and other sources from 1972, the decade when the trend of publications starts to increase little by little. The Journal of the American Leather Chemists Association is one of the first journals where more documents on unhairing and liming began to be published, reaching a total of 68 published documents. The second one with more published documents (48) on the topic of study is the Journal of the Society of Leather Technologists and Chemists, which began to publish in 1996. Table I shows the top journals with at least 3 publications on the topic of the study. Figure 3 also shows that it was not until 2001 when the Journal of Cleaner Production (17) began to publish about the subject of study. Similarly, the Journal Clean Technologies and Environmental Policy (5) did so in 2004. As their proper title says, these Journals also publish documents about cleaner environmental technologies. Therefore, when the environmental concern caused by traditional unhairing began, many authors also decided to publish their documents there.

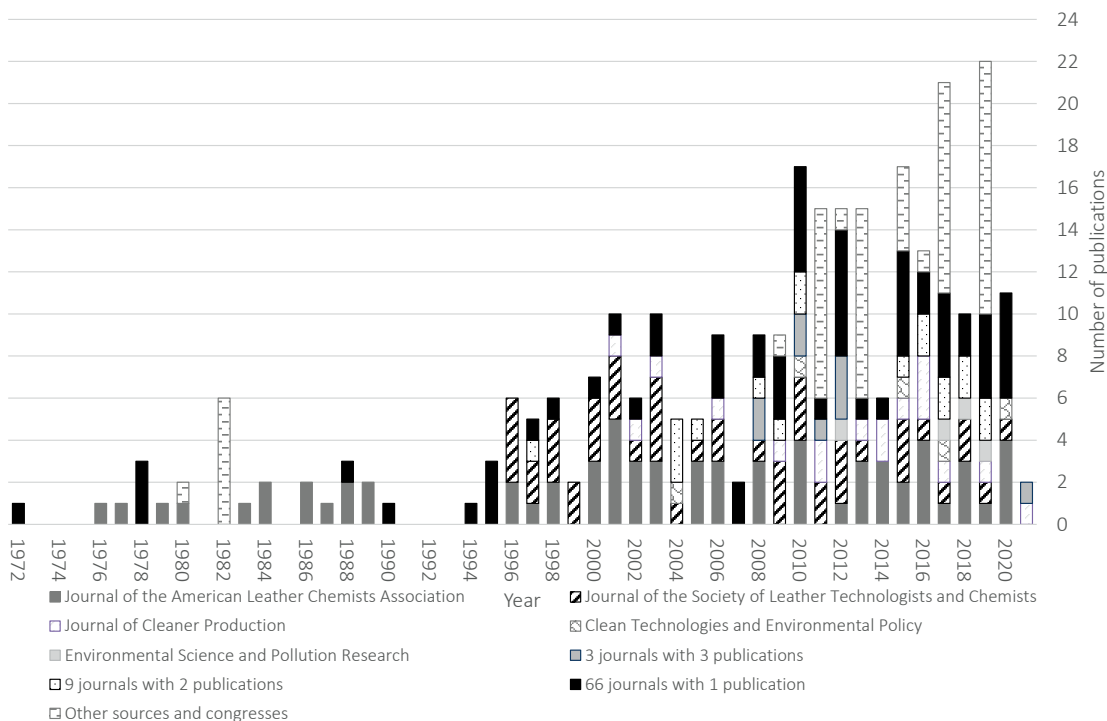


Figure 3. Annual trend of publications by journal.

**Table I**  
Top journals with at least 3 publications on the topic

Journal	Number of publications
Journal of the American Leather Chemists Association	66
Journal of the Society of Leather Technologists and Chemists	48
Journal of Cleaner Production	17
Clean Technologies and Environmental Policy	5
Environmental Science and Pollution Research	4
Advanced Material Research	3
Brazilian Journal of Chemical Engineering	3

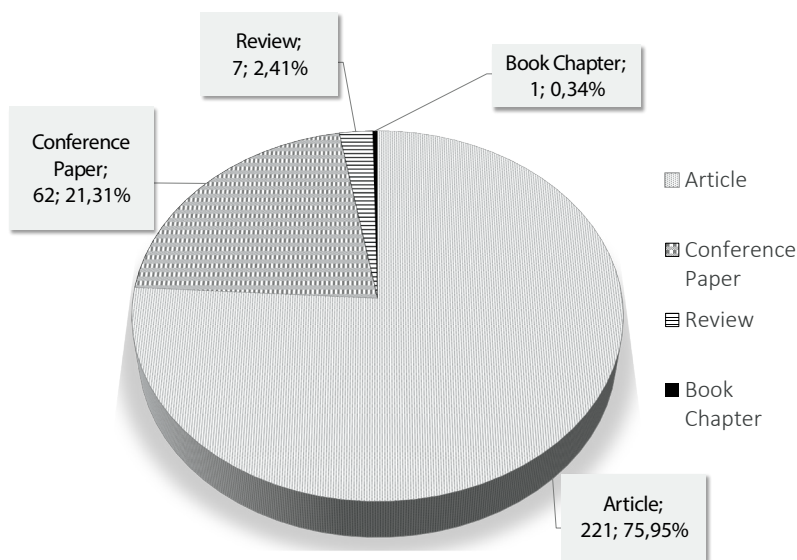


Figure 4. Percentage distribution of the document type of publications.

