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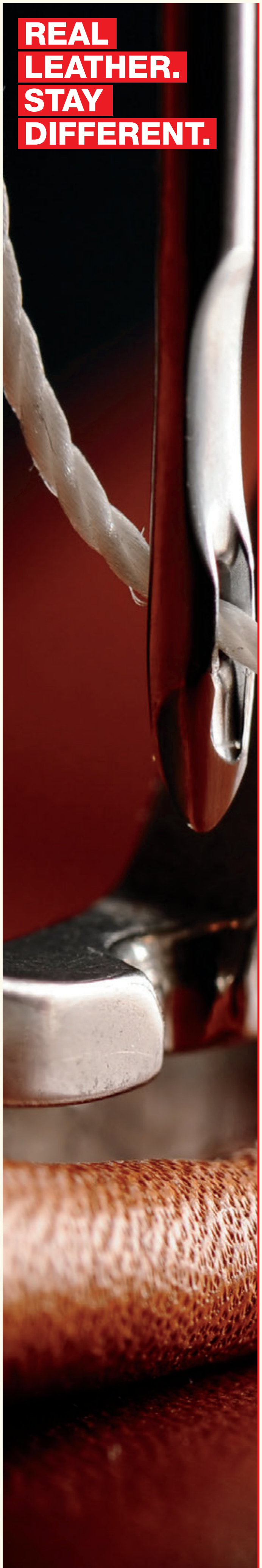

LEATHER BY NUMBERS:

FACTS AND FIGURES FROM THE US LEATHER INDUSTRY AND BEYOND

Note: All figures as of January 2021 or latest available.

ZERO cattle are killed to make US leather. US hides have been valued at JUST 1-2% of a cow's total value for the last two years, which is why they are considered a by-product and often end up as waste. The average price per head of US cattle is $2,000-2.200, while hides vary in price from $5 TO $35 PER PIECE, if sold at all. (1)

330M hides come from the meat and dairy industries around the world. Approximately 34M were processed the US. (2) AS MANY AS 2.4M US HIDES ended up as landfill in 2019, this is 7% of the national total.

Worldwide the waste figure is approximately 40% or 132M hides. With the average hide weighing 25Kg this means that 3M TONNES are thrown away ever year.

Leather production turns more than 4.5M TONNES OF potential waste, every year, into usable, durable goods. This saves 2.7M TONS OF GREENHOUSE GAS EMISSIONS from landfill sites. (3)

Production, processing and distribution of hides and leather products directly employs an estimated 5,486 individuals, who collectively earn more than $384M. US exports of hides and leather was over $1.5BILLION in 2021. (4)

The US exports approximately 95% of all cattle hide and wet blue leather products it produces, worth $2.85BILLION. (5)

Around 45% of global leather production is used to make footwear, 22% for clothing, bags and accessories, 18% for car upholstery, and about 15% for furniture. (6)

Water consumption for the production of leather from cattle hides has fallen by more than 35% in the past 25 years, down from 60 CUBIC-METERS per ton of hides to 38 CUBIC-METERS per ton. US tanneries are required, by law, to connect to effluent treatment plants to prevent pollution. (7)

Leather will biodegrade in LESS THAN 50 YEARS. In contrast, it can take 500 YEARS or more for synthetics, made from petrochemicals, to degrade. (8)

ReFed's conversion rate for food waste is for EACH METRIC TON OF WASTE DISPOSAL there is 9.8 7MT of CO_2 EQUIVALENT emitted. In this case, mostly as methane. (9)

This factsheet is produced by the Leather and Hide Council of America (L&HCA), established to promote the US leather industry which is responsible for a significant proportion of the international trade in hides. The L&HCA works to establish best practice in US leather production and to share this worldwide. Figures quoted refer to the USA unless otherwise stated.

SOURCE:

(1) https://downloads.usda.library.cornell.edu/usda-esmis/files/rx913p88g/w0893q25p/5d86qb66f/lstk0223.pdf

(2) https://downloads.usda.library.cornell.edu/usda-esmis/files/r207tp32d/pg15cj85z/hd76t466z/lsan0422.pdf

(3) 2020 LHCA Infographic

(4) John Dunham & Associates, Economic Impact of the Meat Industry (2016)

(5) https://thesustainabilityalliance.us/wp-content/uploads/2020/04/US-Hide-Skin-and-Leather-Factsheet-0420.pdf

(6) TBC

(7) 2020 LHCA factsheet

(8) https://en.wikipedia.org/wiki/Leather#:~:text=Leather%20biodegrades%20slowly%E2%80%94taking%2025,or%20more%20years%20to%20decompose

(9) https://insights-engine.refed.org/impact-calculator?inputs=%7B%22sector%22%3A%22manufacturing%22%2C%22type%22%3A%22fresh-meat-seafood%22%2C%22unit%22%3A%22tons%22%2C%22alternative%22%3Afalse%2C%22destinations%22%3A%5B%7B%22key%22%3A%22refuse-discards%22%2C%22current%22%3A1%7D%5D%7D

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117TH ANNUAL CONVENTION — JUNE 20–23, 2023

Opening Address

by **Joseph Hoefler**

Greetings, I would like to call to order the official opening of the American Leather Chemists Association's 117th Convention held at the Grand Geneva Resort and Spa in Lake Geneva, Wisconsin. This marks our second conference after missing a few years due to the pandemic and looks to be well attended and hopefully as successful as last year's conference. As one might envision, it takes a lot of effort to pull off a convention as there are so many moving parts. Carol and Sarah and of course John and Steve and to a lesser extent myself worked hard to prepare for this moment and of course the next couple of days. As important I would also like to thank the many sponsors for supporting the conference that are on display next to the podium. There were two last minute sponsors that I will recognize now as they missed the poster, Eagle Ottawa by Lear and Twin City Hide.

We can look forward to a well esteemed speaker for the John Arthur Wilson Lecture, Mike Redwood, fifteen technical papers, lots of discussion related, lots of time getting reacquainted with old friends and meeting new ones. A great deal of this started yesterday on the golf course which is where so much business and fun takes place these days. Maybe I have this backwards, fun first. At least this is what all of the golfers I spoke with yesterday said to me when I asked how they did. The universal response was We Had Fun!

So, what is new with ALCA, well we have a new Executive Secretary Kristina Hall. Sad to say that Carol will be retiring shortly after so many years of dedicated service. We will partake in a cruise tonight to send Carol off on a high note as she sails away into retirement. In the meantime, please extend a hello to Kristina who will likely be very close to Carol throughout the convention, learning the ins and outs of what this conference and association is all about. Another new item is the attendance of many additional members of the Leather and Hides Council of America (LHCA). President Steve Sothmann and Vice President Kevin Latner along with approximately another dozen or so members are in attendance. First considered at last year's ALCA conference it seemed to make sense to extend an invite to the LHCA as we share so many interests, convictions, members as well as our new Executive Secretary.

A common theme at conferences focusing on Leather is sustainability which is very much the flavor of this year's conference and for good reason. The leather industry continues to be threatened as it is often unfavorably portrayed even though it truly begins as a byproduct of the meat industry. A majority of the papers directly or indirectly have sustainability in their titles. Other papers include a focus on specific concerns like alternatives to chemistries once thought to be safe and next generation chemistries developed to improve leather's performance. Lastly there are also a group of papers that examine the way leather is manufacture attempting to account for an improved overall process through traceability. I can't say that I was ever at a leather conference that did not have papers devoted to this important topic. Taken together all the papers can be considered to have the betterment of the leather industry as a focal point.

Are we preaching to the choir? I offer that good science makes for a strong defense and being informed about the critical nuances is something that needs to be continually reinforced since it can be very complicated and is always evolving. Positive, informed messaging is the minimum everyone dedicated to this industry should be able to do at every turn. Participating in conferences, whether speaking or listening is a great way to stay informed and the ensuing dialog is invaluable. As we did last year, let's have an open and lively dialog. Let's listen and ask questions. Thanks.

Introduction to the 62nd John Arthur Wilson Lecture

by **Eric Webb**

Good morning Ladies and Gentleman. My name is Eric Webb, and it is my honor to introduce this year's John Arthur Wilson Lecture. This is the 62nd John Artur Wilson lecture. Looking back at the former recipients of this award you will see strong leaders of our industry in various ways and this year's recipient is another strong leader.

The John Arthur Wilson lecture was initiated in 1959 in memory of the late John Arthur Wilson, who was regarded as a world leader in the leather chemical industry as well as an esteemed member of our association.

I am here as a representative of Stahl, who are proud sponsors of the John Arthur Wilson lecture since 2004. I know our association thanks Stahl for their ongoing support and commitment as the main sponsor for this lecture.

For the last decade our recipient has mixed part-time teaching at the University of Bath School of Management with an involvement in the leather industry which has involved undertaking commercial work with supporting Leather Naturally and being a Trustee of the U.K. Leather Conservation Centre.

Having studied Leather Science at Leeds University, he worked as a technician and general manager in tanneries around the world, including Italy and Latin America before being unexpectedly asked to focus on sales and marketing by a fast-expanding Pittards. Since then, he has concentrated on marketing, innovation and lately corporate responsibility. Mr. Redwood's Ph.D. from Bath University was in marketing and related to the evolution of business networks over long periods of time, with which he mixes an interest in the history of technology.

Ladies and gentlemen, please welcome this year's winner of the John Arthur Wilson lecture recipient Mike Redwood.

Eric Webb presenting Dr. Redwood with the John Arthur WilsonAward

The 62nd John Arthur Wilson Memorial Lecture

Retelling "Viewing Leather Through the Eyes of Science" A Century On

Mike Redwood

Introduction

In the U.K. they say if you remember the sixties you weren't there. But I do and I was. Nearly sixty years ago, still a teenager, I caught a train south from Scotland to the city of Leeds, made my way up the hill to search out the old red brick Leather Industry Building in the University of Leeds. I was directed to the small departmental library with its glass fronted bookcases lining the walls and dominated by a single large table where I was interviewed about joining their undergraduate course in Leather Science.

I was unaware that fifty years before me, a 23-year-old Chicago born graduate of New York University, recently engaged as a chemist in a Milwaukee Tannery also arrived in Leeds by train and made his way to the same red brick Leather Industry Building to be met by staff in that very library. This was 1913 and John Arthur Wilson was there to learn from and work with Professor Henry Procter.

In thanking the Chair and members of the selection committee for the honour conferred upon me by inviting me to give this 62nd John Arthur Wilson Lecture I have discovered that Wilson was a most illustrious alumnus from my own University. I worked in laboratories and sat in lecture theatres and offices unchanged from the ones he used, probably frequented many of the same pubs and travelled in and out of town on the same number one bus route.

The prolific research and writing that Wilson did in those years at Leeds and after his return to Milwaukee culminated in two notable publications. *The Chemistry of Leather Manufacture* was published exactly 100 years ago this year and then in 1924 the Shoe Trades Publishing Co. produced "Viewing Leather Through the Eyes of Science", mostly based on essays he had written for "American Shoemaking" and "The Leather Manufacturer" and it is this which forms the basis for this lecture. Looking at the current landscape what would Wilson be working on if a 2nd edition were being prepared for publication in 2024?

"Viewing Leather through the Eyes of Science"[1] was about communicating the science to a wider audience, nearly all of it established in only the previous 40 years, a lot of that in Leeds. Wilson was convinced that knowledge should not be held by the elite but shared in normal language with others outside the industry. This meant primarily those who used leather in their products, but also those curious about the science involved in the articles of everyday life.

At the start of the 20th century the UK leather industry was slipping behind both the USA and Germany in size but it was still leading in terms of research, with Leeds at the centre.

In Leeds Wilson met Joseph Turney Woods whose work in his tannery laboratory in Nottingham had led to replacing dog dung in bating. Woods was a member of the leather industry advisory board for the University and an external examiner. Edmund Stiasny had moved to Leeds from the Vienna Imperial Research Institute in 1909 in preparation for taking over the department when Procter retired in 1913. In January 1913 Professor Stiasny launched Nerodol, with a lecture in London. It was the first ever synthetic tan based on Stiasny's patent and produced by BASF[2]. Procter had redirected his retirement gifts to fund a research laboratory where he stayed on as an Emeritus Professor[3]. According to Ward, the last leather Professor at Leeds, this was the most prolific research period in the near hundred years of leather at Leeds University[4].

The following year Wilson was reminded of the strategic importance of leather when the Great War erupted. Stiasny did not make it back from a trip to Austria and Procter was asked to return to head the department. The CEO of the Booth Group, George Booth, agreed to become the Director General of the newly formed Ministry of Munitions at the request of Lloyd George who thought The Booth Group had the logistics skills missing in the Ministry of Defence. They owned a shipping line and had decades of experience moving semi processed and finished leather back and forth across the Atlantic. His father Charles Booth returned from a private meeting with Theodore Roosevelt on Long Island to take back control of the Booth leather business. Roosevelt had asked him to come to discuss trade unions.

From Stiasny's arrival through to the end of the War Procter was able to bring to fruition researches he had begun in the 1890s on the swelling of skin and gelatine"[5] aided by R. A. Seymour-Jones, Atkin, Burton and of course Wilson. Each one a well-remembered leather scientist. Wilson was in Leeds during momentous times for both the world and the leather industry.

Shortly after the end of the war other external matters beset the leather industry, with major destocking in the USA starting almost at once. According to Watson[6] demand for cattle hide leather declined considerably from 1920 because of:

- technological change
- the appearance of substitutes
- new modes of living
- economic weakness, finally ending in the Great Depression

Watson says: "*as far as is known, this was the most important shrinkage in demand ever experienced in the indu*stry". You might think you are reading about today with so many similarities. Wilson understood technological change, new materials, geopolitics and societal evolution as the constants we work with.

In the opening lines of "Viewing Leather Through the Eyes of Science" Wilson says: "That leather is the most suitable material known from which to make shoes is so obvious from everyday experience that any argument brought forward would seem to be an unnecessary waste of words." Amazingly this was an industry tale you could still hear until recently.

Wilson's responded by pointing out "it is not so widely understood just why leather is the ideal shoemaking material. Knowledge of the wonderful structure and delicate mechanisms of the skins are too often left to specialists" and he wanted to make this information fully available.

He was of course right that leather was the best material for shoes at that time. For footwear and many other sectors leather was essential, even strategically so, as he had harshly been made aware of during the war. Today there are no such areas where leather cannot be replaced by alternative materials. The competitive environment today necessitates full and continued communication.

This business and technical landscape that we have today, so similar in many ways with that Wilson was dealing with, means we have many major areas of concern. I will use three linked and overlapping leather science topics that I am sure John Arthur Wilson would be wanting raised at this 117th Annual Convention to try and do them justice. These are research, biomaterials and chromium.

Research

Wilson often told his audiences the chemistry of leather had not yet overtaken the art in large aspects of leather making production. He was determined to enlarge the area of fully understood science as he saw the requirement to move leather towards an engineered product, which customers of every sort could always rely on to meet specifications. To achieve this and to advance leather science Wilson was strongly invested in the vital role of research.

His dedication to research hit me strongly when I returned to Leeds earlier this year. The University Archivist carried out a large open notebook on an even larger soft grey cushion. She put in front of me Wilson's laboratory notebook, written entirely in his own hand, where 381 pages detailed his research work in 1915 and into 1916.

Leather Science might no longer be taught at Leeds, the old leather buildings might have been demolished but I did feel as though I was in the room with John Arthur Wilson. He was sitting opposite in his double-breasted suit and colourful tie explaining the effect of acids on chrome tanned leather he had cut neatly into 8 square inch pieces.

As well as looking at chrome tanned leather he continued the work on the effects of acids on the swelling of protein to build a picture of the main features of the changes in volume of hides and skins through the wet stages of the leather production.

His Laboratory Notebook includes notes of a lecture he read to the Nottingham section of the Society of the Chemical Industry. He described theoretical problems he had found while seeing if he could strip the chromium out and then quickly moved to a long list of what he termed "Possible Practical Uses". These included extracting chromium from shavings for glue stock and stripping chromium from splits to make tanning with quebracho easier.

