NOVEL ADVANCED-COATING COMMERCIALIZATION

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Abstract

Antimicrobial coatings nowadays play a vital role in several industries and their implementation is becoming increasingly necessary, especially in the *healthcare* and in the *food industry*, as will be discussed later in this thesis.

This project presents some innovative antimicrobial coatings and provides a step by step management plan for their commercialization in various industries. A review of the spray-coating techniques and equipment will also be present, followed by the realization of a sprayer prototype to be used to perform tests and experiments in the laboratory.

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Keywords

Antibacterial, Antimicrobial, Bacteria, Biofilm, Coating, Commercialization, Food, Management, Medical, Prototype, Solution, Sprayer, System.

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Introduction

This introductory chapter will present the current threats and concerns present in both the healthcare and the food industry, to highlight the urgency to find a solution and to introduce antimicrobial coatings as a possible one. Advanced antimicrobial technologies will be here contextualised, before being analysed in depth in the remaining chapters of this work.

Antimicrobial coatings in the food industry

In the *food industry*, safety and quality of food products are topics which have been consistently raising concerns among the consumers, especially in today's world, demanding for perfect aliments and accustomed to higher and higher quality standards. This consumer behaviour, coupled with poor handling and transportation of food, leads to a global wastage of 1.6 billion tonnes of nourishments every year (Goldenberg, 2016). A change is clearly needed: as the global population grows and the third world countries still face hunger, the most straightforward solution seems to be the full exploitation of the existing resources, attainable by minimising the wastages. Food preservation techniques, such as the application of *edible antimicrobial coatings*, can help in this direction and be beneficial for the environment, which suffers from the production and the disposal of non-consumed food.

Antimicrobial coatings in the medical industry

Concerning the healthcare, one of the main challenges that has manifested in the last decades is the number of post-operation infections generated by the presence of pathogens onto surgical devices and medical protheses. Standard antibiotics are no longer effective for treating some types of pathogens, as they have developed resistance mechanisms over the years. For this reason, bacteria keep proliferating undisturbed onto prothesis and devices until they form biofilms, becoming particularly difficult to eradicate. Such phenomenon has been creating concerns, as new drugs are constantly needed to cope with genetically mutated human pathogens, who have now become immune to the existent treatments.

Alternative antimicrobial agents have been researched and tested in the recent times to tackle this problem. Among these, Silver (Ag) leads the market, as its antimicrobial activity has been proven against several bacteria species; while other non-metallic agents (e.g. Selenium), have been recently arousing interest among the scientists and will also be discussed in this paper.

Significance of the work

The present paper is of great significance to the healthcare industry and to the medical patients who undergo surgeries involving the implantation of a prothesis, as the antimicrobial technologies that will be presented are meant to be a solution to the recurring problem of implant-associated infections.

This study is also relevant to the food industry, as its findings would benefit both the consumers, who would be able to rely on the food they eat thanks to the presented preservation technologies, and the environment, which would benefit from the reduced disposal of food.

Aims

The aim of this research is to provide a description of both the current antimicrobial technologies on the market and some more innovative solutions, which are still at an experimental stage.

A market analysis will also be performed in order to provide insights about the current leaders in this market and to draft a management plan to guide the commercialization of the analysed technologies.

Report Outline

This *introduction* will be followed by a comprehensive *literature review*, composed by a variety of high-quality and mostly recent studies on the topics of interest. This will be divided in 3 sections:

- Antimicrobial coatings in the food industry
- Antimicrobial coatings in the medical industry
- Spray coating technologies

The literature review will lead to an *experimental component*, meant to describe the realization of the prototype of a spray coating system, to be used in the laboratory to perform experiments.

Lastly, the *conclusions* that this research came to, will be summarised in a final closing chapter.

SECTION 1: Food industry

The introduction of edible antimicrobial coatings in the food industry has been proven to prolong the shelf-life of several foods and offers many advantages in terms of both quality and nutritional values. Edible films and edible packaging in general, are also a good option to reduce the use of synthetic films and plastic packaging (Bourtoom, 2008). This makes them a positive influence for the environment. Besides the reduction of plastic disposal, edible coatings may represent one of the biggest contributors to the reduction of food wastages, and hence deserve to be thoroughly analysed.

Materials

The literature offers a number of options in terms of materials that can be used for food-coating applications. Some examples are provided below:

Proteins, for instance, acting as a moisture barrier, represent a relatively cheap option for the food industry. Being hydrophilic, however, they are not ideal to form coatings. To face this issue, hydrophobic additives can be mixed with the solution (Embuscado, 2009).