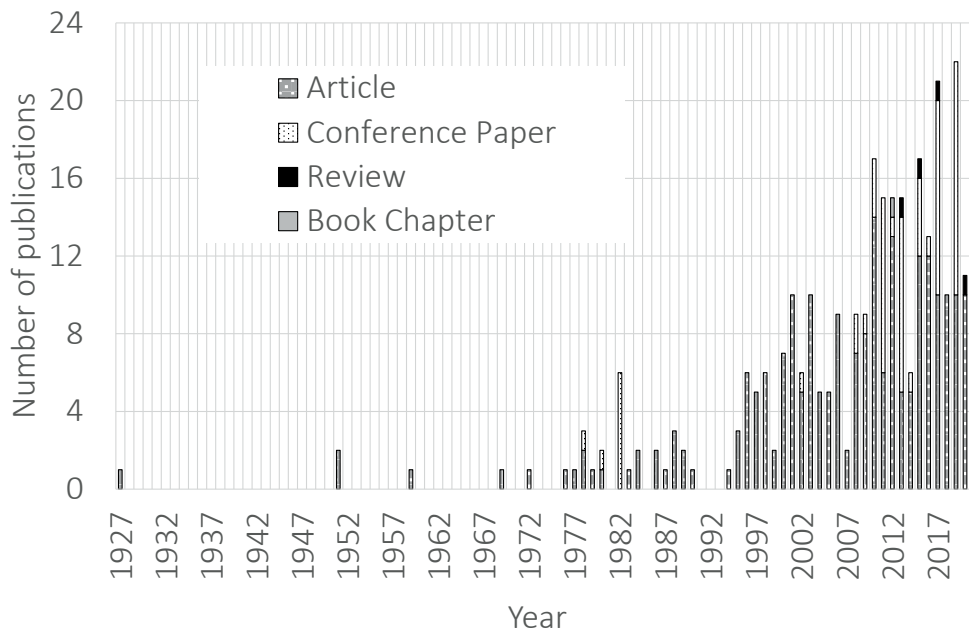


Figure 5. Annual trend of publications by document type.

Figure 4 shows the percentage distribution of publications classified by document type. It is observed that most publications are articles (221), followed by conference papers (62). As for the rest of the documents, 7 reviews have been published and a single book chapter related to unhairing and liming.

Figure 5 presents the annual trend and distribution of publications according to the type of documents, from 1927 to 2021. As mentioned above, the most common format of publications is the article. It is observed that it was not until the late 1970s that conference papers began to be published, but it was not until the end of the first decade of the 21st century that they were published again. On the other hand, it was not until 2013 that documents were published in the form of review. Finally, the only document in book chapter format was published in 2012.

Figure 6 presents the percentage distribution of the documents published according to their thematic area. There is so much diversification of subject areas because some journals deal with various topics at the same time, so some documents may be assigned in more than one thematic area. Chemical Engineering is the subject with the highest percentage of published documents (23%), followed by Chemistry (22%), and Materials Science (19%).

According to the query used and the documents extracted from Scopus, the main institutions and affiliations that have published more than 5 documents on the topic of interest are ordered in Table II. As it can be seen, the Council of Scientific and Industrial Research India (also called the Central Leather Research Institute India) tops the list, being the most active institution on the subject, followed by two Chinese institutions, Sichuan University and the Ministry

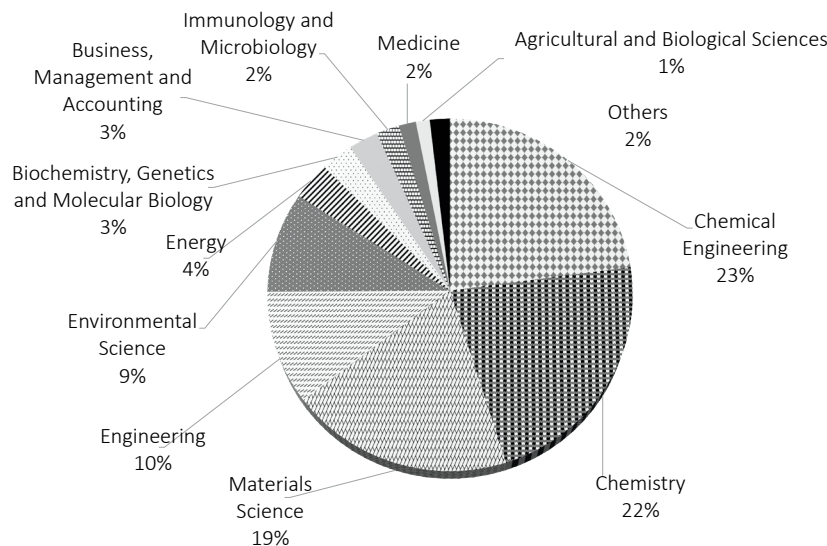


Figure 6. Percentage distribution of publications by subject area.