Chairing that meeting in December 1915 was Joseph Turney Wood, who had just learned of the death of his only son. The machine gun post he was commanding had been overrun and no one survived. War was never far away in those years.

As Ward[7] explains Wilson and Procter jointly produced the full formulation of what became known as the Procter-Wilson theory. Wilson did most of the practical work for two papers they subsequently published in 1916[8,9] setting out the theory and its experimental confirmation. Further work was done in conjunction with Loeb[10] on the swelling of gelatine in acid. Some years later we have the Donnan Equilibrium which probably better explains the overall picture. This is based on the swelling being mostly due to the unequal distribution of the ions of the acid inside and outside the gelatine.

According to Ward this work "formed a fitting intellectually satisfying and practically valuable achievement to crown Procter's scientific career". Having played such a central role Wilson will have returned to the Chief Chemist post at A.F. Gallun in Milwaukee proud of what had been achieved and energised by the importance of research.

Research is integrated throughout his book. Knowledge of the structure of skin is vital to anyone who makes or uses leather, he says, so the Gallun tannery had "equipped a laboratory devoted to studies of the composition and structure of animal skin". The entire

5th floor of the large main building at A.F. Gallun and Sons were occupied by this and other laboratories.

These covered all materials entering the tannery, checks on hides and liquors during process, bacteriological work and the study of microorganisms, with another holding the most advanced testing and control equipment. The final laboratory was a small-scale tannery, not for samples but for testing new processes

Wilson thought laboratories had to cover:

- eliminating problems from variations of incoming materials
- preventing deterioration in the established operations
- advancing the science of leather manufacture

During Wilson's time advancing leather science and work on the structure of skin slipped away from the tannery. Most fundamental work transferred into national research laboratories or moved to the leather chemicals industry. Turney Wood successfully collaborated with German chemical companies to obtain commercially viable bates and Stiasny pushed the concept of academic/industry collaboration further when he took his "super patent" to BASF and persuaded them only a well-resourced company could successfully exploit the many products that could be evolved from it.

In the second half of the 20th century the research organisations lost their local industrial base and most sources of government finance. With only a few exceptions they switched into testing and consulting houses. Universities have also suffered. Chemical companies have been reorganising and consolidating to meet new competitive challenges including the costs of servicing a more dispersed customer base and have had to divert major resources to comply with new regulations such as REACH. All this has made doing fundamental research more difficult.

Research is complex. I was reminded recently that we still wash our clothes in a drum. Fair enough, but is it not wise to question why we continue to depend on aqueous solutions with rapid uptake in the first hour, then hang around endlessly for the last few per cent to get taken up, and still end with dirty water? And should we still be using difficult chemicals like sulphide?

The machinery side has given us many advances in recent times. There are several far thinking companies investing considerable sums searching for not just the known unknowns but the unknown unknowns. And Kanigel[11] explains that one of the reasons nonwovens improved in the 1990s was that collaboration with Italian tanners found that dyeing and fatliquoring in drums gives a much better touch and feel. I am not necessarily opposed to drums.

I do not intend to demean the new materials that have come to market in the last few years; nor the current work ongoing to deal with some of those in current use that are problematic. But I think it is a valid question why we continue to use far from perfect processes for so long and have not jumped far ahead with our product and process thinking. Rather too many items in the agenda of this 117th Meeting feel as though they should have been dealt with a long time ago.

And the work that Procter and Wilson were doing on raw material still feels incomplete even one hundred years and 62 JAW Lectures on.

I have been a Trustee of the UK Leather Conservation Centre since 2005 and a marvellous quote by the Scottish writer and poet Kathleen Jamie came up when we did a recent residential course for international conservators and curators. It fits alongside new thinking that is going on to understanding how humans and their predecessors have made use of hides and skins for most of the last two million years.

Jamie had been looking at ancient cave paintings of horses, cattle and other animals deep underground in Spain:

> "There was a time – until very recently in the scheme of things – when there no wild animals, because every animal was wild; and humans were few. Animals and animal presence over us and around us. Over every horizon, animals. Their skins clothing our skins, their fats in our lamps, their bladders to carry water, meat when we could get it." Kathleen Jamie, *Sightlines*[12]

Because of global warming artefacts that have been buried without air for thousands of years are now being unearthed. Work done by the Leather Conservation Centre and others has made it possible for these to be properly conserved and available for study.

We see that hides and skins were effectively used by humans in every state from raw onwards. They might be totally raw, as parchment, sometimes treated with "leathering" oils which protect but do not tan, and then brain and smoke treated. All appear to have played a more significant role in our history than the fully tanned items that crowd our museums.

Even with no or minimal treatment they functioned perfectly well in the prevailing conditions.

When Rawasami gave his JAW lecture in 2001[13] searching for Wilson's dream of a unified definition of tanning he looked at measures such as shrinkage temperature and structural stabilization amongst other more complex ideas. Later Eleanor Brown[14] suggested that tanning might be better viewed in terms of protein modification than as simple crosslinking, hence the more general term of stabilisation of the collagen structure I have taken from recent correspondence with the Director at the New Zealand Leather and Shoe Research Association.

Rawasami put it simply that in the "new material world, leather needs to perform. While mankind has striven to design and make materials with similar molecular assemblies and network structures, Nature has provided the leather chemist with an architectural marvel in the form of skin."

Central to Wilson's work and consequently to many JAW lectures is this collagen structure – and increasingly we look at its architecture as much as its chemistry. Tanners do not make leather through assembly or synthesis. They do it through conditioning, that is making changes, to the material to make it fit for purpose. With hides and skins that is usually best achieved by doing as little as possible, and history is now showing us that nothing more than cleaning and drying often worked. Perhaps this interface between what is raw and what is tanned is less important than we imagine and is even restricting our ability to seek out creative solutions for maximising this marvelous material.

The measure is more will the leather be fit for purpose than can it stand the boil.

What's more do we consider that our approach to some grades push us too far towards a commodity? Might it be better while looking for new ways to stabilise collagen as leather and to use some hides and skins for other purposes altogether?

Back in the 1980s the late Bob Higham and I started an abortive attempt to look at whether the bottom 10 per cent of hides and skins could be taken out of leather making and used in other ways. This would expand the arrangements some tanners have to send limed splits to the casings market. The project did not go far; those already using hides and skins for products like casings wanted to avoid scar tissue. But times have changed, technology has advanced, more tanners are working with protein for various uses and climate change has rewired the economics.

Currently we have unwanted hides and skins being thrown away around the world at a level no one expected or likes. A way needs to be found to get them back into the chain, but should every hide and every skin end up as leather?

Over and beyond looking at collagen in modern times every researcher must consider the impact of leather manufacture on the planet's resources. Not only hides and skins but water and many other items tanners make use of are in limited supply.

In recent years tanners have reduced the footprint of leather in terms of water, energy, chemicals and all types of waste as a result of a remarkable effort. Wilson wanted well managed effluent and hated waste, even in the 1920s. He was the director of research for the Milwaukee Sewerage Commission as well as Chief Chemist at Gallun when he gave the Chandler Lecture for 1928. His citation[15] talked of his work to improve Milwaukee's sewage plant and to make it "operable in such a way that it may soon be returning revenues to the city".

The work and the associated investment by most tanneries in all environmental areas has been large and consistent. As an industry we can now honestly say that we go beyond complying with legislative demands and are searching out levels of best practice that allow us to face the world of materials with some pride. We have tanneries and organisations that have completed their own Life Cycle Analysis and as well as using them with key accounts have made them public. This has been in stark contrast to the Higg Index, now rebranded Worldly, whose opaqueness led to its own downfall, after many years of doing great harm to natural materials and especially leather.

This hard work never reaches an end point, and we need to keep advancing to stay ahead of competitive materials and be confident we are doing our best. We need our research bodies involved.

It would be incredible to see our few remaining research hubs across the globe obtaining the funding needed to increase their work in all these areas, most of all in fundamental longer-term research. Perhaps also working with some of the new generation of talented leather scientists now working as consultants. If we could get collaborative initiatives funded this could elevate leather to the next level. Eliminating some of the difficult chemicals, making better use of the collagen that enters the tannery, finding new ways to stabilise the collagen structure for leather, and imbuing leather with advanced properties that would make it a genuine competitor with other materials. A material willing to challenge conventions at every step; adapting to changing times as it has all through its long history.

Biomaterials

The argument that more fundamental research is required in the leather industry to stay ahead of competitive offerings flows into discussion of biomaterials where large amounts of finance have been steadily put into research for many years.

Despite this leather has proven difficult to match and we have seen a decade of failure. Currently only Piñatex, a cellulosic non-woven derived from the discarded leaves of pineapples appears to have reached bulk and it has a very distinct aesthetic that is not to the taste of all consumers. A mycelium production can be expected in 2024 and there will be another presentation during this convention. The work is very committed and relentless so it is obvious that before long the gap will be jumped and my argument would be to switch biomaterial producers from enemies into potential partners.

Allied to this the structure of the livestock industry has meant that meeting the demands of a growing population for meat and dairy products does not of necessity lead to an increase in long-term per capita availability of leather. Fewer but larger animals, greater efficiency in raising milk yields and greater consumption of white meat like poultry all mean that the growth of hide supply and thus leather production has been very low for decades.

The simple fact that no one keeps livestock for leather has been obvious throughout the last 100 years and was the major driver for another sixties event – the 1963 announcement by Du Pont that their new material called Corfam that was going to replace leather[16]. We should remember what this caused in the leather industry at the time.

There had been a host of materials such as vinyl, leatherette and leathercloth offering low-cost coverings for books and boxes made to look superficially like leather, but this was the first carefully constructed poromeric (short for porous polymer), supposedly breathable material designed with performance characteristics hoping to match leather.

Corfam failed with amazing speed. No one who bought a first pair ever bought a second. They were too uncomfortable. Corfam was expensive to produce and shiny so put into the more formal footwear category. These were the shoes of the office and the commute where foot comfort mattered.

Apart from creating a textbook marketing disaster Corfam showed how difficult it is to copy leather and how necessary it is to understand how consumers perceive complex subjects such as comfort.

The synthetics industry then searched for other routes into the materials covering markets by offering good properties at low prices, in a process well described by Christensen in the Innovators Dilemma[17]. The introduction of sneakers helped a great deal, while also supporting the split market. Improving generations of synthetic materials could be combined with leather and textiles to make attractive, comfortable footwear. Little mention was made that sneakers were never repaired. The synthetics then began to relentlessly grow market share in all areas.

This century synthetics have gained ground every time raw materials rose in price but not retreated when prices fell as they have before. Their growth in share in footwear alarmed the leather industry who particularly objected to some of their advertising, complaints that have shifted to several biomaterials. Several recent JAW Lectures have discussed this point in detail, particularly well covered by Gustavo Gonzalez-Quijano in the 60th Lecture[18].

The good qualities that made plastic ubiquitous in 20th century life have now been tarnished by critical failings that impact climate change and rapid loss of biodiversity. We should remind ourselves of them:

- They are based on fossil fuels.
- Their useful life is very short and they cannot be repaired
- They shed or degrade into microparticles in ways not previously understood, particularly in salt water.
- In landfill the plastic element will take between 500 and a million years to biodegrade
- They are very hard to satisfactorily recycle.

It is not leather that needs replacing but all these plastic materials. Since there can never be enough leather to fill the gap then biomaterials are the best bet to move into the immense space held currently by Petro-fibres of all types.

So to me it has for some years made sense to support the development of biomaterials and urge that the leather industry should increase the collaboration that has already begun. If we engage with them and share expertise I am confident we have the combined skills to create the best portfolio of materials originating essentially from nature.

Biomaterials would have our knowledge of non-woven fibre structures, on how to refine products for different end uses and access to markets where it is already clear there is interest with the brands. But they would bring expertise and skills of their own.

I should declare an interest here as I have given advice to companies in the sector based on my belief that we need good materials to fight the plastics and to give vegans a better plastic free offering.

Before we go further let me also address a related matter which all partners will have to agree. When people sell something which they say is essentially biobased they need to be honest and transparent about it. The discovery by shoemakers, confirmed later by laboratory test[19] that many materials have close to 50% polyurethane demonstrates a level of deceitfulness. It is nothing to do with marketing. Similarly saying that cows are saved from slaughter by replacing leather is not marketing either, it is a lie. These are areas, along with that of the accurate description of leather, where we must support our national associations to improve the laws and put more effort into enforcing existing laws. And we must police our own industry and ensure our partners adhere to promoting science-based truths.

We should remember that while bioplastics are a major improvement on fossil fuel plastics they are still plastic, so the longevity in use and end of life issues still exist. This can be a problem for leather as well as biomaterials according to a recent study by Carcione et al. Some heavily coated leathers are not much better than many biomaterials[20]. Perhaps tanners should revisit linseed oil and the other natural treatments that were used in patent leather production before the age of plastics.

I also believe that amongst the best biomaterial producers there is full commitment, along with the necessary research funding, to complete the journey to a fully-fledged material suited to work alongside leather.

A collaboration with biomaterials that supported all these objectives would mean that centuries of building product knowledge, process knowledge, market knowledge and our historic understanding of the Circular Economy can be usefully applied in an overlapping area. And I do not believe this will damage leather.

I believe such a move could unlock access to research capital and creative thinking that is so badly needed and even more offer the leather industry future growth potential far beyond the one or two per cent we have had to battle with for so long.

To push plastics out and make a significant difference to the disposable consumer attitude to products would be our target.

Chromium

Today all leathers and biomaterials that the leather industry has a hand in, must consider Circularity.

The main concept behind the Circular Economy, twenty years before Braungart and McDonough's 2002 book Cradle to Cradle[21], came from Walter Stahel's Mitchell Prize winning paper in 1982[22]. He argues that we need to keep goods longer and repair them. His Product Life Extension concept, now sometimes called the Value Retention Process, says we should make articles that last for longer and consumers will want to keep. Using resources for the longest time possible and then repairing and refurbishing them would reduce emissions and the new materials consumed. "A new relationship with our goods and materials would save resources and energy and create local jobs"

Stahel has lately been working with the Ellen MacArthur Foundation and has updated his thinking in several books plus a 2016 article in Nature[23] which emphasises that taking used goods back for recycling is costly in resources and should be delayed as long as possible.

Stahel's paper could have been written with leather in mind. Not all items worked on at the Leather Conservation Centre suddenly appear when glaciers shrink and permafrost melts. Most are centuries old items that have been well used and kept. Many carry initials showing they have passed through generations. Wall coverings last for centuries and the UK has four original copies of the Magna Carta. Often items were repurposed if they ever did reach end of life.

To maintain and improve this longevity and circularity philosophy a barrier for the leather industry exists with the continued use of chrome. I want to commend those who have put so much effort into producing viable alternatives for replacing chrome. But let me expand on why we must do more and move faster to eliminate chromium from leathermaking.

Amongst the press articles I keep is one from the Financial Times in 1994 entitled Green Leather in Fashion.[24] It is an environmental piece promoting the concept of wet white and intended to start the transition away from chromium.

Thirty years on chromium still predominates. It has been the subject of major research projects to bolster its defence and for much of that time I joined that defence, but now I think change is imperative.

Chromium is undoubtedly an excellent tanning material when managed properly in the tannery. That fact has not been enough to reverse the irretrievable damage created by the 1990s briefing against it. The target was to persuade the automobile industry to switch but it simultaneously created a consumer fear over chromium in leather which got linked to popular movies and legal cases about chromium VI. This has dogged the reputation of leather since, and all the statements, academic papers and research produced have failed to move the dial. Our industry does not have funding to defend chromium as well as to fight for leather. And it should not be trying to do so.

Beyond the well managed tannery the baseline arguments for chromium have changed. Few if any of the analyses of the different tanning methods, or current LCAs consider leather after it leaves the tannery, yet for the circularity to be complete it is one of the key areas. It is an area where leather offers magnificent benefits to society but it highlights the difficulty with chromium.