Cellulose based coatings represent another possible choice: a tendency of fruits and vegetables to preserve their qualities has been noticed, after these coatings were applied.

Prickly pear cactus mucilage has been used as a food coating to increase strawberries shelf-life without altering their original taste and colour (Del-Valle, 2005). This solution is usually chosen for its low cost (El-moniem, 2012). The method used for the application of such material is called *dipping* and consists in the immersion of the commodity in the solution, followed by draining and forced-air drying.

The effect of *aloe vera gel*, applied as a coating on cherries, has also been studied by Valverde in 2005: a delay in the decay process was registered as a consequence of the application of the gel.

Selenium's antioxidant properties have been analysed in a 2016 study conducted by Vera et al. In this study, solutions containing Selenium nanoparticles (SeNPs) were used on packaging materials to assess any potential effects on the shelf life of hazelnuts. SeNPs solutions were found to have higher antioxidant effects compared to their equivalent blank solutions. The findings of this study lead the authors to the conclusion that SeNPs are suitable to be used in food applications to improve the storage conditions and prolong the life of groceries, without compromising their perception and appearance.

Chitosan is another material suitable for the realisation of biodegradable coatings (Singh & Ray, 1998). The recent literature proved it able to extend the shelf-life and maintain the nutritional values of foods such as: grains, fish, but mostly fruits and vegetables (Sinha, 2014; Aranaz et al., 2009), by inhibiting microbial activities.

Among all these available options, **chitosan** stands out as one of the best, thanks to its excellent ability to form films and to its biochemical and anti-fungal properties (Ghaouth et al., 1991; Zhang, 1998; Jiang, 2001). For this reason, it will be discussed more in detail in the next section.

Chitin and Chitosan

Chitin is the second most abundant natural polymer after cellulose (Synowiecki, 2003; Xu et al., 2013). It is mostly found in the exoskeleton of crustaceans, such as shrimps, crabs and lobsters, but is also present in some fungi (Shiekh, 2013) and insects, as shown in table 1.

Crustacean exoskeletons, due both to their high percentile chitin content and to their abundance, are the main chitin source. To extract chitin, it is necessary to demineralise and deproteinise these shells. Chitin possesses some interesting features, such as: non-toxicity, biodegradability and biocompatibility, but it has the downside of being insoluble in water.

Organisms	Chitin content (%)	References
Crustaceans		
Nephro (lobster)	69.8[a]	Synowiecki & Al-Khateeb, 2003
Euphausia superb (krill)	24[a]	Arbia et al., 2013
Homarus (lobster)	60–75[a]	
Crangon crangon (Shrimp)	17.8[a]	
Lepas (goose barnacle)	58.3[a]	
Chionoecetes opilio (Crab)	26.6[a]	
Insects		
Blatella (cockroach)	18.4[a]	Kaur & Dhillon, 2013
Coleoptera (ladybird)	27–35[a]	
Diptera	54.8[a]	
Pieris (butterfly)	64.0[a]	
Bombyx (silk worm)	44.2[a]	
Galleria (wax worm)	33.7[a]	
Fungi		
Aspergillus niger	42.0[b]	Synowiecki & Al-Khateeb, 2003
Penicillium notatum	18.5[b]	
Penicillium chrysogenum	19.5–42[b]	
Saccharomyces gutulata	2.3[b]	
Mucor rouxii	9.4[b]	
Siboglinidae	33[c]	Crini, Guibal, Morcellet, Torri, & Badot, 2009
Cnidaria	3–30[d]	Crini et al., 2009
Brachiopod	4–29[a]	Crini et al., 2009
Mollusks	6–40[e]	Crini et al., 2009
Squid, cuttlefish, octopus		

Table 1: Sources of chitin and relative percentile content (Hamed, 2015. Industrial applications of crustacean by-products (chitin, chitosan, and chitooligosaccharides): A review, p.41).

Chitosan is a polysaccharide obtained through a chitin alkaline deacetylation process. Its standard form is not soluble in water, but only in acidic solutions (Sashiwa et al., 2002; Zhang et al., 2010). However, its structure is often modified and made water soluble, widening its fields of application. Its use in coating applications allows to enhance food properties, by adding functional ingredients, vitamins or flavours to the coating solution (Ribeiro and others 2007; Falguera and others, 2011; Avena-Bustillos and McHugh, 2012; Zhao, 2012).

Most of the industries which use chitosan for their final products, are chitosan manufacturers as well. But it is possible to purchase the product from other sources, if needed. Globally, the main chitosan manufacturers are found in Asia: Japan leads the production, followed by China (Global Market Insights, 2016).