**Table II**  
**Top 10 institutions and their corresponding country**

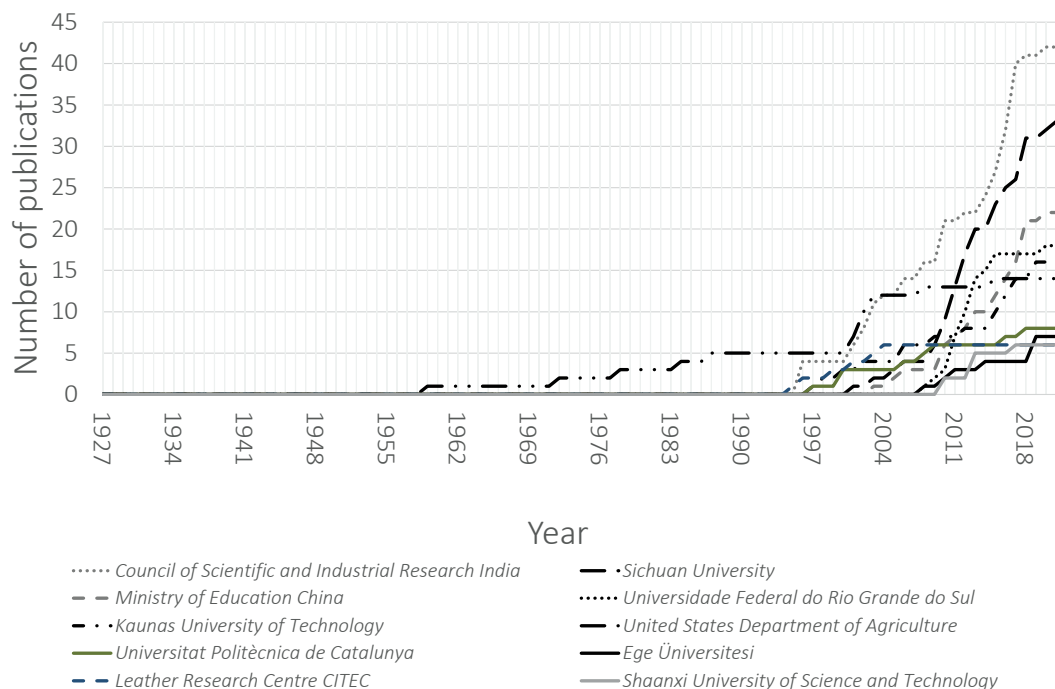
Affiliation/Institution	Country	Number of publications
Council of Scientific and Industrial Research India	India	42
Sichuan University	China	33
Ministry of Education China	China	22
The Federal University of Rio Grande do Sul	Brazil	18
Kaunas University of Technology	Lithuania	16
United States Department of Agriculture	United States	14
Polytechnic University of Catalonia	Spain	8
Ege University	Turkey	7
Leather Research Centre CITEC	Argentina	6
Shaanxi University of Science and Technology	China	6

of Education China, with 33 and 22 publications, respectively. This suggests that India and China are the main most active countries in the subject of interest. Other countries interested on the topic are Brazil, Lithuania, United States, and Spain. It is also observed that most institutions are universities or research centers (independent or belonging to governments).

Figure 7 presents the accumulative annual trend of the publications of the first 10 institutions (Table II). From 1927 to 1958, none of these institutions published documents about the topic of interest. It was not until 1959 when the United States Department of Agriculture published its first paper on the subject. Then, in 1995, so did the

Leather Research Centre CITEC institution. It should be noted that most of these institutions, their trend of publications begins in the late 1990s, publishing between 2 and 5 documents per year.

Figure 8 presents a world map of the different countries that have published more documents on unhairing and liming between 1927 and 2021. Search results in Scopus show that only 45 countries are involved in the topic of interest. As it can be seen, countries with the highest number of publications are colored with more intense orange, such as China and India (60 and 53 publications, respectively), compared to other countries with fewer published documents, for example, Spain (12) and Turkey (10).