Some of the sizeable problems with chromium tanned leather can be demonstrated in shoemaking. Footwear companies find it hard to manage shavings and trimmings that contain chromium when trying to move towards circularity. There are also problems when the consumer is finished with the shoes. Incredibly large numbers of pairs are disposed of annually. Collection is hard and very few schemes have so far been successful.

So nearly all shoes are discarded, ending up incinerated, in landfills, or shipped to developing countries in Africa with unmanaged landfill that is always alight. The footwear industry has a big task ahead to become circular given most shoes are multi component. But if the tanning industry can offer a good chrome free biodegradable leather it would make life a lot easier, and replacing difficult plastic linings and footbeds with suitable leathers their circularity task gets easier and the consumer's foot more comfortable.

In addition, the California Proposition 65 and other new regulations to reduce the maximum chrome VI permitted in consumer goods add an extra layer of difficulty, exacerbated by costly penalties and contested test methods. Pyrolysis can deal with chrome leathers and pieces but there are very few plants in the world. Using chromium will continue to be fraught with difficulty. It is time to move on.

We do have better alternatives now in the market after concerted efforts in the past few years, although some older ones use worrisome chemicals. But until recently apart from some hydrothermal stability gains in the automobile sector new leathers without chromium have been mostly uninspiring and not been in easy to manage in areas formerly working with wet blue.

Footwear producers have largely stayed with chromium while many leather goods manufacturers have returned to vegetable leathers. We now need to see more support for a wholesale move away from chromium.

It took decades for the right processing parameters to be set for chromium along with the correct choice of fatliquors and retanning agents. When Wilson was worried about the performance of chromium uppers he had almost no options for retanning or fatliquoring. With a multitude of products today some committed collaboration with chemical companies should be able to fast track products with even better good aesthetics and performance. A much stronger uptake should also dispel the overblown fears about cost as volume benefits come through and development costs get paid off.

And I think the wet blue industry is big and strong enough to make and even to lead that change if they push harder with chemical industry suppliers and their own technical teams to get the technology perfected.

Conclusion

As the last century ended our trade organisations appeared in disarray. The International Council of Tanners of the 1990s was a far cry from the well represented body that filled the hall in Buenos Aires in 1978 for a big agenda. That was my first ICT meeting with the industry still talking about what if Corfam had succeeded.

In the last decade all our institutions appear to have transformed. Image, thinking, narratives are totally refreshed. Great moves are being taken to promote leather solely based on proven facts and science. We have even re-remembered longevity as a feature and a benefit – one of those givens that Wilson thought we had talk about more. But too many countries are still missing from the ICT and we need them involved and participating. There is so much to be done. We cannot drive our industry forward if we do not join and support or national, regional and voluntary bodies and get them collaborating. And making better leather through great research and manufacturing requires the full support of strong institutions.

At his Chandler lecture Wilson was commended for his "researches in physical chemistry, colloid chemistry, and the chemistry of proteins; his application with great daring and acumen of wide and exact knowledge of the most modern advances in chemistry to the complex problems of leather chemistry have resulted in valuable improvements in processes."

Wilson crossed the Atlantic, he corresponded globally and worked with intense application to take leather into a new more scientific era. He was able to handle multiple challenges at once. He helped the industry make huge progress and his thought processes continue to help us now. I am proud to have got to know him these last few months.

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117th ALCA Annual Convention
June 20-23, 2023
Grand Geneva Resort & Spa
Lake Geneva, Wisconsin, USA

Technical Program starting Wednesday, June 21

John Arthur Wilson Memorial Lecture
Retelling "Viewing Leather Through the Eyes of Science" A Century On
by Mike Redwood, Leather Naturally, Somerset, UK

A big thank you is extended to The Leather & Hide Council of America (LHCA) for holding their Spring Board of Directors Policy Meeting at our location and as key contributor for the presentations on Thursday

Other Papers to be Presented on Wednesday and Thursday:

From Waste to Resource. Available Technologies for a Sustainable Leather Process by Daniele Bacchi and Sergio Dani, Italprogetti S.p.A., San Romano, Italy

Enzymatic Applications for Sustainable Leather Processing by Olga Ballús, Cromogenia S.A., Barcelona, SPAIN

Bisphenols — Threat for the Leather Industry? — Strategy to Overcome This Problem by Harald Bauer, Stahl Chemicals German GmbH, GERMANY

Sustainable Hide Sourcing and Traceability by Danielle Dotzenrod, BEHUMANE Leather, Decorah, Iowa

Managing Potential PFAS Liability in the Leather Industry by Kelley Drye, Kelley Drye & Warren LLP, Washington, D.C.

Making Sustainability Measurable: Biobased Content, Biodegradability and EPD of Retanning Chemicals by Jordi Escabros, Trumpler Espanola, Barcelona, SPAIN

Environmental Update by Joe Green, Kelley Drye & Warren LLP, Washington, D.C.

Next Generation Dulling Technology Application: A New Way to Matte Leather by Myron Hooks, The Dow Chemical Company, Collegeville, PA

Showcasing Sustainability, Investing in Our Future by Kevin Latner, Leather and Hide Council of America (LHCA), Washington, D.C.

Key Modifications to Silicone Polymers That Have Enabled Their Utility in Leather by Pete LeBaron, CHT USA, Cassopolis, MI

The Leather Industry as a Driver for Change within the Context of Global Warming by Guilherme Motta, JBS Couros, BRAZIL

Identification of Bacterial and Fungal Damage in Leather by Joseph Ondari Nyakundi, Leather Research Laboratory, University of Cincinnati, Cincinnati, OH

Traceability, How to Mark and Read Hides during the Process by Marc Oomens, im innovating, The Netherlands

Market, LCA, and User Data in an Emotionally Driven Decision about Leather — Our Responsibilities by Roger Pinto, Pangea Made, Inc., Rochester Hills, MI

Update on Leading Issues Impacting the Leather Industry by Stephen Sothmann, Leather and Hide Council of America (LHCA), Washington, D.C.

With TFL Through the Legislation Maze to Renewable Leather by Christopher S. Tysoe, TFL, Germany

Overview and Performance of a New Substrate for the Tanning Industry by David Williamson, Modern Meadow, Inc., Nutley, NJ

Council Meeting Minutes

AMERICAN LEATHER CHEMISTS ASSOCIATION
Grand Geneva Resort & Spa, Lake Geneva, WI
June 20, 2023

Officers:	Joseph Hoefler, John Rodden
Councilors:	Shawn Brown, Myron Hooks, Steve Lange, Lee Lehman, and Roger A. Pinto
Executive Secretary:	Carol Adcock; Kristina Hall
Convention Chair:	Sarah Drayna

1. **WELCOME** – Joseph Hoefler, President

   President Joseph Hoefler called the meeting to order and welcomed everyone. He introduced Kristina Hall to Council as the new Executive Secretary that was hired by Council to take the place of Mrs. Adcock upon her retirement. As is customary per the Association's by-laws, Ms. Hall has full authority to open new bank accounts in Cincinnati, Ohio for the Association. She will need to open an operating account as well as a wire account.

   Results from electionbuddy.com were announced. New councilors will be Goetz Hagen and Todd Salzman. Mrs. Adcock announced that 81 votes were cast out of the 213 ballots sent out which is 38%. This was a little higher than 2022.

2. **OLD BUSINESS** – Joseph Hoefer, President

   LİFE MEMBER

   There were no candidates for life membership in the Association. The criteria for life status in the Association is that the member has been a paying member or paying and then retired member of the Association for forty (40) years. Prior to the convention Council did approve Scott Beloli for life membership in the Association noting he had attended more conventions than anyone else during the tenure of Mrs. Adcock.

3. **CONVENTION ITEMS AND REVIEW OF CONVENTION** – Sarah Drayna

   Mrs. Drayna reviewed the schedule for the convention noting several room changes. She felt having the LHCA join the convention was very successful, bringing more people and sponsorships to the convention. She recommended asking the LHCA to join the ALCA convention next year.

   Members of the hotel staff joined the meeting to introduce themselves. Mrs. Drayna pointed out that the hotel's AV person was very helpful in lowering the original bid for audio visual equipment.

4. **REPLACEMENT OF EXECUTIVE SECRETARY** – Steve Lange

   Mr. Lange reported that Kristina Hall has been hired to become the Association's Executive Secretary beginning May 8. Ms. Hall had created a card to hand out at trade shows to get new members in the ALCA. It contains a Q code which directs people to the Association's website for more information. She handed out the cards to Council.

   Mr. Lange has bought Ms. Hall a new computer and software. When the office in Lubbock, TX is officially closed, he will also get the latest version of QuickBooks for Ms. Hall. Ms. Hall's salary and benefits will be billed to the Leather Research Laboratory and then reimbursed by the LHCA. When the bills are received, the ALCA will be billed by the LHCA for their part which is to be 60%. Discussion continued about a training plan and moving plan. It was agreed that Ms. Hall will fly to Lubbock, TX for training the week after convention and will discuss moving plans while she is there.

5. **EDITOR'S REPORT** – Steve Lange

   Mr. Lange submitted the following written report dated June 15, 2023:

   We have published 22 papers in 2023 so far. Confirmed manuscripts are scheduled through October 2023. Five papers have been rejected to date in 2023. Submissions have slowed in recent months. (Received 6 viable submissions in March, 4 in April and only 1 in May.)

   Publication cost averaged $2,136 in 2023 and $2,089 in 2023 to date.

Working with UC Press to correct errors in the website postings (some articles missing and/or incomplete). They have agreed to train someone from the LRL to post archival issues. We have all the issues back to 1973 scanned and ready to post. These archival issues should be fully searchable via normal Internet search engines.

Respectfully submitted,
Steve Lange
Journal Editor

Discussion was held regarding the Editor's Report. Mr. Lange pointed out again that the publication cost is still running half as much as the previous printer. He also said that the Editorial Board tries not to reject papers but helps to fix them so they are publishable. More members are needed on the Editorial Board.

Motion was made, seconded, and carried to accept the Editor's Report as written.

6. **FINANCIAL REPORT** – Carol Adcock
The Council was sent the Financial Analysis for 2022 as well as the first quarter 2023 financials including the Profit and Loss Statement, Balance Sheet and Budget vs. Actual prior to the meeting. Mrs. Adcock reviewed all these items with Council. The Financial Analysis is attached to these minutes. Mrs. Adcock also reported to Council that since the Association was moving to another state and the current auditor was shorthanded, he has declined to be the auditor for the Association in the future. He recommended finding an auditor in the new location. Ms. Hall has some contacts that she will contact to get an estimate on handling the needs of the Association concerning doing a financial analysis and the yearly income tax return.

The Membership and Subscription Report was also reviewed. The ALCA currently has 275 members consisting of 120 active, 46 active life, 4 active life mutual, 22 active life retired, 15 active mutual, 39 active retired, 25 SLTC, 2 SLTC students, and 2 ALCA students. It was noted that The Association had been notified that 4 members and/or friends of the leather industry had passed away since the last ALCA Annual Convention in 2022. They are Jean Tancous, Maurice J. Plumez, Carl R. Bagg and James E. Cartier. A moment of silence will be held for all of them at the Annual Business Meeting. It was also noted that one member, Scott Beloli, was given life status in the Association as noted at the beginning of the meeting.

For 2023, 132 paying members contributed $32,848. There is outstanding approximately $1,442 in dues from the SLTC after subtracting the dues of our mutual members. Subscriptions for 2023 have brought in $10,680 in fees postage and handling charges. Discounts have been given in the amount of $585, making a total of subscriptions and postage and handling charges minus discounts in the amount of $10,095. Nineteen new members have joined ALCA since the last Annual Convention: eighteen active members and one student member.

Motion was made, seconded and passed to accept the Financial Report as presented.

7. **WAYS AND MEANS COMMITTEE** – Shawn Brown and Steve Schroeder, Jr., Co-Chairs
Mr. Brown suggested that Council should take over the duties of the Ways and Means Committee and gets reports from Steve Ford, our financial advisor for the Association's portfolio with Ford Fowler. He felts this should be done at least twice a year and can be done via a zoom call. Mr. Brown said the portfolio was designed for a non-profit and has only one major stock. Ms. Hall read the actual duties of the Ways and Means Committee as in the bylaws, stating the following under section VI. Finances, Number 6:

Ways and Means Committee:

(a) To promote the financial welfare of the Association there is established a Ways and Means Committee. This committee shall consist of a chair, appointed by the Council, and as many members as may be necessary, appointed by the chair with approval of the Council. Appointments to the Ways and Means Committee shall terminate at the close of the annual meeting held in even-numbered years.

(b) The Ways and Means Committee shall aid in increasing the income of the Association by securing advertisers, new members, or any other proper financial support. The committee shall advise the Council and the Executive Secretary regarding financial matters, and shall assist in the preparation of the annual budget.

Motion was made, seconded and unanimously approved that the new Chair of the Ways and Means Committee will be the President of the Association, Joseph Hoefler, with the entire Council being members of the committee.

Mrs. Adcock gave the following numbers on the investment account:

First Quarter 2023 earnings - $612.85 compared to first quarter of 2022 of $573.43; have not received any dividend checks from the company this year;

Value of Portfolio as of March 31, 2023 - $127,862.6825; was $179,830.68 end of March 2022;

Withdrawals in 2022 and 2023 were $22,000 received on 7/28/2022 and $20,000 received on 2/23/2023.

Motion was made, seconded and carried to accept the Ways & Means Committee Report.

7. ANNUAL CONVENTION 2024

Convention Chair for 2024 will be Donis Bosworth. Several sites have been investigated with only two being viable at this time. The ones under consideration are Oglebay in Wheeling, WV and Hershey Lodge in Hershey, PA.

Council ran out of time to discuss this matter. This item will be revisited again at the next Council meeting on Thursday, June 22.

8. COMMITTEE APPOINTMENTS -

President Hoefler's recommendations for the following appointments were announced:

2024 Nominating Committee: John Rodden (Chair), Shawn Brown, Todd Salzman
2024 ALSOP Committee: Joseph Hoefler (Chair), Mike Bley, Luis Zugno
2024 O'Flaherty Award Committee: Sarah Drayna (Chair), Lori Hyllengren, Beat Schelling
2025 Wilson Selection Committee: Katie Kutskill (Chair), Eric Webb, Jordan Kaiser

Motion was made, seconded, and can-ied to accept the appointments as presented.

9. NEW BUSINESS - Joseph Hoefler, President

This item was tabled until the next Council meeting.

10. ADIOURNMENT

The next Council meeting will be Thursday, June 22, at 8 am in Loramoor A. It will be a short meeting before the technical sessions begin for the day and will include the current Council as well as the new members of Council.

There being no further business, the meeting was adjourned.

Respectfully submitted by:

Carol Adcock, Executive Secretary

Signed and Approved by:

Joseph Hoefler, President

John Rodden, Vice President

SCOTT NORTHAM, CPA, PC
Certified Public Accountants

INDEPENDENT ACCOUNTANT'S REPORT ON THE APPLICATION OF AGREED-UPON PROCEDURES

American Leather Chemists Association
1314 50th Street, Suite 103
Lubbock, TX 79412

We have performed the procedures enumerated below, which were agreed to by American Leather Chemists Association (ALCA), solely to assist you in evaluating the revenue and expense transactions of the Organization for the fiscal year ended December 31, 2022. ALCA's management is responsible for the presentation of the revenue and expense transactions. This agreed-upon procedures engagement was conducted in accordance with attestation standards established by the American Institute of Certified Public Accountants. The sufficiency of these procedures is solely the responsibility of those parties specified in the report. Consequently, we make no representation regarding the sufficiency of the procedures described below either for the purpose for which this report has been requested or for any other purpose.

We are required to be independent of the Association and to meet our other ethical responsibilities, in accordance with the relevant ethical requirements related to our agreed-upon procedures engagement.