Chitosan applications

As previously mentioned, chitosan's ability to form films, together with its antibacterial properties, make it particularly suited to the *food* and *supplements* industry. Chitosan can in fact be used for: edible coatings, thickening and lipids binding for cholesterol reduction (Rinaudo, 2006).

Chitosan, due to its non-toxicity, biocompatibility and biodegradability, can also be used in a variety of other fields, like:

- *agriculture*
- *water & waste treatment*
- *biomedical* (e.g. sutures, dental implants)
- *beauty products*

(Rinaudo, 2006).

Safety and regulations

Many studies have been carried out in the last three decades to assess the safety of chitosan supplementation, all with similar results: positive outcomes were often achieved in terms of health, with few to none minor adverse effects. In a study carried out in 2016 by Amaral, for instance, 13 patients with severe allergies to shrimps, were given wine treated with chitosan. The result was the following: "None of the 13 shrimp allergic patients and none of the control participants had immediate or late-phase reactions to any of the wines" (Amaral, 2016. Safety of chitosan processed wine in shrimp allergic patients, p.462).

Despite these studies, the use of chitosan in food has not been globally approved yet (Kanatt, 2013), due to the fact that countless modifications to its principal structure can be done, making it impossible to effectively assess all the risks that one chitosan compound may have. For this reason, it is not possible for the Food and Drug Administration (FDA) to *globally* declare chitosan as "Generally Recognised as Safe (GRAS)" (Kean, 2010). In each study involving chitosan, it is in fact necessary to know the exact formulation of the compound used, and to assess it individually for the grant of the GRAS status.

The next section provides a summary of the legal status of chitosan in different countries.

Chitosan legal status

Chitosan has been granted the *Generally Recognised as Safe* (GRAS) status in the ***United States*** in 2001 by the *Food and Drug Administration* (FDA).

Europe, on the other side, still seems to be conservative from the food innovation point of view, and only few European countries have been somewhat open to this kind of technologies: Poland and Norway produce it (Kumar, 2000), while Italy and Finland commercialise it in the supplement industry (Kean, 2010).

The reason why chitosan cannot be freely used for food applications in Europe is that the European regulation requires to have a complete toxicological analysis of the product to mark it as safe, even when the quantities used are far below the hazardous threshold (Restuccia, 2010).

Some ***Asian*** countries such as China and Korea, similarly to European countries, commercialise chitosan as a supplement in capsule form (Kim, 2014), while others, such as Japan, do not have restrictions in using the product as a food additive (Fang, 2015).

Australia also allows chitosan commercial production (Kumar, 2000) and dietary supplementation.

Chitosan market

Active packaging materials, including edible coatings, were first introduced in the market in the 1970s by Japan. Their diffusion in the United States and in Europe started only 20 years later and has been constantly growing since (Restuccia, 2010).

Chitosan market is following the same trend: a lack of suppliers is expected by 2018 (Global Industry Analysts Inc., 2014) and its market size is forecasted to reach USD 7.9bn by 2024 (Global Market Insights, Inc., 2016). However, Kim (2016) points out how chitosan market is affected by the seasonality factor, as it needs fish by-products as raw materials. To make this market more stable during the year and less influenced by seasonality, new chitin sources are being searched in silk-worms, honey bees and other insects, as well as in mushrooms, moulds and bacteria.

So far, the main chitosan manufacturers and suppliers worldwide are Asian countries, Japan being the biggest, with over 90% of the total production (Palpandi et al. 2009). However, today's changing scenario and growing demand is offering a change of perspective: western countries might soon start taking advantage of their raw materials and compete with the abovementioned Asian countries in this field.

New potential global suppliers

The vast majority of chitosan produce derives from the fishing industry, and in particular from shrimp wastes, which constitute about 20% of the total weight of these crustaceans (Gómez-Ríos, 2017). The Latin-American region is one of the biggest shrimp suppliers, with over 40% of the exportations worldwide. It could become a global producer and exporter of chitosan, considering the need for new suppliers and the increasing demand for the product. To make this possible however, it is necessary for these countries to implement the right technologies to be able to exploit the wastes produced during the shrimp-processing operations and use them for chitosan production. This would help their economy thrive, as high-quality chitosan is currently sold for USD 50 to 100 per kilogram (Gómez-Ríos, 2017).

Post-harvest food processing

Losses

Bio-coating technologies would be beneficial in food processing, as the advancement of technology in a country has great impact on the extension of the post-harvesting losses (Parfitt, 2010). According to Wisniewski (1992), the percentile losses of fruits and vegetables, subsequent to their harvesting, are approximately 24% in the United States, and about the double in underdeveloped countries.