**Figure 7.** Annual trend of publications by institution or affiliation.

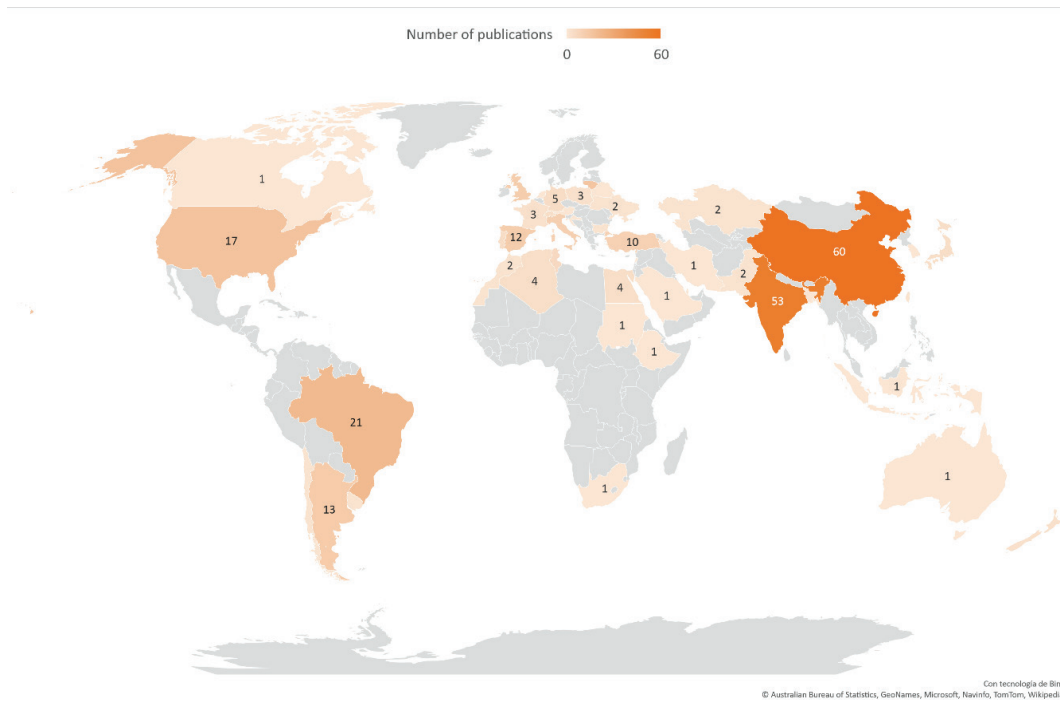


Figure 8. World map of the publications distributed for each country.

Figure 9 shows the cumulative annual trend of the top 10 countries with the highest number of published documents. According to the data extracted from Scopus, the United States was the first to publish an article about unhairing and liming operations, specifically in 1927 (*Action of Ammonia on Calfskin*). The following countries to publish their first paper on the topic of the study were United Kingdom and China (which is not seen in the graph since it is overlapping with England), specifically in 1988: *Enzymes in the tannery - catalysts for progress*<sup>34</sup> and *Improvement of Unhairing Enzyme for Leather Processing*,<sup>35</sup> respectively. As it can be seen, these two documents study the influence of enzymes on leather tanning.

It can also be seen that the two countries with the most documents published so far are China and India. This is due to the large increase in the publication of papers due to the development of the tanning industry. Italy is the third country to publish documents on the topic of study in 1990 (*Environmental impact of the tanning industry*<sup>36</sup>).

Table III presents the top 10 authors with the highest number of documents published on the topic of study. Mariliz Gutterres leads the list, with 18 documents published, followed by Virgilijus Valeika and Kęstutis Beleška, with 16 and 15 publications related to unhairing and liming, respectively. Both authors are from the

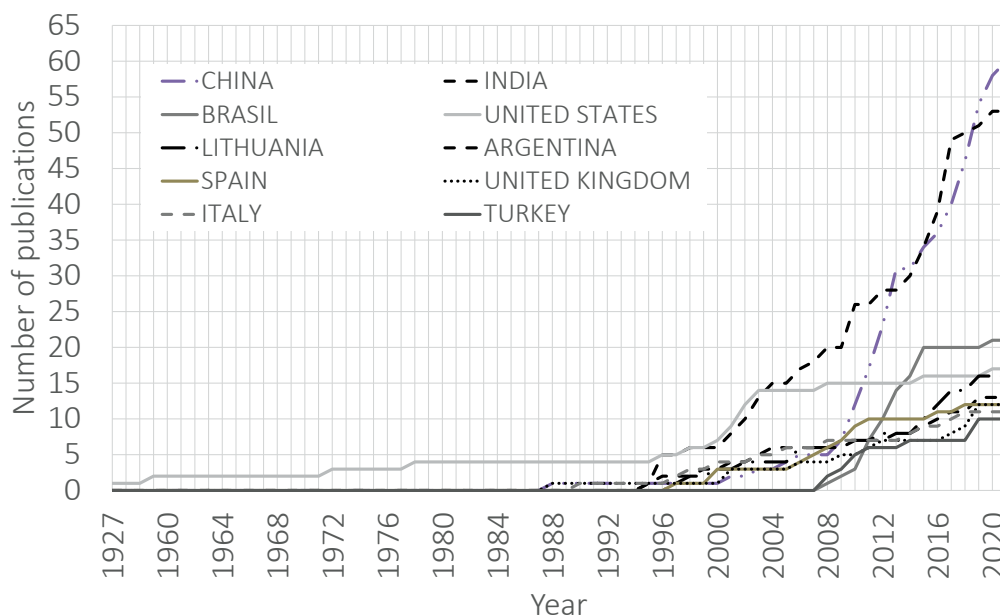


Figure 9. Accumulated annual trend of publications by country.

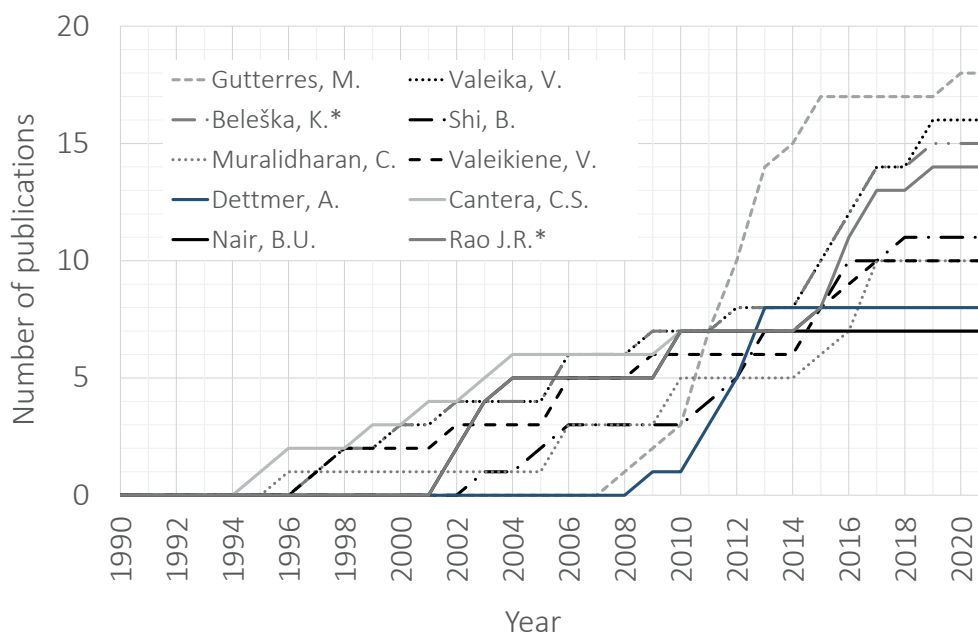
**Table III**  
List of the top 10 authors including institution, country, total publications on Scopus and h-index