We examined the detailed general ledger and a representative sample of the revenue and expense transactions and the related underlying supporting documentation for the organization for the fiscal year ended December 31, 2022 for the purpose of determining whether the documentation presented properly supported the revenue and expense transactions and were properly categorized within the financial records. We found no significant exceptions within the revenue and expense transactions tested.

This agreed-upon procedures engagement was conducted in accordance with attestation standards established by the American Institute of Certified Public Accountants. We were not engaged to, and did not conduct, an examination or review, the objective of which would be the expression of an opinion or conclusion, respectively, on the Association's financial position and operations as of and for the year ended December 31, 2022. Accordingly, we do not express such an opinion or conclusion. Had we performed additional procedures, other matters might have come to our attention that would have been reported to those parties specified in the report.

This report is intended solely for the information and use of by the directors and management of American Leather Chemists Association and is not intended to be and should not be used by anyone other than those specified parties.

SCOTT NORTHAM, CPA, PC
Ruidoso, New Mexico
May 15, 2023

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(575) 258-5559
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A Bittersweet Occasion

After almost 24 years we had to say farewell to our beloved Executive Secretary, Carol Adcock. Over that time Carol came to be much more than just the secretary, she was the heart and soul of the organization. Carol was the one who knew the history and, very importantly, knew the bylaws that the ALCA was supposed to operate under, and she was a stickler to make sure all Officers and Councilors followed the bylaws to the letter. Carol always made sure to follow-up with the various award / nomination committees to ensure that they did what they were supposed to do in a timely manner so that everything would be done and ready for the next Convention.

To ease Carol into retirement, we chartered the largest boat we could find on Lake Geneva and held a wonderful party.

And, once our Guest of Honor arrived, the party was off and sailing!

Later, at the awards banquet, Carol was presented with a commemorative hide signed with notes of appreciation from all the attendees.

Carol will always have a special place in the hearts of all those many ALCA members that have come to know her over the years. We will miss her steadying presence at the Convention and the ready answers to any questions posed to her when called on the phone. She always insisted that she didn't know anything about the leather industry but the leather industry knew her and will miss her deeply.

Lady of the Lake, Lake Geneva, Wisconsin

And, of course, we had cake!

Retiring Executive Secretary Carol Adcock

Editor Steve Lange presenting Carol with a Commemorative Hide

Awards Banquet Opening Remarks

President **Joseph Hoefler**

Greetings, welcome to the 117th Convention Awards Banquet. I trust everyone has enjoyed this year's convention. I would like to recognize John Rodden for arranging a super line-up of presenters. Having to personally support the same endeavor last year, I know the effort needed and how stressful it can be. I would also like to thank Carol and Council for their dedication and the sponsors who came through and exceeded expectations. Lastly, I want to acknowledge and thank the LHCA for participating to a greater extent in this year's convention. Though several ALCA members are also LHCA members, there was a much higher LHCA turnout and contribution to the technical session which has had a very positive impact.

ALCA President Joseph Hoefler

This year, from my perspective, is truly when we are free of the shadow of Covid. Though we had a well-received conference last year, it was more like a combination of a reunion of sorts and a conference. I suppose being an annual event this conference will always have some reunion attribute to it. As this night goes on, we will see that part of our ALCA family is moving on and with that a new part is added. I personally, like many here, can reflect on all the past members that have similarly moved on with others stepping up to fill their shoes but unfortunately there seems to be less and less replacements to step up as time goes by. ALCA has a long history and it is not going to diminish on my watch and I can assure John feels the same way, hence the outreach to the LHCA and other new ideas we are currently considering to further enhance this event. We are open to suggestions as well.

ALCA really had to address a few critical issues this year and these are not finished related to Carol's retirement, Kristina's hiring, moving of the office in Texas, to really a remote position shared between ALCA and LHCA. This makes sense to both parties and hopefully the dust will settle from all of this change, and we can identify an area or two that ALCA can take on to better support this great industry and prepare it for the future. Again we are open to suggestions.

Awards Banquet Closing Remarks

President **Joseph Hoefler**

In my earliest days at Rohm and Haas some 35 years ago one of the first things a manager said to me that really seemed to have stuck with me all these years is that *There is no progress without change*.

At the time, being a young new hire, I didn't realize how true these words would be. Before us we have Carol moving on and Kristina taking over. This is certainly change but not progress at all, as there is so much work related to this change that must take place in the immediate future. We have said our so-longs and now it is time to also think about the future of ALCA. We certainly are going to look for progress and it seems that change is in the air. Exactly what those changes are will be the subject of future meetings and with some hard work should begin to be seen by next conference. Going forward, John or I, will look to Council for added support, compared to where this has traditionally stood, and without doubt others will be called on as well. Please begin to consider how each of you can contribute to bring added value to ALCA, to attract a bigger audience yes but truly to have a bigger impact on our much-cherished industry.

With this I call a close to this year's convention and I will hand the Gavel to Carol to officially close the meeting.

Bactericidal and Fungicidal Action of Copper Nanoparticles on Leather Surface

by

Deepak N, Inbasekar C, Nishad Fathima Nishter*

Inorganic and Physical Chemistry Laboratory, CSIR-Central Leather Research Institute, Adyar, Chennai-600020

Abstract

Although tanning makes the collagen matrix resilient against microbial attack, the chemicals used in the finishing process are susceptible to microbes. Hence, it is imperative to develop a finishing process with inherent antimicrobial properties. Leathers with antimicrobial properties evoke a considerable array of interest in consumers. The present study aims to enhance the antimicrobial properties of the leather using copper nanoparticles in the finishing and retanning process. Copper nanoparticles have been synthesized by chemical reduction using copper sulphate pentahydrate as the precursor with dialdehyde starch and gallic acid. The prepared nanoparticles have been characterized using UV-Visible spectrometry, dynamic light scattering, scanning electron microscopy, transmission electron microscopy, and X-ray diffraction techniques. The prepared nanoparticles have been used in both retanning and finishing processes. The experimental leather retanned using copper nanoparticles possess good mechanical strength properties and color index value compare to the control. Nanoparticles are effective against both gram negative and positive bacterial organisms. The nanoparticles also inhibit the growth of common fungus, which can colonize on leather. Thus, the current study paves the way for a novel solution that is an alternative to biocides and antimicrobial chemicals and is more effective in inhibiting microbial growth.

1 Introduction

The extracellular matrix is a natural barrier that protects against invading microbes and other external factors. Collagen is the major protein in the extracellular matrix that provides structural integrity to the skin and is commonly known as leather making protein.[1] The leather process comprises pretanning, tanning, post tanning, and finishing. The post-tanning process imparts functional properties to the tanned leather by employing polymeric fillers, dyes, and lubricating agents. The selection of the post tanning process relies on the end product.[2] The finishing process enhances the aesthetic value and imparts other functional properties such as the leather's super hydrophobicity and antimicrobial properties. To prevent the growth of microbes in leather products, biocides and antimicrobial chemicals are widely used in the finishing process.[3]

The presence of microorganisms on the leather surface causes deterioration of raw materials at various stages of tanning or visible defects in finished leathers.[3] Especially vegetable-tanned leather is prone to microbial attack.[4] Fungi and bacteria also colonize finished products.[4] Sweat from footwear and lining in socks in shoe materials will be a carbon source for microbial growth.[5]

Several antimicrobial compounds have been utilized in the leather industry; however, some of these materials are ineffective owing to their composition, high cost, and pose a pollution risk, thereby limiting their application.[6] The use of biocides endangers the health of humans, animals, and the natural environment.[7] Metallic nanoparticles have distinct toxicity mechanisms in different microorganisms. The majority of metal oxides are lethal to all types of bacterial cells.[8] Some transition elements and coinage metals have all been found to have antibacterial properties.[9] For ages, copper and its compounds have been employed as disinfectants.[10] Many studies have been carried out on the antibacterial effects of metals such as copper as a result of research into the creation of antimicrobial agents, particularly antibacterial agents.[11] Copper nanoparticles cause plasmid DNA degradation in gram-positive and gram-negative pathogens in a dose-dependent manner.[12] Contact kills bacteria, yeasts, and viruses on copper surfaces.[13]

Copper nanoparticles can provide site-specific and targeted reactivity owing to their smaller sizes and large surface area, which promotes their penetration inside the bacterial cell.[14] The reduction of copper ions causes cascade events such as DNA degradation and the generation of Reactive Oxygen Species (ROS), which induces cell death by membrane damage.[15,16] Thus, the current study explores the antimicrobial properties of copper nanoparticles in the post tanning and finishing process.

2 Experimental

2.1 Materials

Copper sulphate pentahydrate, gallic acid monohydrate, polyethyleneimine (PEI), sodium periodate, sodium borohydride, 3,3'diphenylthiocarbocyanineiodide,2,7dichlorodihydrofluorescein diacetate (DCFHDA) were purchased from Sigma Aldrich. Mueller hinton agar (MHA), nutrient broth (NB), sabouraud dextrose agar (SDA), and potato dextrose broth (PDB) were purchased from

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HiMedia. Experiments were carried out by using analytical-grade chemicals. Two Gram-positive (*Staphylococcus aureus* and *Bacillus cereus*) and two gram-negative (E*scherichia coli* and *Pseudomonas aeruginosa*) bacterial strains and a fungal strain (A*spergillus niger*) were obtained from the MTCC. All the chemicals used for leather processing were of analytical grade. The chrome tanned wet blue goat leather and goat crust leather was collected from the Tannery division of CSIR-Central Leather Research Institute.

2.2. Methods

2.2.1. Preparation of Dialdehyde starch (DAS)

The dialdehyde starch was prepared using the standard procedure. About 20 g of corn starch and 10 g of sodium periodate (1:0.5) were dissolved in 100 ml of water in a round bottom flask with vigorous stirring at 37°C for 12 h. Then 5 ml of propylene glycol was added to the reaction mixture to quench the reaction. The resulting slurry was filtered and washed with water thrice and freeze-dried. The dialdehyde starch powder was used without further purification.

2.2.2. Synthesis of Copper nanoparticles

Copper nanoparticles were synthesized by the chemical reduction method. Copper sulphate pentahydrate was used as a precursor, with dialdehyde starch as a reducing agent and polyethyleneimine as a capping agent. Dialdehyde starch (DAS) solution was prepared by adding NaOH, Urea, and DAS (3:2:1) in water and 2% of this solution was cooled to -20°C for 12 h and thawed under stirring at room temperature. $CuSO_4$ solution (15 mM) 1 mL was taken in the round bottom flask and 5 mL of DAS solution and 1mL of polyethyleneimine (PEI) was added to this under magnetic stirring. The reaction mixture was thoroughly stirred and passed through N_2, and the round bottom flask was placed in an oil bath at 50°C for 3 h. Copper nanoparticles were synthesized using dialdehyde starch and polyethyleneimine as a reducing and capping agent, respectively. Dialdehyde starch was dissolved in NaOH/urea system to form a light-yellow colored solution. As the reaction proceeded, the mixture showed a gradual color change from light yellow to reddish-brown. After washing and purification, a reddish-brown solution was obtained. The resultant copper nanoparticles were freeze-dried and used without further purification.

For the retanning process, copper nanoparticles were synthesized using sodium borohydride and gallic acid. $CuSO_4$ solution (5 mM) 10 mL was thoroughly mixed with 10 mL (5mM) of gallic acid solution. Then 30 mL (10 mM) of $NaBH_4$ solution was added dropwise into the above mixture for 2 h in the dark. The obtained copper nanoparticles solution was further purified by centrifugation at 15,000 rpm for 20 minutes. The resultant copper nanoparticles were freeze-dried and used without further purification.

2.2.3. Characterization of Copper Nanoparticles

FTIR measurements were performed using an infrared spectrometer (JASCO IR). Infrared spectra were taken with a scan range of 400-4,000 cm^{-1}, and resolution of 4 cm^{-1}. Particle size and zeta potential analysis were performed using a high-performance particle analyzer (Zetasizer Nano series, Malvern) at 25°C. The samples were dissolved in a water medium for measurements. X'Pert Powder X-Ray Diffraction obtained the crystallographic studies and diffraction peaks. The samples were analyzed by powder diffraction using samples prepared as finely ground powders. An FEI Quanta 200 scanning electron microscope was used to study the morphological characteristics, and all specimens were then coated with gold using a palaron range CA7620-sputtering coater. Energy dispersive X-Ray was used to study the elemental composition of the nanoparticles. Fluorescence spectra were recorded on a Cary eclipse fluorescence spectrophotometer using quartz cuvettes at room temperature. BET-specific surface determination was based on an N_2 isothermal measurement at 77 K performed with an IMI-HTP manometric sorption analyzer (Hiden Isochema, Inc). Before the measurements, the samples were degassed at 420 K for 16 h. Transmission electron microscopy (TEM) samples were prepared by casting a drop of the as-prepared copper nanoparticle suspension on a carbon-coated copper grid and then drying them in air. The dried grid was placed under a JEOL 1200 EX transmission electron microscope. The images were taken at an acceleration voltage of 120 kV.

2.2.4. Finishing process

Goat crust leather was used for spray coating using High-Volume-Low-Pressure (HVLP) gun. A mixture of isopropyl alcohol and water was sprayed as a clear coat to remove the dust and increase the finishing formulation's penetration. Base coat formulation was prepared, and two cross coats were sprayed and dried. Top coat formulation with lacquer, copper nanoparticles, and water were prepared, and one cross coat was sprayed on the leather surface.

2.2.5. Post tanning leather process

Chrome tanned wet blue leather was used for retanning process, pH of the leather was adjusted to pH 5.5. Copper nanoparticles synthesized using gallic acid was used for the retanning process.

2.2.6. Characterization of Leather

The color values L*, a*, b* were determined using UV-Vis-NIR spectrophotometer Agilent CARY-5000. Tensile and tear strength was tested according to SATRA TM 43 and 162. The wet and dry rub fastness test was measured according to IUF 450 by veslic C-4500. Measurement of color fastness to water was carried out by SATRA TM 335-1.

2.2.7. Antibacterial Activity of Copper Nanoparticles

The antibacterial activity of synthesized copper nanoparticles and coated leather was assessed using the agar diffusion method. The bacterial culture broth was prepared by inoculating the bacterial strains in nutrient broth and allowed to grow overnight at 37°C. Two Gram-positive (*Staphylococcus aureus* and *Bacillus cereus*) and two gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacterial strains were cultured. Mueller Hinton Agar was prepared and poured into the sterile petri dish, and the bacterial strains at $1x10^6$ CFU/mL concentration were uniformly spread on plates using sterilized cotton swabs. Then the wells were made on the inoculated plates using a sterile gel borer. Wells were filled with 100 *μL of* different concentrations of synthesized copper nanoparticles (10, 20, 30, and 40 %), and the plates were incubated overnight at 37°C. The antibacterial activity of copper nanoparticles coated leather was assessed by placing the sample cut with a 2 cm radius compared with control leather.

2.2.8. Antifungal Activity of Copper Nanoparticles

The fungal culture broth was prepared by inoculating the fungal strain in potato dextrose broth and allowed to grow for 72 h at 28°C. A fungal strain (*Aspergillus niger*) was cultured. Sabouraud dextrose agar media was prepared and poured into a sterile petri dish, and the fungal strain at $1x10^6$ CFU/mL concentration was uniformly spread on plates using sterilized cotton swabs. Then the wells were made on the inoculated plates using a sterile gel borer. Wells were filled with 100 *μL of* 40 % of synthesized copper nanoparticles and the plates were incubated overnight at 37°C. The antifungal activity of copper nanoparticles coated leather was assessed by placing the sample cut with a 2 cm radius compared with control leather.

2.2.9. Determination of Membrane Potential of Intact **E. coli** *Cells*

The membrane potential of bacterial cell was determined by spectrofluorimetric methods, using the dye 3', 3'diphenylthiocarbocyanine iodide. To carry out the experiments, synchronized cells of *E. coli* were newly grown to the log phase in Luria–Bertani (LB) medium. The grown cells were then treated with 3.0 µg/mL CuNPs (the minimum inhibitory concentration (MIC)) for 1 h, centrifuged at 8000 rpm for 5 min, and the cell pellets were resuspended in starvation buffer (SB). As negative and positive controls, cells alone and cells treated with 3.0 µg/mL $CuSO_4$ (the precursor of the NPs) were also taken.