The main factor that spoils the crops and causes these losses is fungal activity. For this reason, the application of *antifungal coatings* such as chitosan would inhibit the decay process of the crops and significantly decrease the amount of wastes.

Post-harvesting wastes however, are not only due to external factors such as the inefficiency of the supply chain and natural decaying of fruits, but are also due to "post-consumer waste": a phenomenon present mostly in the industrialised countries, where consumers tend to dispose groceries even when still edible, as the value of food is perceived as constantly decreasing due to both the increase of disposable incomes and the global competition in the food industry, which makes groceries cheaper and cheaper (Parfitt, 2010).

Edible coatings can be the right way to reduce both these types of wastages: first in the supply chain, by helping protect the food from bacterial and fungal threats, and second in households, by allowing the commodities to maintain a good appearance over time, hence reducing its disposal.

Mechanization of post-harvest processing

For the reasons mentioned above, the food industry should consider an upgrade in the post-harvesting processing, and in particular the extensive application of edible bio-coatings. The literature on the topic offers practical examples of how improvements in the food processing bring several advantages: in a study carried out by Abass (2017) it is analysed how the mechanization of the postharvest processing of cassava, leaded

African villages to a 49% reduction in poverty. This was achieved thanks to less wastes and higher volume of production, leading to an increase in incomes and a decrease in unemployment.

Implementation of the technology: financial aspects

The implementation of a spray coating technology implies a ***cost*** due to the additional equipment required. It is in fact necessary to:

- Expand of the facility;
- Extend the conveyor system;
- Buy and install appropriate atomisers, containers for the chitosan solution, and ovens to speed up the drying process.

The cost of such equipment can vary considerably, depending on the type of machinery employed and on the size of the facility.

With the exclusion of the facility enlargement, it is possible to make a rough estimation of such cost, after having selected the exact equipment to be used:

Rubber belt conveyor systems can be found of many different types, and cost about US $350 to $700 per meter of length. However, if the conveyor system is initially designed considering the presence of a spray coating system, as opposed to extending it afterwards, it is possible to find cheaper options.

Regarding the *atomisers*, prices are not available in the online catalogues. It is necessary to directly contact the suppliers and inquire. Obviously, the price will be dependent both on the quality and the quantity of the nozzles to be employed.

Tanks for the solution and *ovens* for the drying process also require to be accurately selected, to be able to estimate their cost. Ovens, for instance, have a wide price range: usually US $600-8,000, but, in some cases, up to US $35,000.

Besides these expenses, industries need to take into consideration other variable costs, such as: increased electricity usage, maintenance of the additional equipment and the purchase of chitosan itself. For this reason, it is necessary to make sure that the yield derived from the sales of better quality products and from the reduction in wastages, exceeds the additional expenses, or at least balances these, allowing to reach a break-even point.

An estimation of the extra costs due to an increase in the electricity consumption and to the maintenance of the spray coating equipment, cannot be done uniquely, as these costs are heavily dependent on the location of the facility and on the magnitude of the additions in terms of equipment.

The price of chitosan, on the contrary, is retrievable: *chitosan powder* for food applications can be bought online from Chinese suppliers. Its price varies depending on the quality, origin source and ordered quantity; it is usually in the range US $30-150.

The *automatization* of the spray-coating equipment and its integration in the production line would be a good solution for the food industry, as it would increase the revenues by delivering higher quality products and reducing the wastes, without heavily affecting the production time. This automation can be realised through programmable sprayers (Tharanathan, 2003), ovens and conveying systems.

All information about prices have been retrieved online from the following links:

- https://www.ebay.com.au/sch/i.html?_odkw=conveyor+system&_osacat=184169&_from=R40&_trksid=p2045573.m570.l1313.TR0.TRC0.H0.Xrubber+belt+conveyor+system.TRS0&_nkw=rubber+belt+conveyor+system&_sacat=184169).
- https://www.alibaba.com/trade/search?fsb=y&IndexArea=product_en&CatId=&SearchText=drying+oven+for+food+industry
- https://www.alibaba.com/trade/search?fsb=y&IndexArea=product_en&CatId=&SearchText=chitosan+food+grade

Management concepts

The value of the final product is mainly dictated by its quality, which is dynamic and ever changing, especially in perishable commodities like groceries. Quality is associated not only with the product, but also with services, processes and people involved in such processes. For this reason, to make sure that the quality is kept high enough to meet and exceed customers' needs and expectations, the post harvesting processes of fruits need to be as fast and delicate as possible, and the management of these processes must be particularly scrupulous.