Author	Affiliation/Institution	Country	Publications (Topic of study)	Publications (Totals)	h-index (Scopus)
Gutterres, M.	Federal University of Rio Grande do Sul	Brazil	18	118	21
Valeika, V.	Kaunas University of Technology	Lithuania	16	40	11
Beleška, K.*	Kaunas University of Technology	Lithuania	15	32	9
Rao, J.R.*	Central Leather Research Institute India	India	14	186	24
Shi, B.	Sichuan University	China	11	270	39
Muralidharan, C.	Central Leather Research Institute India	India	10	70	19
Valeikiene, V.	Kaunas University of Technology	Lithuania	10	22	7
Dettmer, A.	Federal University of Rio Grande do Sul	Brazil	8	47	13
Cantera, C.S.	Leather Research Centre CITEC	Argentina	7	21	10

\*Authors presents in the database with more than one different name.

same institution, with a total of 40 and 32 published documents, and an h-index of 11 and 9, respectively. In fourth place is the author Jonnalagadda R. Rao, from India, with 14 documents published on the subject. Table III shows that Lithuanian authors have published the most documents on unhairing and liming operations, compared to their total publications. The same can also be said of the author Carlos Santos Cantera, who has published 7 documents about the topic of interest from a total of 21 publications.

Figure 10 presents the accumulated trend from the documents published by the authors of Table III, year by year, from the early 1990s to the current year (2021). Indeed, the years before the 90's were not contemplated because, among these authors, until 1995 only Carlos Santos Cantera was the first one to publish a document about unhairing, specifically aiming to recycle the effluents from the hair-saving chemical unhairing process.<sup>37</sup> The following year, Chellapa Muralidharan published his first document on the subject,



**Figure 10.** Accumulated annual trend of publications by author from 1990 to 2021.

with the aim to study an alternative non-enzymatic but sulfide free unhairing of goat skins<sup>38</sup> and again C.S. Cantera published one more document that year, focusing on a hair saving enzyme-assisted unhairing.<sup>39</sup> As it can be seen, the main common topic of these 3 documents is the study of alternative methods to traditional unhairing, free of sulfides: hair-save unhairing and enzymatic unhairing. Mariliz Gutterres began publishing in 2008, a few years later compared to other authors, but its trend has been increasing, becoming the author with more documents published so far (a total of 18 publications on this field of research), as seen in Table III.

### Co-authorship analysis

Most scientific research projects are increasingly being developed in groups. Currently, completing research on a particular topic individually is quite difficult. Co-authorship analysis is essential for any bibliometric study, as it helps to know the level of collaboration and interaction existing between different authors who research the same specific field.<sup>40</sup> In this section, two types of co-authorship analyses are presented: by country and by author.

Figure 11 shows the co-authorship relationships between the countries that have published on the topic of study. The size of the circles determines the number of published documents in a country on the topic.<sup>41</sup> Then, the main countries with the highest number of publications are China, India, and Brazil. It seems to be no link between the countries that make up the graph. It is true that countries such as Austria, Chile, Egypt, etc., do not have any co-authorship relationship with other countries. However, in Figure 12 it can be seen in more detail the collaboration between different groups of countries (or clusters). China is not only one of the countries with the most published documents, but it is also one of the countries with the most co-authorship relations with countries such as the United Kingdom, Turkey, New Zealand, and Taiwan. Similarly, in

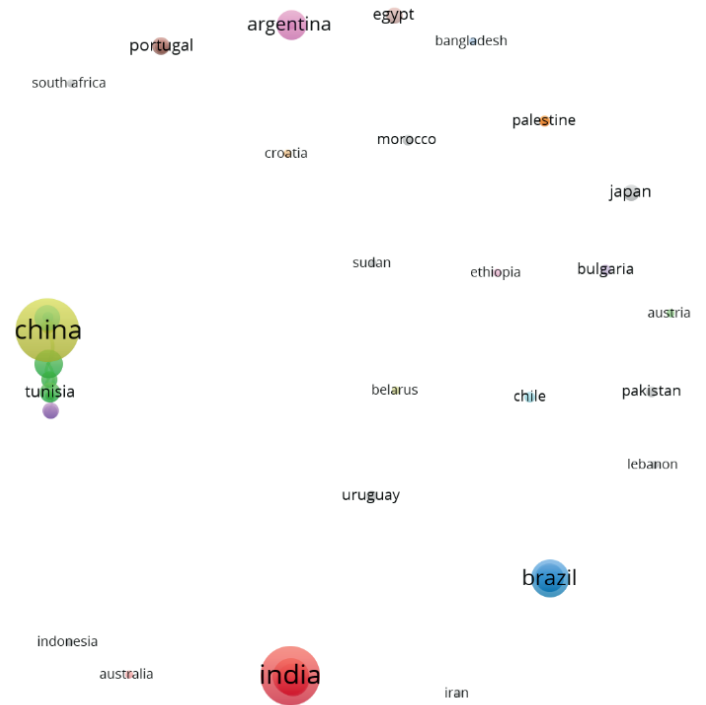


Figure 11. Country co-authorship network.