2.2.10. Determination of the Production of Reactive Oxygen Species (ROS) in **E. coli** *cells*

ROS production in bacterial cells was estimated using the chemical 2', 7' dichlorodihydrofluorescein diacetate (DCFHDA) as a marker to visualize the bacterial cell. Log phase grown cells, were prepared by treating with 3.0 µg/ml CuNPs for 1 h, centrifuged, and suspended in saline (8.0 g/L NaCl, 0:2 g/L KCl). The negative and positive control experiments were also done. The probe (1 µl of 10 mM DCFHDA) was added to each of the four sets and incubated for 2 h at ambient temperature in the dark. The fluorescence of each sample was then measured in the spectrofluorometer with excitation and emission wavelengths of 485 and 530 nm, respectively.

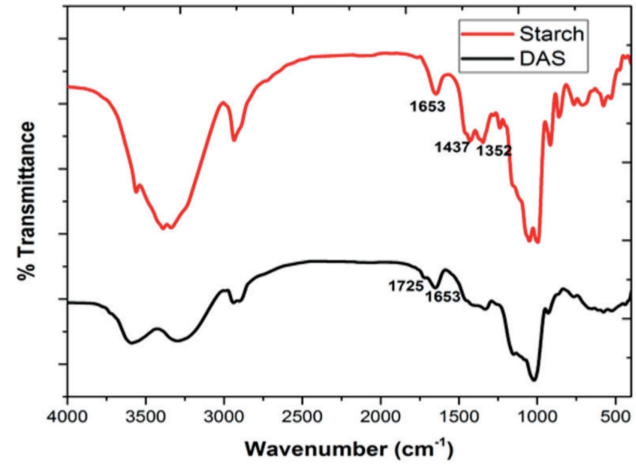

Figure 1. FT-IR Spectra of Starch and DAS (Dialdehyde starch)

3 Results and Discussion

IR spectroscopy has been used to study the functional groups present in the starch and dialdehyde starch. Figure 1 shows the FTIR spectra of starch and dialdehyde starch. The periodate oxidation of starch is characterized by the targeted cleavage of the C2-C3 bond of glucose residues in the starch.[17] The characteristics band at 1352 cm^{-1} corresponds to the C-H alkane bending and the band at 1725 cm^{-1} corresponds to the stretching vibration of the carbonyl C=O bond confirms the presence of aliphatic aldehyde group.[17] The results confirm the aldehyde group modification in the starch.

UV-Visible spectroscopy has been used to elucidate the formation of the nanoparticle. Nanoparticles size and shape are regulated by the precursor choice and the reaction conditions. For instance,

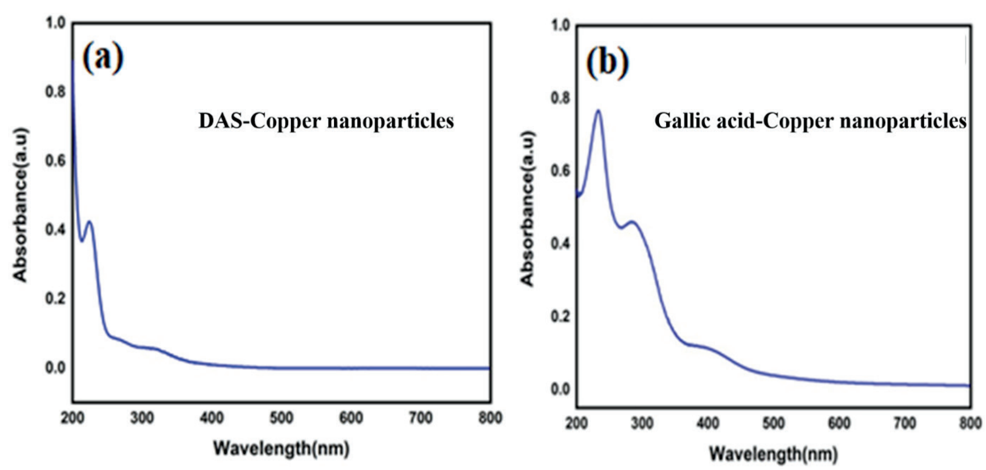

Figure 2. UV-Visible spectra of copper nanoparticles using (a) DAS and (b) gallic acid

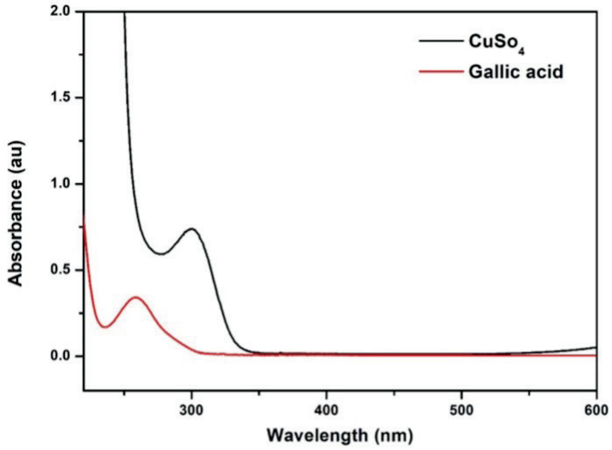

Figure S1. UV-Visible spectra of copper sulphate and gallic acid

the peaks of copper oxide nanoparticles usually occur in the 220–350 nm range and is attributed to Cu^{2+}–O– charge transfer transitions.[18] The copper nanoparticles synthesized using DAS exhibit a maximum absorption peak at approximately 253 nm, corresponding to a characteristic Cu nanoparticle peak (Figure 2 a).[20] The peak at 290 nm corresponds to the n→π* transition due to the presence of the carboxylic group of gallic acid.[22,23] The UV-Visible spectra of copper sulphate and gallic acid are given in supporting information (Figure S1).

Dynamic light scattering measurement has been performed to measure the nanoparticles' hydrodynamic diameter and surface charge. From Figure 3 (a) and (b), copper nanoparticles synthesized using DAS and PEI has a hydrodynamic diameter value of 105 ± 5 nm, PDI value of 0.325 and nanoparticles synthesized using sodium borohydride and gallic acid have a hydrodynamic diameter value of 280 ± 14 nm, PDI value of 0.387, respectively. The zeta potential of copper nanoparticles synthesized using DAS and PEI is 24.2 ± 1 mV and -38.8 ± 1.5 mV, respectively. The increase in D_H and ζ indicates that the presence of gallic acid influences the nanoparticle size and provides more stability to the nanoparticles. The negative zeta potential of copper nanoparticles synthesized using gallic acid is due to the presence of the deprotonated carboxyl group.

X-ray diffraction pattern measurement have been performed for copper nanoparticles synthesized using dialdehyde starch and gallic acid. Figure 4 (a) shows the major diffraction peaks at 2θ = 42.8°, 52.4°, 70.2° are assigned to be Miller indices plane (111), (200), and (220) correspond to the crystal planes of copper nanoparticles[19] and the Figure 4 (b) 2θ values 46.2°, 53.6°, which are indexed to planes (111), (200) has the significant variation in the crystallinity of copper nanoparticles due to the presence of gallic acid.[19]

The morphology of PEI stabilized Cu NPs was examined by FESEM. Figures 5 a and b show the fast emission SEM image of the spherical copper NPs, which are consistently dispersed due to the presence of capping agent PEI, which prevents the aggregation of the nanoparticles and results in uniform particle size.[24,25] EDAX

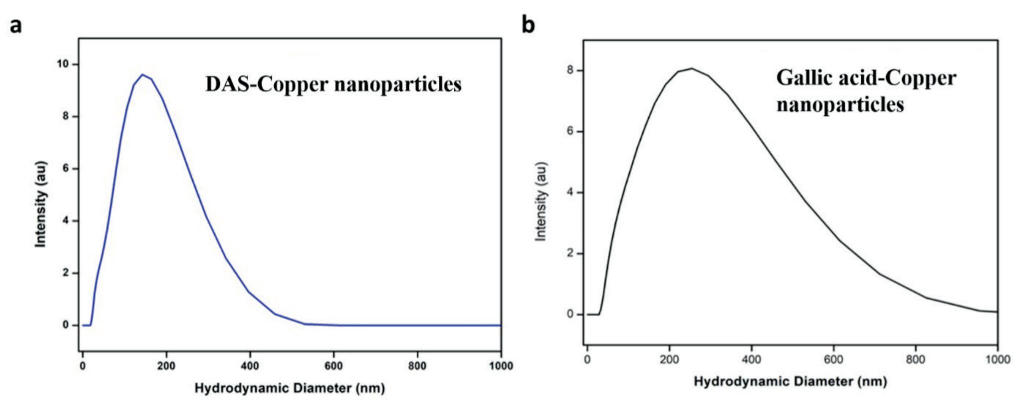

Figure 3. Particle size of copper nanoparticles using (a) DAS and (b) gallic acid

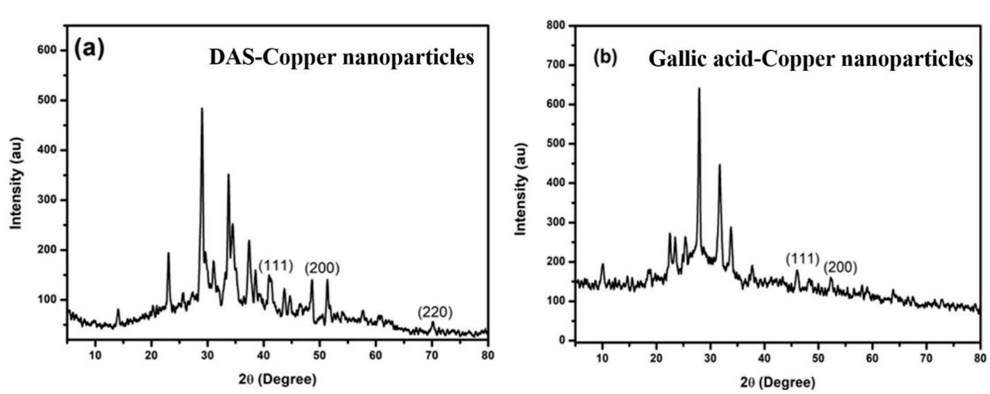

Figure 4. XRD pattern of copper nanoparticles using (a) DAS and (b) gallic acid

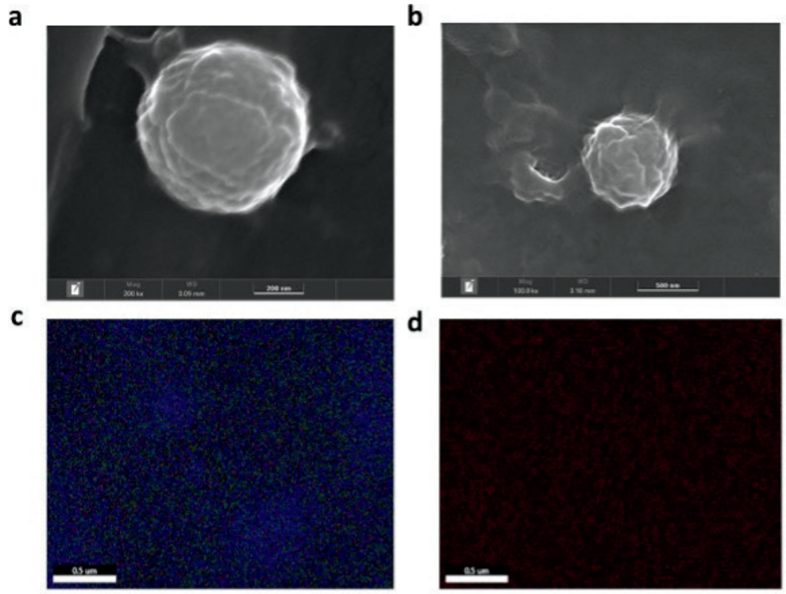

Figure 5. FESEM images of copper nanoparticles at magnification (a) 200 nm (b) 500 nm (c) overall E-DAX mapping of copper nanoparticles, (d) Copper E-DAX mapping of copper nanoparticles

mapping of copper nanoparticles are shown in Figures 5 c and d. Figure 5 c shows the overall mapping of copper nanoparticles with an elemental composition of carbon, nitrogen, oxygen and copper. Figure 5 d copper mapping shows the uniform distribution of copper in the synthesized nanoparticles.

Using TEM, the size and morphology of copper nanoparticles has been investigated. TEM images (Figure 6) further confirmed that the nucleation and growth of copper nanoparticles progressed with the reaction time. Most of the nanoparticles show contrast regions within one nanoparticle, indicating their polycrystalline structure spots confirm the presence of copper nanoparticles, and the results support the XRD pattern and SEM.

The Brunauer–Emmett–Teller (BET) analysis has been measured to assess the surface area molecules in the pores of nanoparticles.[15] The specific surface area and pore size distribution of copper nanoparticles has been measured by nitrogen adsorption/desorption at 77 K. The N_2 adsorption–desorption isotherms of copper nanoparticle samples, belonged to type II adsorption isotherms with flatter region in the middle represents the monolayer formation, indicating the presence of mesopores (6.7702 nm) and multilayer adsorption where the amount of adsorption increases with increase in pressure are shown for copper nanoparticles in Figure 7.[26] The BET surface area of the copper nanoparticles is 20 m^2g^{-1}. The most abundant pore size for the copper nanoparticles is the range of 2-10 nm also confirms the mesoporous nature of the nanoparticles.