The total-quality management

The rationale behind this management approach is that the quality should be continuously improved by monitoring all its aspects: products, services, processes and people. Firms which adopt this approach tend to compete in the global market and thrive, as opposed to smaller firms, where high quality standards are not seen as such a relevant matter (Goetsch, 2014).

The total quality method is composed by various principles, all aiming at better quality, solid education and training. The few principles that this project focuses on are:

- Continual process improvement
- Prioritising of quality
- Customer focus, through statistical analysis/benchmarking

All the principles listed above help to keep high quality standards and make *sustainable* the *supply chain management* (SSCM).

The total quality management might hinder profits in the short term, but increases them over time. Long term profit should be the prime objective of the firms implementing this approach. This management methodology would be a perfect fit for the food market, as quality and safety are vital in this industry (Manning et al., 2005) and consumer requirements are continuously evolving.

RFID

Another aspect that the supply chain management has to deal with in the food industry, is the tracking of commodities (Wang et al., 2009): several studies have been carried out on this topic, many of which seem to focus on Radio Frequency Identification (RFID). Li et al. (2009) believe that RFID will be able to revolutionise the supply chain management in the near future, by providing a better traceability of the inventory and a faster and more accurate stock control. This in turn, will help reduce the cost of both storage and handling (Loebbecke and Palmer, 2006). With RFID it is possible to reduce barcode reading-time. This is because radio-frequency readers, by working with electromagnetic waves, are not sensitive to dirt and bending, do not need line of sight with the tags, and can read multiple tags simultaneously (Karkkainen, 2003).

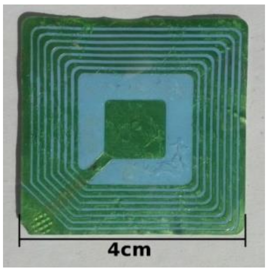

Figure 1: RFID tag.

The implementation of this identification system in the food industry implies important capital gains and savings, which, according to Karkkainen (2003), sum up to over USD 11 million a year, mostly due to a reduction in both inventory loss and operational costs. Many foods need to be processed under controlled temperatures and in high amounts. For this reason, even very small percentile increases in efficiency bring significant reductions in cost. A real example of the use of RFID technology on food can be found in a case study of the Italian cheese company “Parmigiano Reggiano”, which was summarised by Regattieri et al. (2007): The company decided to implement the technology for traceability purposes, by adding a mere 0.5% to the original cost.

In this way, the food was always localised and the whole supply chain was informed about the delivery route whenever needed. By using RFID, the company could see tangible improvements in different areas, such as production, delivery, customer satisfaction and effectiveness of communication between supply chain parties, all leading to a better overall efficiency.

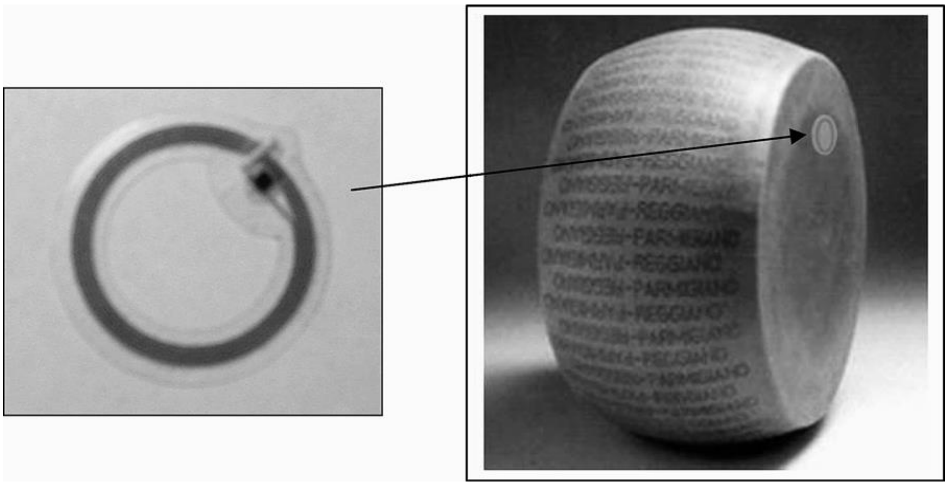

Figure 2: One whole Parmigiano Reggiano cheese (33-35 kg) can be localised by using one only tag (Regattieri et al., 2007, p.353).