the red cluster, the relationship between Ukraine and Lithuania is very close, although only Ukraine has shared authorship with the United States. The last blue cluster shows that each country is connected only to two other countries. Brazil has shared authorship with Italy and Germany, but not with Spain.

As it can be seen, countries very close to each other such as China and India do not have any co-authorship relationship. As mentioned before, in these two countries, there has been a large increase in publication production due to the rapid and very important development of the tanning sector in recent years, so their tradition

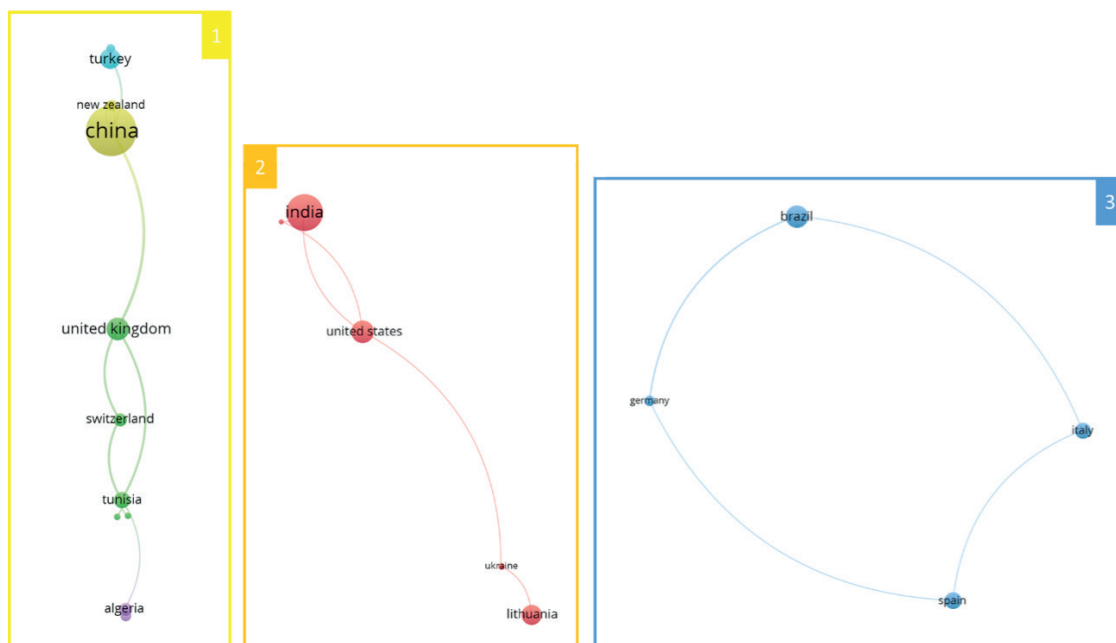


Figure 12. Co-author links between different countries.

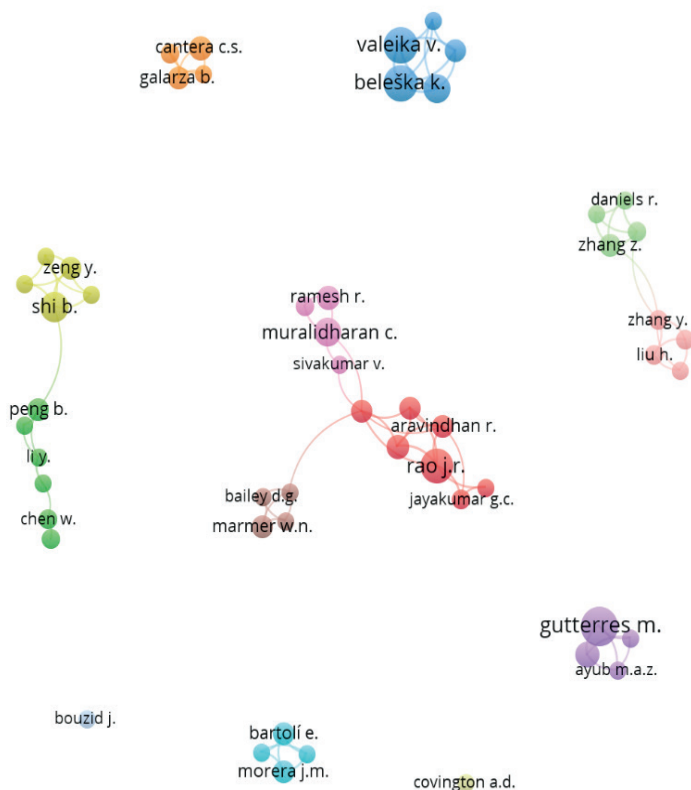


Figure 13. Author co-authorship network.

of research in this field is quite new. That is why they collaborate with other countries where there is a strong tradition of research for years but with very little production at an industrial level, such as the United States or United Kingdom.