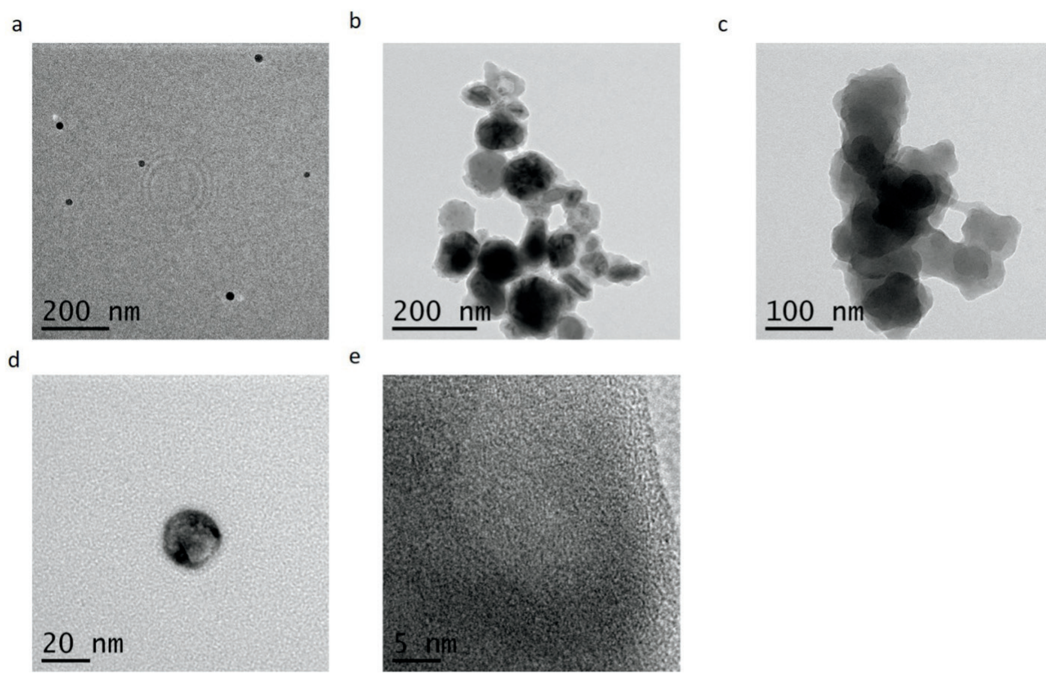

Figure 6. HRTEM images of copper nanoparticles at different magnifications (a) 200 nm (b) 200 nm (c) 100 nm (d) 20 nm (e) 5 nm

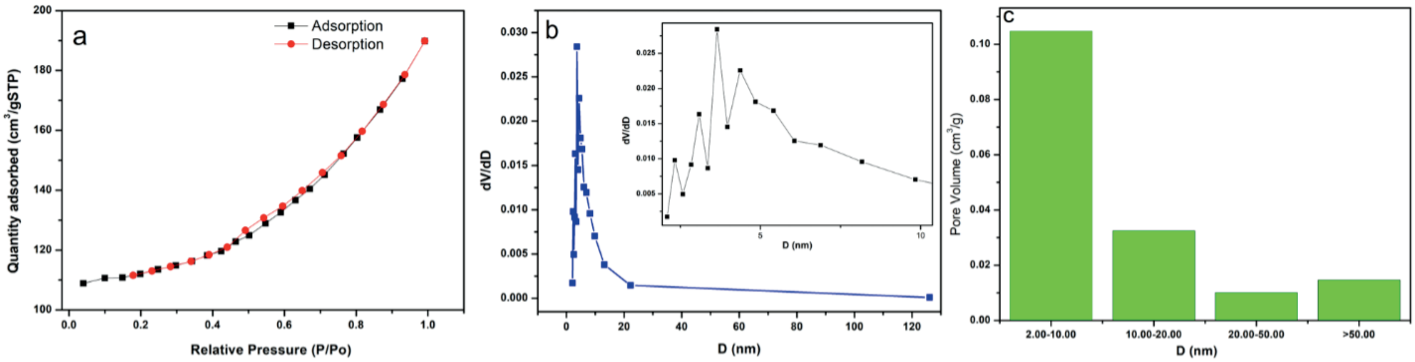

Figure 7. (a) Adsorption Desorption isotherm of copper nanoparticles (b) BJH Adsorption pore size of copper nanoparticles and (c) Pore volume of copper nanoparticles

The copper nanoparticles synthesized using sodium borohydride and gallic acid has been used in the retanning process. Figure 8 shows the photographic images of control retanned leather and copper nanoparticles incorporated in retanned leather. The leather retanned with copper nanoparticles shows high color intensity due to the presence of gallic acid. Gallic acid is used to functionalize the copper nanoparticles, thereby increasing the leather matrix's reactive sites and enhancing dye uptake in the experiment. Tables I and IV show the color fastness values of control and copper incorporated retanned leather; the color rub fastness ratings of both leathers are similar. After 256 and 512 cycles, it is found that both the leathers have excellent color rub fastness properties. From Table III, it could be observed that the physical strength properties exhibit a significant difference compared to the control leather. The experimental leather's organoleptic properties are relatively better than the control leather. The leaching studies were performed at regular intervals to check the copper nanoparticles leaching, and there was no leaking of nanoparticles after 24 h; the result is given in the supporting information (Figure S2).

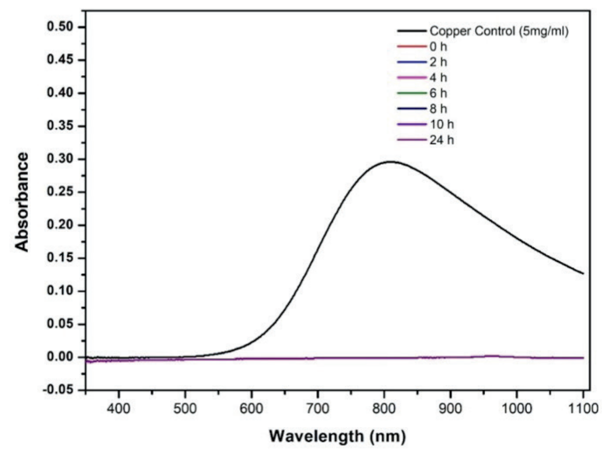

Figure S2. Leaching studies of copper nanoparticles

Antibacterial Activity of Copper Nanoparticles

The antibacterial activity assay has been investigated by the agar diffusion method. The nanoparticles synthesized using DAS has been used in the finishing process and nanoparticles synthesized using gallic acid has been used in the retanning

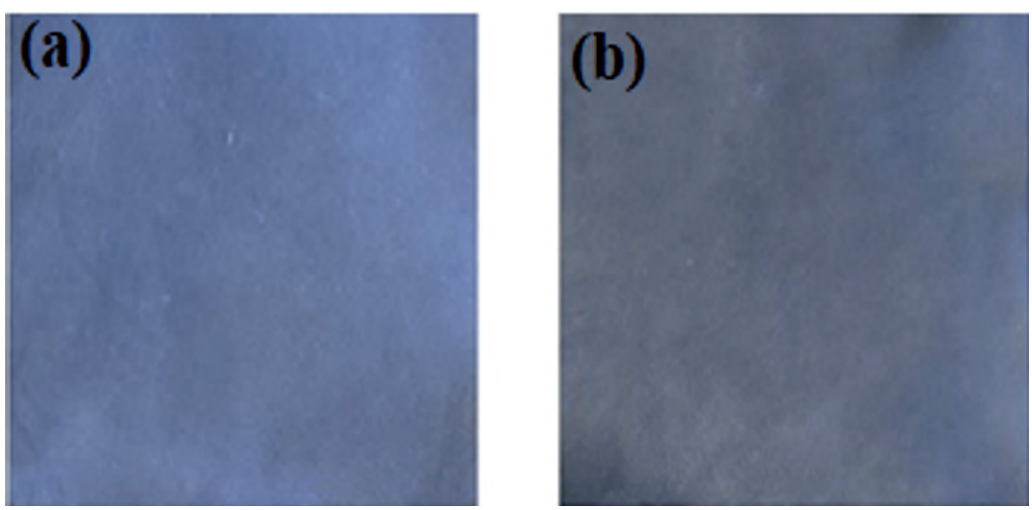

Figure 8. Photographic image of (a) control leather and (b) copper nanoparticles retanned leather

Table I

Color fastness values of control leather and leather finished using copper nanoparticles

Color fastness to rubbing	Control	Copper coated
Dry 512 rubs (material)	4/5	4/5
Wet 256 rubs (material)	4/5	4
Dry 512 rubs (felt)	4/5	4/5
Wet 256 rubs (felt)	4	4

Table II

L*a*b* values of control leather and leather retanned using copper nanoparticles

Values	Control	Experimental	Difference Δ
L*	99.78	88.17	11.61
a*	0.01	1.11	1.1
b*	0.06	9.95	9.89

Table III

Strength properties values of control leather and leather retanned using copper nanoparticles

Sample	Tensile strength (MPa)	Tear strength (N/mm)	Elongation at break (%)
Control	19.23 ± 0.5	52.27 ± 0.5	72.34 ± 0.5
Experiment	25.43 ± 0.5	71.39 ± 0.5	87.01 ± 0.5

Table IV

Color fastness values of control leather and leather finished using copper nanoparticles

Color fastness to rubbing – Greyscale	Control	Experiment
Dry 512 rubs (material)	4	4
Wet 256 rubs (material)	3/4	3/4
Dry 512 rubs (felt)	4/5	4/5
Wet 256 rubs (felt)	2	3

process. The antibacterial activity of copper nanoparticles coated leather was assessed by placing the leather samples on the agar surface against gram-positive and gram-negative bacteria. However, various mechanisms behind the bactericidal activity of metallic nanoparticles have been well studied earlier, commonly followed mechanism where an accumulation of nanoparticles in the bacterial membrane alters its cell permeability, with consequent release of LPS, membrane proteins, and intracellular components.[5] It is evident from Figures 9, 10, and 11 that the increasing concentration of copper nanoparticles effectively inhibits the growth of bacterial species both in the finished and retanned leather.

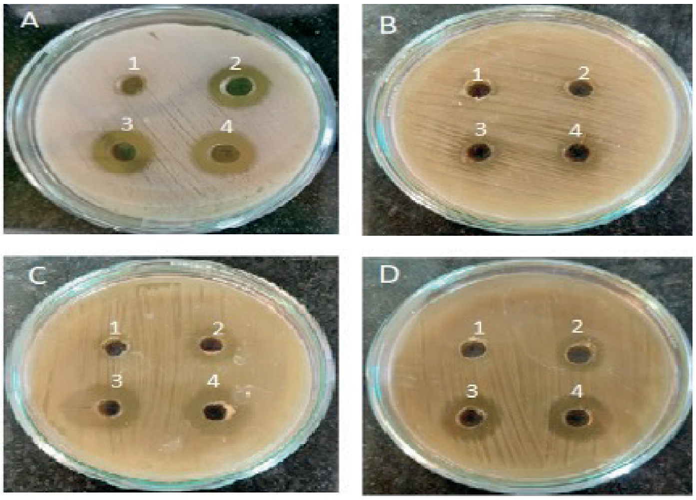

Figure 9. Effect of various concentrations of copper nanoparticles using DAS on growth inhibition zone of bacterial species (**A**- *B. cereus*, **B**- *S. aureus*, **C**- *E. coli,* and **D**- *P. aeruginosa*), 1- 10 % nanoparticles, 2- 20 % of nanoparticles, 3- 30 % of nanoparticles, 4- 40% of nanoparticles

Mechanism of Bacterial Killing

Changes in the bacterial cell membrane potential has been studied using 3’, 3’ diphenylthiocarbocyanine iodide. This is a non-fluorescent dye that binds with cell membrane protein and becomes fluorescent which can be quantified in a spectrofluorometer. The fluorescence intensity is directly proportional to the extension of cell lysis and alteration of cell membrane potential. It is evident from Figure 12 a that the copper nanoparticles cause modification of membrane potential in the bacterial cell wall and cause disruption of cytoplasm, which results in the increased fluorescence intensity due to the leached cells compared to the positive and negative control. Similarly, 2’, 7’ dichlorodihydrofluorescein diacetate (DCFHDA) is a reduced form of fluorescein commonly used as a marker for reactive oxygen species in cells. Copper nanoparticles disrupt the bacterial cell wall, resulting in the cleavage of membrane protein and increased generation of reactive oxygen species. The mechanism of this assay is that DCFHDA could easily cross the cell membrane and hydrolyze the diacetate groups by cytosolic

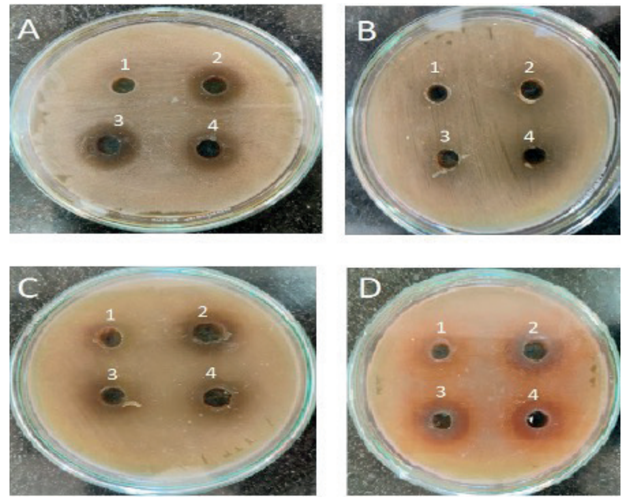

Figure 10. Effect of various concentrations of copper nanoparticles using gallic acid on growth inhibition zone against bacterial species (A- *B. cereus*, B- *S. aureus*, C- *E. coli,* and D- *P. aeruginosa*), 1- 10 % nanoparticles, 2- 20 % of nanoparticles, 3- 30 % of nanoparticles, 4- 40% of nanoparticles

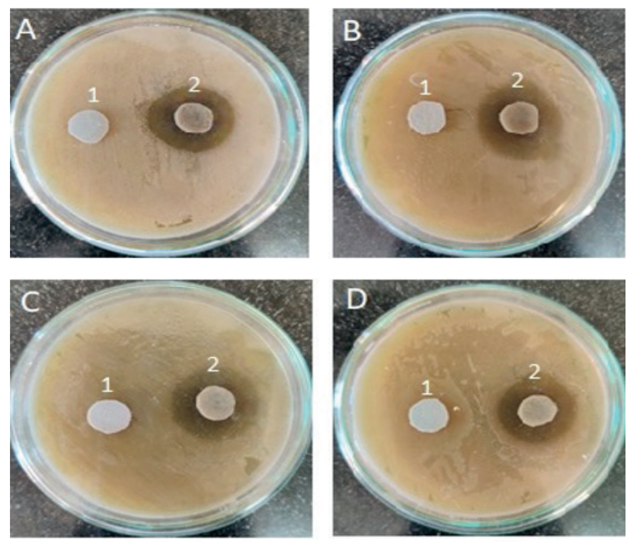

Figure 11. Effect of control finished leather and copper nanoparticles coated finished leather against bacterial species (A- *B. cereus*, B- *S. aureus*, C- *E. coli,* and D- *P. aeruginosa*)**,** 1- control leather, 2- nanoparticles coated leather.

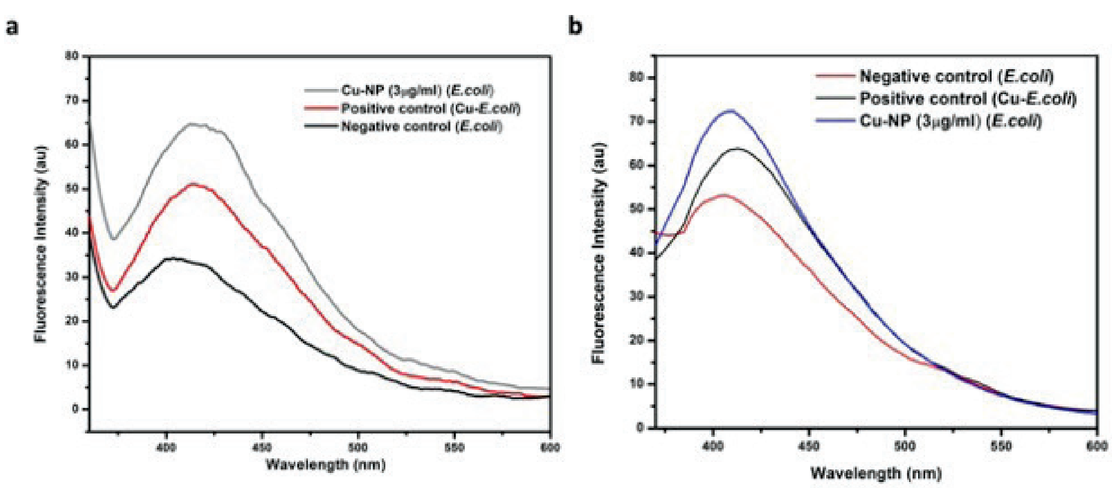

Figure 12. Fluorescence spectra of (a) *E. coli* bacterial cell membrane potential, (b) ROS generation in *E. coli* bacterial cell

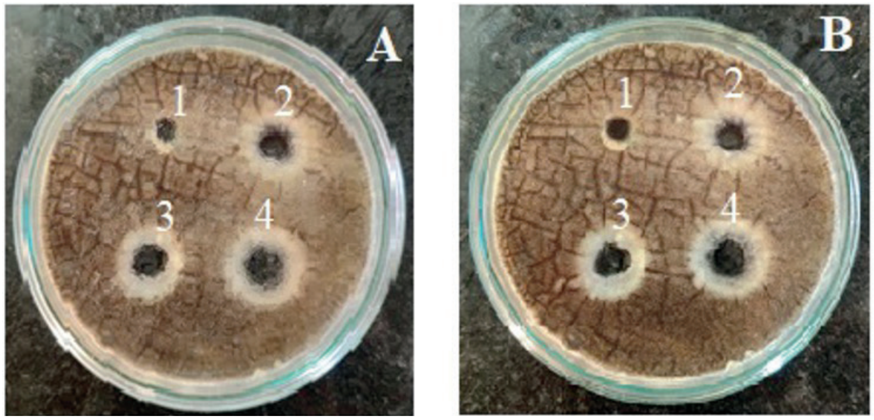

Figure 13. Growth inhibition zone of copper nanoparticles using (A) DAS and (B) gallic acid against *A. niger,* 1- 10 % nanoparticles, 2- 20 % of nanoparticles, 3- 30 % of nanoparticles, 4- 40% of nanoparticles

esterases; subsequently, DCDHF is oxidized by peroxynitrite to the highly fluorescent product dichlorofluorescein. Therefore, the fluorescence intensity of DCF is proportional to the ROS generation within cells. It is evident from Figure 12 b that there is an increased fluorescence intensity for the copper nanoparticles due to the increased production of reactive oxygen species compared to the positive control and negative control.