Other studies, contrarily, found that RFID implementation in the supply chain management leads to non-promising results, and doubt that the benefits offered by such technology would be able to pay off the initial investment (Ha et al., 2013). This indicates that RFID might not be essential to some companies as they do not respond in the same way as others (such as Parmigiano Reggiano) to this identification system.

SECTION 2: Medical industry

Antimicrobial coatings are becoming more and more necessary not only in the food industry, but in today's medical implants as well, since device related infections are in an uptrend (Holinka, 2013). This can be attributed to the increasing number of surgeries performed every year and to the fact that more bacteria are becoming harder to eradicate with conventional methods.

Antibiotics have become ineffective against several bacteria, and finding an effective replacement or additive to these has been the aim of many scientists. That's why, in the past few years, several attempts were made to create new antimicrobials. Many studies showed promising results, though mostly on a short-term basis, and rarely at a clinical stage (Cloutier, 2015).

Silver

Silver has so far been the most popular element implemented in coatings as an alternative antimicrobial agent. Its use has been widely investigated by the scholars and its effectiveness in inhibiting the formation of biofilms has been shown in many studies. Ag-nanoparticles coatings are in fact able to stop the proliferation of different types of antibiotic resistant bacteria such as Staphylococcus aureus and Pseudomonas aeruginosa (Verma, 2017). Furthermore, studies have revealed that Silver shows synergistic features when coupled with antimicrobials (Cloutier et al., 2015), making it an ideal supplement to standard antibiotics.

Ag has been shown to work in synergy not only with antimicrobial drugs, but with metals too: a 2013 study carried out by Samani et al., revealed that solutions containing Silver and Zinc ions outperformed their individual counterparts in terms of antimicrobial properties, with the highest bactericidal effects obtained at Zn: 1.5 wt% and Ag: 0.6 wt%, indicated as "Z15A6" in the graph below.

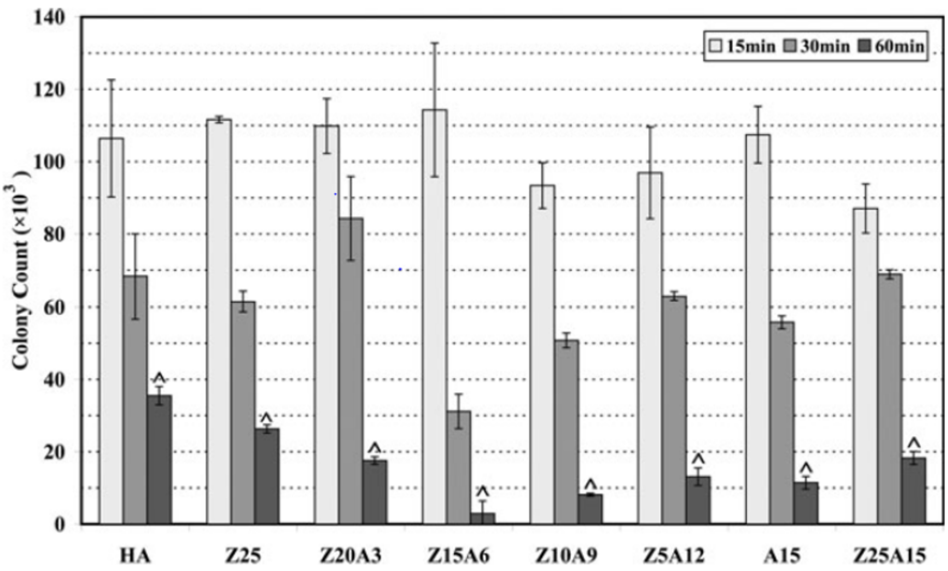

Figure 3: Antimicrobial solution used vs. Colony count after 15, 30 and 60 minutes of incubation (Samani et al., 2013, p.228).
Note: HA stands for Hydroxyapatite, a calcium phosphate-based coating.

The presence of Zinc in Ag coatings, moreover, promotes the growth of bone cells and makes coatings less expensive. Besides this, Zn is considered one of the most important trace elements for the human body, thanks to its countless essential functions. This suggest that Zn-doped Silver coatings would be preferable compared to simple Ag-based coatings, as they are characterised by better antimicrobial properties, higher biocompatibility and lower cost (Samani et al., 2013).

Despite its popularity, Silver has shown to be ineffective in some applications, as reported by Tran and Webster (2013): studies in fact showed that implementing Ag coatings on catheters did not inhibit bacteria proliferation, demonstrating Ag unable to prevent infections associated with these implants. The extensive use of Ag as an antimicrobial agent, moreover, has the potential to generate unwanted outcomes. The literature offers a few possible effects that might derive from the metal's broad implementation, some of these are: pathogens' adaptation to Silver, interference with other antimicrobials and cytotoxicity to some cells (Verma, 2017; Romanò, 2015). These potential side effects have been one of the reasons why researchers are constantly trying to come up with new antibacterial agents and formulations.