The analysis of co-authorship by authors allows us to know the main links that exist between the most outstanding authors with publications on the subject in question. It broadly reflects social relations and interactions between members of different institutions.<sup>42</sup>

Figure 13 shows the relationship between the different authors who have published a minimum of 4 documents on the subject. As can be seen, there are a total of 13 clusters, most of them linked to each other. However, in the analysis some authors are not related to any other author. The red cluster is the one that brings together the largest number of authors, all of them from India, and currently belongs to the Central Leather Research Institute India. The only author linked to other authors from other clusters (the pink and brown clusters) is Thirumalachari H. Ramasami. At the left, the green cluster is linked to the yellow one. The only line that connects these two clusters is the one that links the authors Bi Shi and Biyu Peng. Both authors are from the same Chinese institution (Sichuan University). Similarly, at the right, in the cluster in salmon pink is linked to the light green one. Both clusters also bring together Chinese authors but, in this case, from different institutions.

### Co-citation analysis

The analysis of co-citations consists of knowing the frequency in which two items, whether documents, authors, or journals, are cited together in the list of references of another document. According to H. Small, this type of analysis is one of the best indicators to know the thematic similarity between two documents.<sup>43</sup> In this section, two types of co-citation analysis are presented: by author and by the journal.

For the construction of the co-citation network using VOSviewer software, from the total of 7459 authors cited, those who were cited at least 20 times were selected, obtaining a total of 74 authors cited. Bigger items are linked to a high number of citations made to a cited author,<sup>44</sup> such as Jonnalagadda R. Rao, Palanisamy Thanikaivelan, etc. Five clusters were formed by different researchers, classified by groups of countries. The first cluster is the largest of them all, consisting of 31 authors from different countries (United States, Spain, India, Argentina, Italy, and Great Britain). The second cluster brings together 15 authors mostly from China and Brazil, while the third cluster also contains 15 authors from India. Finally, the last two clusters group 7 and 6 authors, respectively. One cluster contains only Indian authors, while in the other cluster, all authors are from Lithuania except Bi Shi and Yunhang Zeng, who are from China. Countries such as China, Brazil, India, and Lithuania may work more individually since these authors did not appear with links to any cluster.

For the elaboration of the journal co-citation network, a total of 2327 journals were cited, of which 17 were cited at least 15 times. These journals are divided into 4 clusters of different colors, indicating the subject area which is assigned:

1. Technical leather industry journals.
2. Journals related to wastewater treatment.
3. Journals of sustainability and environmental technologies.
4. Journals of microbiology, biochemistry, and molecular biology.

According to the data provided by VOSviewer, the journals with the most co-citation links among other journals are the Journal of the American Leather Chemists Association and the Journal of the Society of Leather Technologists and Chemists, with 572 and 357 citations respectively, followed by the Journal of Cleaner Production, with 316 citations.

### Keyword co-occurrence analysis

The concept of co-occurrence in keywords analysis refers to the frequency of appearance and proximity between similar keywords.<sup>45</sup> Of the 291 publications extracted from the query, a total of 2024 keywords were obtained, of which 149 appeared at least 5 times. Before viewing the co-occurrence network, the elimination of some unnecessary keywords such as “article”, “nonhuman”, and

“controlled study” was considered. Special attention was also paid to replacing keywords written almost identically (e.g., animal for animals). Finally, a total of 144 words, distributed according to its thematic area, were found:

1. 40 keywords related to the study and treatment of water and environmental management.
2. 39 keywords referring to the main chemical compounds and other elements present in the tanning process.
3. 35 keywords linked to the biochemistry involved in the tanning process.
4. 30 more generic keywords such as metabolism, temperature, pH, animals, etc.

It could be noted that the word that stands out the most on the map, that is, with a more frequent appearance in publications, is “leather”, followed by “tanning” and “enzymes”, from different clusters but very close to each other.

Analyzing the keyword “leather”, multitude of links with other keywords were seen. The thicker the line that links two words (link strength), the greater the co-occurrence between them. The distance between words also plays a significant role, since the less distance between words, the stronger the relationship between them.<sup>51</sup> So, the word “leather” is strongly linked with the words “tanning”, “enzymes”, “sulfur compounds”, “collagen”, “effluent”, “leather industry”, etc.