Antifungal activity of Copper Nanoparticles

The antifungal activity assay was investigated by the agar diffusion method. The zone of inhibition in the radius of copper nanoparticles synthesized has been measured against fungal species on the agar surface against *A. niger* as shown in Figure 13. The plausible mechanisms of action of copper ions and copper nanoparticles are based on altering the structure and function of the fungi cell; furthermore, these particles can affect DNA and disrupt its replication and transcription, ultimately leading to the death of fungal microorganisms.[21]

Conclusion

The current study deals with the synthesis of copper nanoparticles by chemical reduction method using dialdehyde starch and polyethylene diamine, sodium borohydride and gallic acid and applied in the finishing and retanning process, respectively. The nanoparticles retanned leather imparts both antimicrobial and functional properties such as good mechanical strength to the experiment leather. The fluorescence assay measurements clearly indicate the inhibitory efficiency of the nanoparticles in the bacterial cell. The nanoparticles coated leather finished leather effectively inhibits the growth of both bacterial and fungus growth. Thus, the present study paves the way for effectual utilization of nanoparticles in the leather process.

Conflict of Interests

No conflict of interest is associated with this manuscript.

Author Contributions

The manuscript was written through the contributions of three authors. All the authors have approved the final version of the manuscript.

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Fungal Deterioration on Ancient Leather Artifacts

by
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Abstract

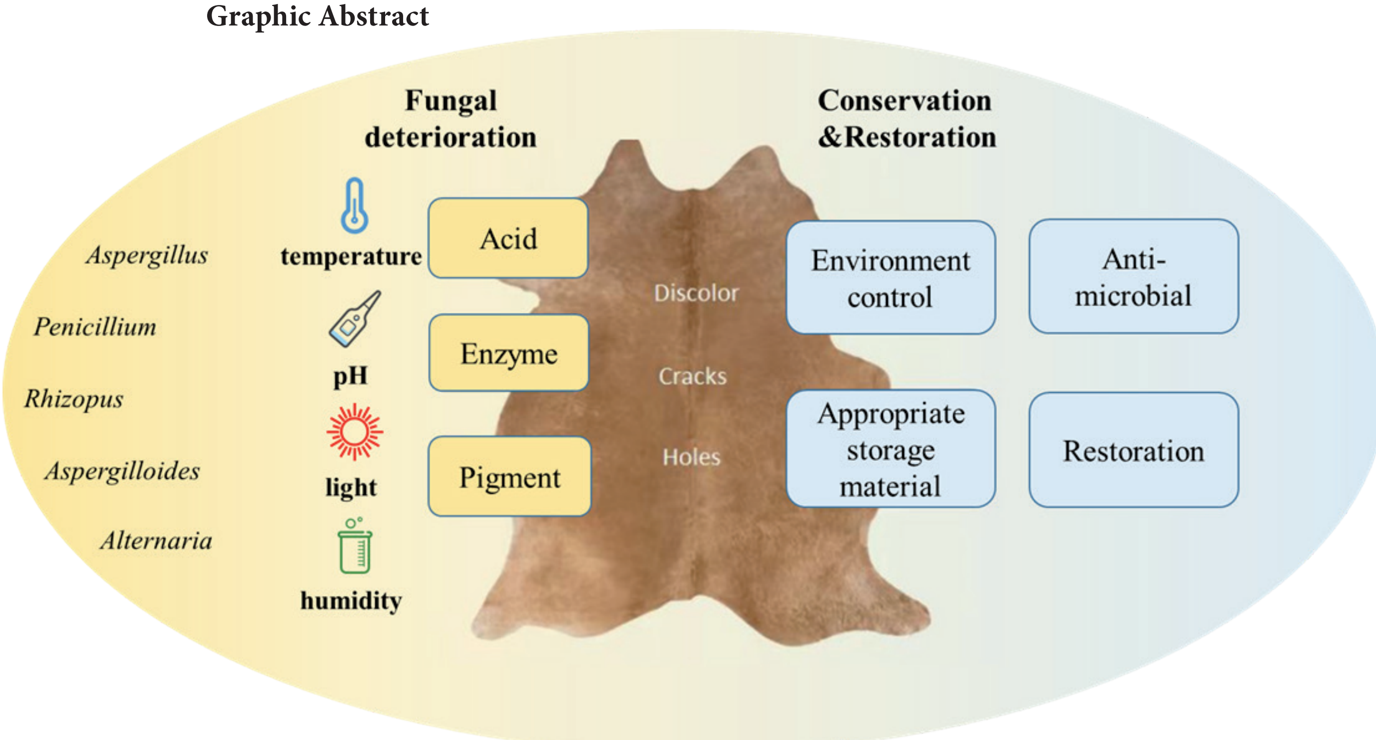
Fungal deterioration of ancient leather artifacts is a significant problem for museums and archives, as it might cause significant damage to the valuable cultural heritage. The growth of fungi on these artifacts is affected by such environmental factors as temperature, relative humidity, pH, and light exposure. The environmental factors that contribute to fungal growth and the impact fungi on the deterioration of ancient leather artifacts are discussed here. An overview is summarized on the strategies to prevent and control fungal deterioration, including the environmental control, the use of biocides, and conservation treatments, which is proposed to provide a valuable guidance for the preservation of ancient leather artifacts.

Introduction

Leather artifacts have played significant roles in human history, which might provide insight into ancient life with historical significance through its various uses, especially with evidence of their use dating back to the Neolithic period.[1] From clothing and footwear to bookbinding and upholstery, leather has been used for various purposes across different cultures and civilizations.[2]

However, over time, ancient leather artifacts can be susceptible to various forms of deterioration, including fungal decay, because of their high organic compound content and the suitable moisture, dark environment for fungal growth. In leather artifacts, there are organic compounds such as collagen, keratin, tannin, lipids, oils and others which are ideal sources of nutrition for fungal growth and proliferation.[2] Fungal deterioration of ancient leather artifacts is a complex issue that poses a significant challenge to

Graphic Abstract



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the preservation of ancient leather artifacts.[3] Fungal deterioration might cause the discoloration, weakening, structural integrity damage, and degradation of the ancient leather artifact, which changes the appearance and reduces their value in culture, history, science, etc.[4] Although there are fewer species of fungi on the substrate than bacteria, fungi tend to take more vital places for biodeterioration, because fungi can grow and reproduce even at lower temperatures and humidity levels than bacteria.[5] The growth of fungi on ancient leather artifacts is influenced by several environmental factors, including temperature, relative humidity, pH, light, and ventilation.[6] High levels of relative humidity and temperature provide ideal conditions for fungal growth and reproduction, while low levels of light and air flow might contribute to the development of anaerobic conditions, which could also promote the fungal growth.[7] The interaction of these environmental factors with the organic compounds in leather could create complex and variable conditions difficult to control and predict.[8] It is necessary to know the factors affecting the fungal growth and to develop strategies to prevent and control the deterioration for the preservation of these valuable ancient leather artifacts. The study of fungal deterioration on ancient leather artifacts is therefore of utmost importance.

This present review is aimed to provide an overview of the mechanism of fungal deterioration of ancient leather artifacts and the strategies used to prevent and control the biodeterioration by fungi.

Factors Affecting Fungal Growth

Fungi are diverse groups of microorganisms found in almost all environments, including museums and archives. They have been playing a crucial role in the decomposition of organic compounds and are responsible for the breakdown of dead plants and animal tissues. The availability of carbon sources, such as cellulose, collagen, oil, and starch are critical factors in determining the ability of fungi to colonize a substrate. However, for supporting fungi to thrive on a substrate, different conditions such as temperature, humidity, and water have to be met.[9,10] Therefore, how to design and control the environmental conditions, such as temperature and humidity, is crucial to inhibiting the growth and reproduction of fungi in order to prevent the damage to materials.

Temperature is critical for the growth and survival of fungi. Belli *et al.* tested the growth rate of *Aspergillus niger* under different temperatures by measuring the diameter of the colony every day and discovered that it grew quickly at the temperature between 30°C and 37°C.[11] Using the same techniques,[11] Plaza *et al.* discovered that *Penicillium* was able to germinate and grow between 4°C and 30°C, with the best growth at 25°C,[12] while Alwatban *et al.* found that *Cladosporium* grew quickly between 23°C and 25°C. Stevenson studied the germination behavior of *Eurotium halophilicum,* with the result that it could germinate between 20°C and 40°C, optimally at 30°C.[13] *Aspergillus*, *Penicillium, Cladosporium,* and *Eurotium* are four genera of fungi that are dominant on ancient leather artifacts, and their optimal temperature are summarized in Table I.

Relative humidity is particularly significant for fungal growth as well. Water might provide essential prerequisite for the growth and reproduction of fungi, as it could affect the amount of water available for the spore germination and growth of fungi.[16] Micheluz *et al.* found that in library bookshelves, a relatively closed environment would facilitate the germination of fungal spores due to the lack of ventilation and the condensation of water on the books during winter.[7] Additionally, vegetable-tanned leather is prone to fungal attack because of its more water-soluble

Table I
The optimal temperature of *Aspergillus, Penicilium, Eurotium and Cladosporium*.

Fungus	Found	Temperature	Reference
Aspergillus	Leather samples & air in the vicinity	30°C -37°C	5, 11
Penicillium	Air in the vicinity of leather samples	4°C-30°C, optimally at 25°C	5, 12
Eurotium	Leather samples	20°C-40°C, optimally at 30°C	5, 13
Cladosporium	Leather bindings	Optimally between 23°C-25°C	14, 15

nutrients for microorganisms, compared to the chrome-tanned leather. The latter is usually heavy oil and difficult to wet, making it less supportive of fungal growth. The ideal conditions for fungal growth include a relative humidity (RH) of 95-100% and a temperature (T) of 30°C, which is beneficial for the substantial fungal growth on the surface of the material.[10] Therefore, both guidance of Australian Institute for the Conservation of Cultural Material (AICCM) and American Institute for Conservation(AIC) recommend RH= 45%-55% and T= 15-25°C for preservation of ancient leather artifacts.[17] It is interesting to note that some xerophilic fungi, such as *Penicillium* and *Aspergillus halophilicus*, could still survive under relatively low temperatures (T= 23°C) and relative humidity (RH= 56.3%). In museum collection stage, the controlled temperature and humidity can be precisely maintained, while the fluctuations in these factors could still provide opportunities for the growth and reproduction of certain fungi, particularly for xerophilic fungi.[7]

The pH of the ancient leather artifacts and environment could affect the growth and reproduction of fungi as well. Most fungi could grow under a broad range of pH values, depending on the environment of germination and metabolic production of the fungi. Gock *et al.* studied the influence of pH on some xerophilic fungi (*Eurotium rubrum*, *E. repens*, *Wallemia sebi*, *Aspergillus penicillioides*, *Penicillium roqueforti*, *Chrysosporium xerophilum* and *Xeromyces bisporus*), and found that they could produce a range of acid by the anaerobic respiration of fungi. It was revealed that these fungi favored slightly acidic condition (pH=4.5-5.5) more than a neutral one,[16] making it easier for these fungi to settle on acidic materials like ancient leather artifacts. On the other hand, however, some early phase ammonia fungi (eg. *Amblyosporium*, *Peziza*, *Ascobolus*, *Tephrocybe*, *Coprinus*) favored the pH between 7 and 8, which was probably correlated to the soil pH where the fungi were sporulated.[18] Once buried in alkaline soil, leather artifacts might encounter these fungi.

Light is a key factor in the regulation of fungal metabolic pathways and is one of the many signals for fungi to perceive and interact with environment, thus affecting its behavior.[19] The structure in fungi responsible for the interaction of fungi with light is called photoreceptor, which is activated by light exposure and starts the signal pathway to arise the cellular response.[20] Among all the fungi studied, *Neurospora crassa* is the best known for deep investigation of the function of White Collar-1 (WC-1) and VIVID (VVD), which is the gene for the light sensing behavior.[20-22] Light might affect different aspects of fungal growth, including conidiation, germination, and pigment accumulation. Lee *et al.* found that when exposed to white, blue and red light, the activity of *Aspergillus oryzae* was greatly suppressed.[21] *Aspergillus fumigatus* was commonly found on ancient leather artifacts, while Fuller found that red and blue light had a strong negative effect on the germination kinetics,[23] as shown in Figure 1. Regarding the pigment accumulation, different fungi exhibit different behavior. Velmurugan studied five pigment-producing filamentous fungi and found that darkness might lead to the best pigment production,[24] which explained the reason why ancient leather artifacts buried deep under the soil still could not avoid discoloration. Fuller further proved that *Aspergillus fumigatus* could produce a lot more pigment in white or blue light than in the dark.[23]

Fungi on ancient leather artifacts

Fungi rely on the carbohydrates, fats, and proteins in ancient leather artifacts for metabolism and are commonly found in genera such as *Cladosporium*, *Rhizopus*, *Scopulariopsis*, *Aspergillus*, *Penicillium*, *Chaetomium, Candida, Alternaria, Phaeosphaeria* and *Eurotium*,[5,14,25] with the most abundant genera of *Aspergillus*,

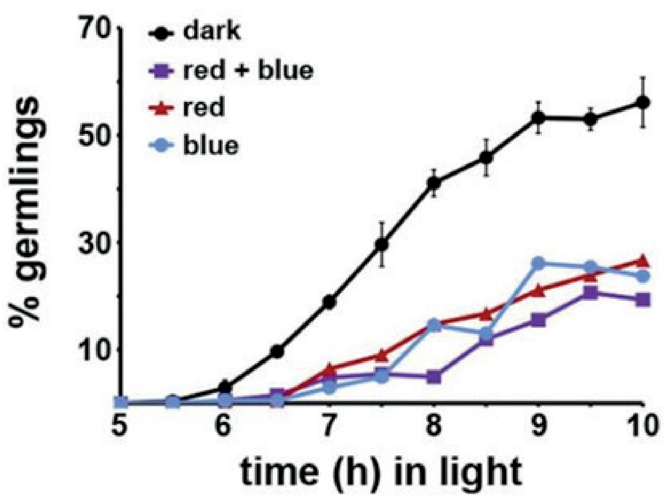

Figure 1. Germination rates of Af293 conidia under constant illumination conditions.[23]

Penicillium and *Eurotium*. Filamentous fungi and actinomycetes are the main microorganisms that cause the biodeterioration of ancient leather artifacts.[2] Compared to bacteria, even under lower temperature and humidity conditions, fungi have a stronger growth vitality and destructive potential. Mold might exist in the form of spores under conditions unfavorable for reproduction and start their life cycle at the proper conditions. In common sense, the contamination of leather by fungi appeared during the long time of storage or burial. However, the contamination during leather processing stages were consistent with the fungi found on ancient leather artifacts, as shown in Table II,[4,26] which proved that a considerable proportion of contamination was from leather processing stages instead of storage.[4] There is a plethora of microorganisms in animal hides from air, water, soil, and feces. These microorganisms exert minimal effects on the hide while the animal is alive, and they will proliferate rapidly after the animal is dead. The proteolytic bacteria in hides could adversely impact the soaking process and leather quality.[27,28] Despite the use of modern tanning methods, microbial contamination is still inevitable. Not to mention collagen-based artifacts that have been in different natural environments for many years, and even centuries.