Selenium: a valid alternative

One of the elements that have been in the spotlight during the last decade is Selenium (Se). This trace element, similarly to Ag, shows remarkable features in terms of antimicrobial/antioxidant activity and exceptional biocompatibility in humans. When compared to commercial Silver-coated polymers, Selenium nanoparticles-coated PVC was shown to be a more effective bactericidal against Staphylococcus aureus (at least in the short term), proving to be an ideal candidate in the medical field for the prevention of implant-related infections (Tran and Webster, 2013). Another recent study carried out by Biswas in 2018 compared once again the antibacterial efficacy of Ag and Se solutions, but this time on chitosan scaffolds to be used for the treatment of chronic wounds. The two solutions were tested against three types of antibiotic resistant bacteria: Staphylococcus aureus, E. coli and Methicillin-Resistant S. aureus (MRSA). The study concluded that both solutions were highly effective against all three species of bacteria, however, the Ag solution appeared to be cytotoxic to the mammalian cells used in the experiments, while the Se solution did not interfere with these, suggesting that humans might show better tolerance towards this latter solution.

Se intake is not simply tolerated by humans, but plays an important role in our health, as it provides several benefits to the immune system, helps prevent cancer and detoxifies our bodies from heavy metals (Stiefel, 2016).

Selenium to stop cancer

The cancer inhibiting effects of Se coatings on orthopaedic applications have been investigated in an *in vitro* study conducted by Tran et al. in 2010. In this study, Titanium substrates were coated with Se nanoclusters and the activity of both cancerous and healthy osteoblast cells was monitored and confronted to the one of uncoated Ti substrates. The results showed that the density of healthy cells barely changed over time in the control sample, while the cancerous osteoblasts proliferated. The substrates coated with Selenium, on the other hand, showed an increase in normal cells density and nearly constant density values for the cancerous cells. As graphically reported by the following figures.

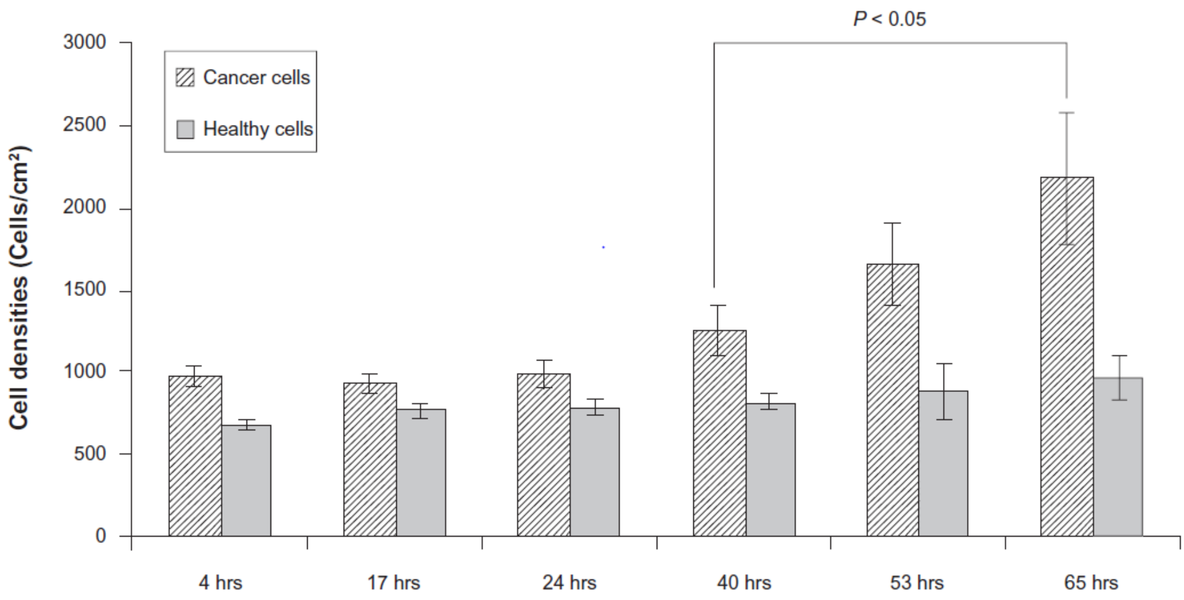

Figure 4: Densities of cancer cells and healthy cells on control Ti substrate after 4, 17, 24, 40, 53 and 65 hours after culturing (Tran et al., 2010, p.356).