Similarly, if the keyword “unhairing” was studied, a strong relationship with the following keywords was found: “leather”, “enzymes”, “tanning”, “sulfur compounds”, “leather processing”, “protease”, “scanning electron microscopy”, etc. Therefore, it is likely that those publications where the “unhairing” appears as one of the keywords of the study, more generic keywords could also appear, such as “leather”, “enzymes” and “tanning”, but also more specific ones, such as “sulfur compounds”, “leather processing”, “protease”, and “scanning electron microscopy”, as some publications could be studies on unhairing process either using enzymes such as protease, or applying the scanning electron microscopy, which allows obtaining information from the surface of a sample.<sup>52</sup>

VOSviewer also allows visualizing data in another type of network: overlay visualization. This type of visualization is almost identical to network visualization. The only difference is that the items are colored differently, as they are assigned a score of a certain color. In this case, this score is called “average publication year” (a.p.y), which is the average year of the published documents in which a keyword occurs. An overlay visualization of the different keywords contained in the publications allowed an evaluation of such indicator. Before 2005, the published documents focused mainly on liming, processes such as ultrafiltration and nanofiltration, as

well as the effects of pH and skin swelling. From 2006 to 2010, research on unhairing and liming began to increase, causing more variety of keywords to appear, such as “hydrogen peroxide” (a.p.y = 2006), “environmental impact” (a.p.y. = 2007), “proteins” (a.p.y. = 2008), “wastewater” (a.p.y. = 2009), “sodium compounds” (a.p.y. = 2010), and so on. From 2011 to 2016, wastewater treatment of the unhairing process and the use of enzymes were some of the most studied topics in the publications. Some of the most popular keywords were “wastewater treatment”, “enzymes” (which a.p.y. = 2011), “effluents”, “collagen” (which a.p.y. = 2012), “enzyme activity”, “leather processing” (which a.p.y. = 2013), “lime”, “pollution” (which a.p.y. = 2014), “leather manufacturing” and “glycoproteins” (which a.p.y. = 2015). Finally, after 2016, chlorine compounds, hydrated lime, together with sustainable development, are some of the new topics used in this period.

Table IV lists some of the keywords added in the publications according to their frequency of occurrence and average year of publication classified into different periods. The fact that a keyword has an associated average year of publication does not mean that it has been appeared only in that period. That is, if 2011 is the average year of publication of the documents for a given keyword, these documents may have been published around 2016 or later, or even before 2005, but in less quantity. Therefore, as seen above, this also means that topics of study such as enzymes and the environment continue to be studied in the publications over these years. For example, the keywords related to the topic of enzymes may be “enzymatic unhairing”, “enzymatic treatments”, “enzyme synthesis”, “proteolytic activities”, etc. Regarding the topic of environment, the main keywords related to it may be “environmental impact”, “environmental protection”, “environmental pollutions”, etc. All these keywords have appeared in many documents from 2006 to after 2016.

## Conclusions

The big environmental issue generated by the traditional unhairing and liming operations of the leather tanning process has become one of the most important topics for researchers investigating this sector of leather.

The application of Bibliometrics has been a successful methodology to analyze the evolution and current state of this line of research. First, the study has allowed us to observe a notable change between the objectives pursued in the study conducted until the end of the 20th century and in subsequent research. The aim of most articles published until the end of the 20th century falls within the field purely of engineering and production process (quality, productivity, etc.). For some years now, the priority aims of the research conducted have to do with the environment and sustainability. Indeed, in recent years, new alternative and less polluting methods are being investigated that can replace traditional unhairing or somehow reduce the environmental impact and improve the sustainability of the process.

**Table IV**  
Average year of publication of some keywords according to their frequency of occurrence in publications.

Periods	Keywords		
	More than 30 occurrences	10 – 30 occurrences	5 – 10 occurrences
Before 2005		tannery liming ultrafiltration pH effects	swelling quality control physical properties nanofiltration dyes
2006–2010	leather tanning unhairing wastewater chemical oxygen demand	environmental impact sodium compounds proteins hydrogen peroxide industrial waste bacteria etc.	alkaline protease hair removal waste water management peptide hydrolases environmental protection enzyme synthesis etc.
2011–2016	enzymes leather industry effluents sulfur compounds lime collagen sodium sulfide etc.	wastewater treatment pollution biochemical oxygen demand enzyme activity alkalinity biodegradation keratin water recycling biotechnology enzymatic unhairing etc.	metabolism waste disposal fermentation silicates glycoprotein tannery wastewater ammonia <i>Bacillus subtilis</i> hide unhairing enzymatic treatments etc.
After 2016		mammals fibers sustainable development	hydrated lime chlorine compounds proteolytic activities environmental pollutions protein degradation etc.

The study also highlights a rapid increase in scientific production in this field of research, with an increasing number of countries and institutions around the world involved in the sector. Despite the first document on skin unhairing, found in Scopus, was published in 1927, the trend of publications did not begin to increase until the late 1990s. From this decade, the number of articles published annually increased dramatically. The reason is the incorporation of Indian and Chinese authors, to the point that the institution with the highest number of publications on the subject is from India. Enzymatic unhairing has been one of the most studied alternatives, accounting for 46% of all documents published from the beginning of the century to 2021.

The number of journals published on the subject has also increased. In front of the two specific journals on tanning have been taking on relevant journals related to topics of sustainability and environment.

Regarding the co-authorship relationship, it is shown that the advantage of geographical proximity between countries is not the main factor that influences cooperative relationships. Rather, cooperation is established between countries where there is an important research tradition but with little production at the industrial level (e.g., United Kingdom or the USA), with countries with a big tanning industry, but with a very new research tradition in this field (e.g., China or India).

The results of the bibliometric analysis were conducted to give a reliable portrait of the “State of the art” of research, which is of significant help to the researcher when deciding what the lines of research should be in which to go deeper and which new lines of research are worth exploring. For example, in the case studied seems clear that it is necessary to deepen the search for an enzymatic product that allows eliminating the use of sodium sulfide and related products to increase the sustainability of the process.

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