Biodeterioration mechanisms of leather by fungi

The most common forms of spoilage in leather include the formation of discolored, non-bleachable spots, molds, and holes due to the degradation of leather components such as collagen and water-soluble substances, resulting in a loss of durability and rendering the leather. The collagen and water-soluble substances in the leather might act as essential nutrients for fungi during the proliferation and multiplication of microorganisms at proper relative humidity and favorable temperature.[10,29]

Various fungi, including *Cladosporium*, *Fusarium*, *Aspergillus*, *Penicillium*, and *Mucor*, have been known to attack leather and ancient parchment.[30] Fungi might cause various types of biodeterioration for ancient leather artifacts, which in turn leads to physical and chemical changes. Most reports about fungal deterioration of leather are focused on enzymatic degradation. The proteases, metalloproteinases, and other enzymes they produced could change the softness, properties and structure of leather.[31-33] Fungi such as *Aspergillus niger* and *Penicillium spp.* could produce cellulolytic enzymes to break down the collagen fibers, resulting in the loss of strength, mechanical stability, and flexibility of the ancient leather artifacts. This process could also

Table II

Fungi found on ancient leather artifacts associated with leather process.

Processing	Damage	Source of damage	Enzyme optima[26]	
Biodeterioration before tanning[4]				
Raw hides:	Discoloration	*Halophilic* and other bacteria	pH	Temperature
Green hides		*Micrococcus*		
Salted hides	Putrefaction	*Bacillus*		
Soaking:	Hairslips	*Pseudomonas*		
Liming	Perforation	*Proteus*		
De-liming		*Escherichia*		
Bating				
Biodeterioration after tanning[4]				
Chrome tanning	Colored stains	Moulds		
Wet blue	Mouldy smell	*Aspergillus*		
Vegetable tanning	Lower quality	*Penicillium*		
Fat liquoring	Downgrade of economic value of finished leather	*Paeccilomyces*	4-4.5	30°C
Drying		*Scopulariopsis*		
Finished leather		*Trichoderma*		
		Rhizopus and others		

cause discoloration, brittleness, and changes in the texture of the materials.[34] The fungi such genera as *Arthroderma*, *Aphanoascus*, *Onygena*, *Epidermophyton*, *Microsporum*, *Trichophyton*, *Chrysosporium*, etc., are highly specialized organisms biologically capable of metabolizing horny products of the epidermis with keratin.[35] Under the condition of low water activity, fungi are still able to degrade leather due to their high enzymatic activity and growth ability. In addition, by the accumulation, fungal metabolites would cause pH changes, further promoting the colonization.[29] Additionally, the emergence of various colored spots on materials is usually attributed to a phenomenon, known as foxing. This process involved the discharge and elimination of pigments and acids by fungi, which gave rise to the formation of brown-yellow specks on the surface.[9] The acidic nature of microbial metabolites could instigate the breakdown of collagen fibers and the depolymerization of collagen molecules, resulting in the chemical deterioration of leather, known as acid-deterioration or red-rot. This phenomenon was initially described by Michael Faraday in 1842.[29] Ancient leather artifacts suffered by red-rot typically exhibits a powdery surface, usually tinged with reddish or brownish hues, and a cracked grain structure with partial or total destruction of the grain. The acid metabolites of fungi could further damage the materials to form microcracks and holes.[36] Sometimes, fungal growth might even cause the complete destruction of the artifacts. Moreover, certain microorganisms, such as *Bacillus spp.*, could generate pigments to change the color and reduce the visual appeal.[37,38] Overall, the mechanism of microbial deterioration of leather is complex with various microorganisms and environmental factors. To avoid this deterioration, it is important to design and control the environmental conditions, with the consideration of specific types of microorganisms likely to colonize the leather.

The leather shoe dating back to the 11th-13th centuries was scrutinized by scholars hailing from Art University of Isfahan, Iran.[39] By SEM micrograph analysis, they discovered that hyphae had infiltrated the red stained segment of the leather, prompting the hydrolysis and subsequent flaking of the collagen fibers, thereby leading to the formation of cracks on the surface. The resemblance between this crimson stain and ret-rot was noteworthy, as ancient leather artifacts that underwent combination tanning of vegetable and alum exhibited analogous deterioration features.[39] According to Fontoura *et al.* discoloration caused by fungi might manifest in diverse hues contingent upon the fungal genus and the kind of leather studied such as pickled hide, wet-blue, and vegetable-tanned leather, as shown in Figure 2.[27] Elimination of such stains still pose significant challenges. The SEM microscopy unveiled a marked alteration in the layer structure of the leather. While the uncontaminated samples displayed a smooth and undamaged surface, with distinct pores and fibers, the infected samples exhibited damaged surfaces and irreparable harm. The appearance of variously colored spots stemmed from the discharge of water-soluble pigments by fungi, hydrolysis of fats and oils, and degradation of proteinaceous and hide substances.[27] Alicja *et al.* studied the microscopic morphological deterioration of leather. The leather samples were subjected to high humidity conditions, and after 19 months, their whole structure displayed severe decay. SEM analysis revealed that various microorganisms had solubilized the tanning aggregates encasing the collagen fibers. In addition, evident craters were observed near fungal spores, indicating that the spores could excrete substances capable of dissolving the tanning agent.[29]

Fungi might decolorize leather by attacking the dyes in leather too. The enzyme responsible for this decolorization is laccase.[40] There are various white rot fungi (WRF) that could excrete laccase, including *Dichomitus squalens*, *Ischnoderma resinosum*, *Pleurotus calyptratus*, *Pycnoporus sanguineus*, and *Trametes hirsute*. A new strain called *Trametes villosa* SCS-10 was found to be a significantly active strain in the biodecolorization of leather dyes. Among the strains frequently found on leather artifacts, *Penicillium oxalicum* SAR-3A was reported to degrade a broad spectrum of industrially relevant azo dyes,[41] while *Aspergillus flavus* was capable of decolorizing Azo (Acid red) and Anthraquinonic (Basic blue) dyes.[42]

Conservation and Restoration

Proper preservation and restoration techniques are essential for preventing and controlling fungal deterioration of ancient leather artifacts. Several strategies can be employed to achieve this goal. One of the most effective strategies is to design and control the environment, which involves maintaining optimal temperature and relative humidity levels in museums and archives. It can be achieved by using climate control systems, such as air conditioning and dehumidification systems.[6] Regular monitoring of temperature and relative humidity is crucial for identifying the changes of fungal growth. The standard relative humidity range of 50-65% recommended for artifact preservation in many American and European collections might encourage the further deterioration of degraded collagen in ancient leather artifacts. Therefore, it is recommended to store the ancient leather artifacts at a lower relative humidity of 30% with a cyclic variation of ±5%.[43] Another strategy for preventing fungal deterioration is the use of appropriate storage materials, such as archival-quality boxes and acid-free paper, which could help to prevent fungal growth and to minimize the damage to the artifacts.[44] When it comes to the restoration of ancient leather artifacts that have suffered fungal attack, proper restoration techniques are crucial. These techniques should be able to stabilize and reinforce the leather, preventing further damage and helping to

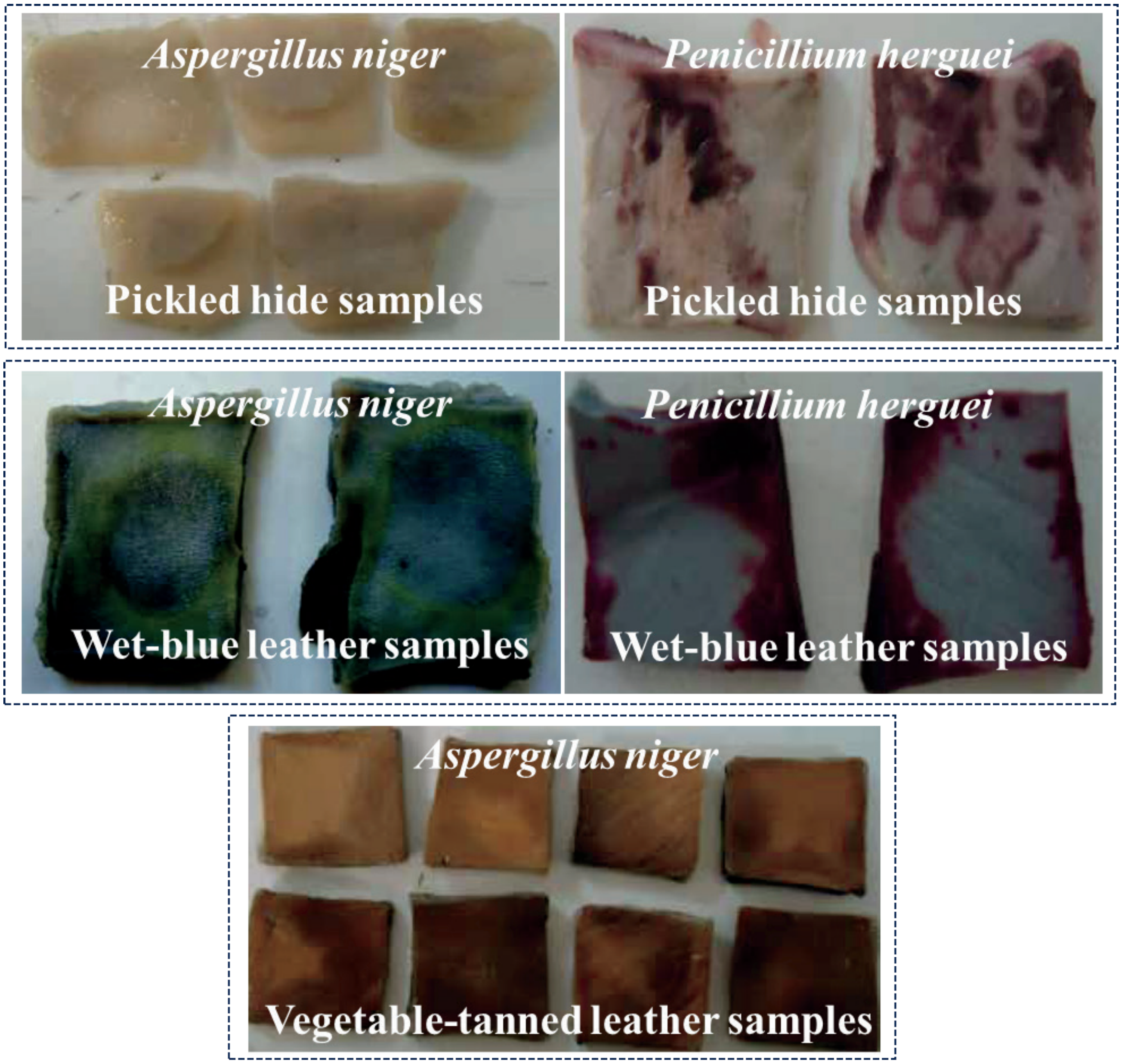

Figure 2. Stains and degradation of pickled hide samples, wet-blue leather samples, and vegetable-tanned leather samples degraded by *Aspergillus niger* and *Penicillium herguei*.

preserve the artifact's original appearance. Conventional methods such as solvent dehydration,[45] freeze-drying,[46] fat liquoring coating[47] and silicone filling[48] have been used, but they might have drawbacks over time, such as becoming hard, brittle, or sticky.[49] Biocides could be effective in preventing and controlling fungal growth, but special caution must be exercised in their use. Some fungicides and disinfectants might be harmful to the artifacts and further damage might be caused. Excessive use of fungicide might also lead to drug resistance.[50] As an alternative, irradiation has emerged as an important technique in the conservation of ancient leather artifacts. Gamma radiation might damage the DNA molecules in microbes, effectively preventing their growth, with little harm to the structure of leather fibers.[51,52] So, it is considered a safer and greener approach, compared to the one using biocides. By these strategies and techniques, it is possible to prevent and control fungal deterioration of ancient leather artifacts.

For the restoration of ancient leather artifacts, special materials with excellent properties might be used to stabilize their structure and increase their properties. Hydroxyapatite (HAp), commonly used as a bone substitute, is biocompatible and can form a cross-linked network structure with collagen, preventing deformation and improving the hydrothermal stability.[53] Nano-hydroxyapatite (nHAp) had good dispersibility because of the nanoparticles, which has been used to repair damaged artifacts, with the flexibility, compactness, and hydrothermal stability of collagen fibers increased.[54,55] Halloysite, a natural nanoclay, is a promising polymer filler because of its good biocompatibility, dispersibility, porosity, as well as high surface area. After dispersing in the polymer matrix, halloysite nanotubes (HNTs) could enhance the tensile strength. The potential of HNTs was demonstrated in the similar thermal stability and fiber cohesiveness in ancient binding leather and artificially aged leather, as well as in repairing fiber pores in ancient paper.[56-58] The current trend in restoring cultural relics involves the use of materials more compatible with similar composition, structure, and properties of leathers.[59] Zhang *et al.* utilized a reinforcement material for decayed leather, significantly improving its physical properties.[60] Nano-collagen produced by the use of chronoamperometry was reported promising in treating vegetable-tanned lambskin leather, with increased mechanical properties, elasticity, softness, and unchanged color.[61] The choice of treatment methods depends on factors such as the type of ancient leather artifacts, the extent of damage, and the desired outcome. However, special attention should be paid to the choice of repairing materials for cultural relic restoration. Further research is needed to explore new materials and techniques for long-term restoration of ancient leather artifacts.

Conclusion and outlook

Fungal deterioration of ancient leather artifacts poses a significant threat to valuable cultural heritage, especially those in museums and archives. Increasing attention has been paid in the restoration and preservation of ancient leather artifacts, and fungal deterioration has been studied with a growing understanding of the deterioration factors. The future research should be focused on the biodeterioration mechanisms and preservation strategies. With the advances in biotechnology and materials science, new and improved preservation methods should be provided for long-term artifact protection with reduced risk of fungal deterioration. However, challenges do still exist, and more effective methods are needed to monitor and control environmental conditions. Deeper and more specific understanding of the fungal growth mechanisms should be studied. Despite these challenges, the study on the fungal deterioration shows a positive outlook due to the recognition of cultural heritage's importance and commitment to preservation. Further research is needed to better know the fungal growth mechanisms and affecting factors for the development of more effective preservation strategies for ancient leather artifacts.

Acknowledgements

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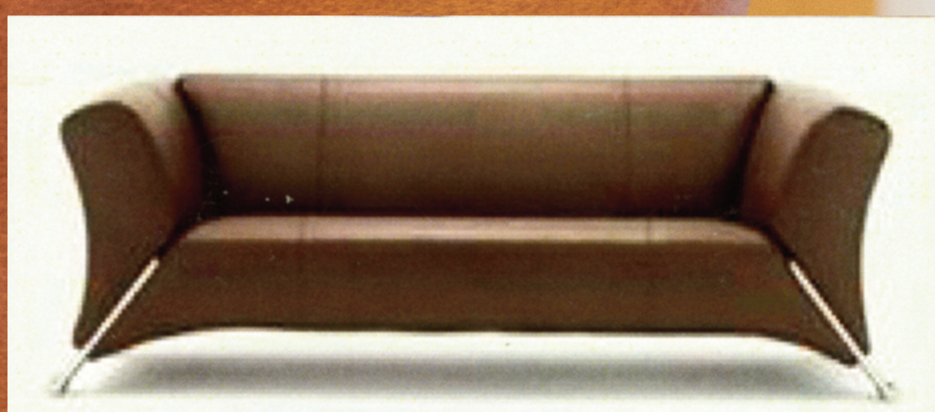

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Deepak N. completed his M.Tech in leather technology. He carried out his M Tech project at the Inorganic Physical Chemistry Laboratory, CSIR-CLRI under the supervision of Dr. N. Nishad Fathima, Chief Scientist. His research interest includes synthesis and characterization of nanoparticles and their application in leather processing. He is also interested in developing antimicrobial compounds for finishing processes.

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