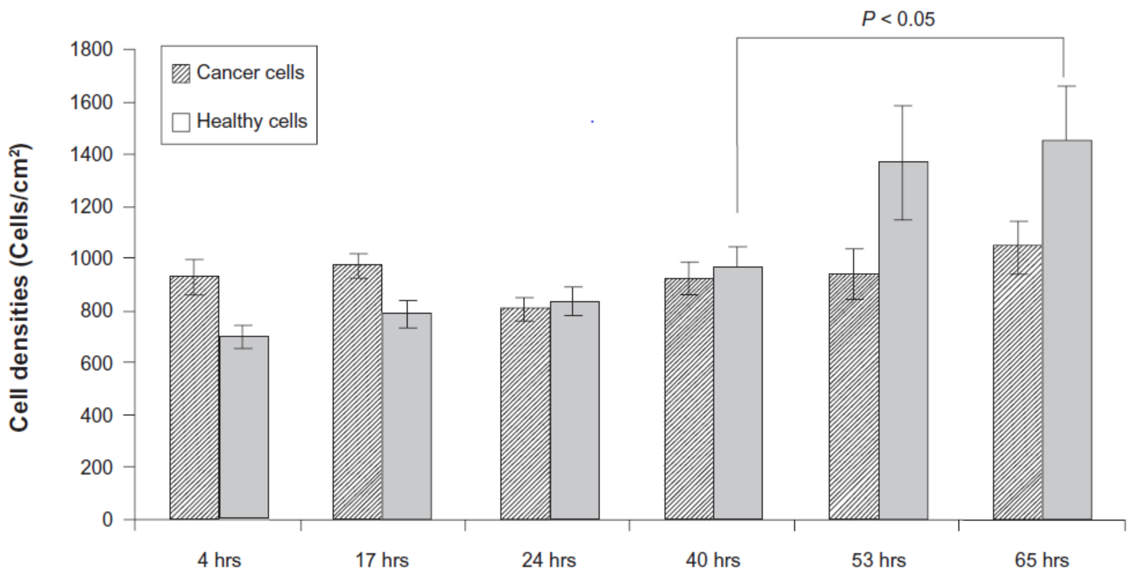

Figure 5: Densities of cancer cells and healthy cells on Se-coated Ti substrate after 4, 17, 24, 40, 53 and 65 hours after culturing (Tran et al., 2010, p.357).

These results are particularly relevant to the orthopaedic industry, as they could contribute to the production of anticancer implants.

Another study by Holinka et al. (2013) showed that coating Titanium discs with sodium selenite helped decrease the attachment of antibiotic resistant bacteria S. aureus and S. epidermidis onto the discs with a concentration-dependent fashion, while keeping unchanged the growth rate of osteoblast cells. These results imply that Se is biocompatible and non-cytotoxic, and show that Se coatings in different forms and compositions offer several benefits for prosthetic applications.

As pointed out by Romanò et al. (2015), the methods currently used to prevent infections, even though helpful in reducing the occurrence of such events, are not enough to completely eradicate them: periprosthetic joint infections keep affecting patients, creating several concerns in the healthcare system.

Coating technologies seem to be the solution to this problem; however, they have to meet several strict requirements before being widely implemented as a replacement of the current prevention methods. Some of these requirements are:

- Safety and efficacy over both short and long-term
- Non-cytotoxicity
- Non-interference with osteointegration
- Non-interference with the implant's mechanical properties
- Inexpensiveness
- Non-induction of resistance mechanisms

Selenium coatings, according to the available literature on the topic, meet most of these requirements (except for the long-term safety and efficacy, due to the lack of adequate studies) and seem to be one of the most appropriate technologies to face the issue of device associated infections.

Selenium: more applications

Besides its implementation in the healthcare and in the food industry, as already discussed, Se has the potential to be used in many other applications. An example is its implementation in contact lenses, meant to improve the lenses' safety and promote the health of the cornea. Se coatings have in fact proved to be able to reduce the bacterial colonization, without having any adverse effects towards the eye (Mathews, 2006).

A 2015 study showed that coating paper towels with SeNPs inhibited the growth of four antibiotic resistant bacteria: Staphylococcus aureus, Staphylococcus epidermidis, Pseudomonas aeruginosa and Escherichia coli, with bacterial density reduction rates ranging from 57.52% to 92.16% after the first 72 hours of exposure (Wang, 2015).

The graphical results obtained in this study are reported in the pictures below.

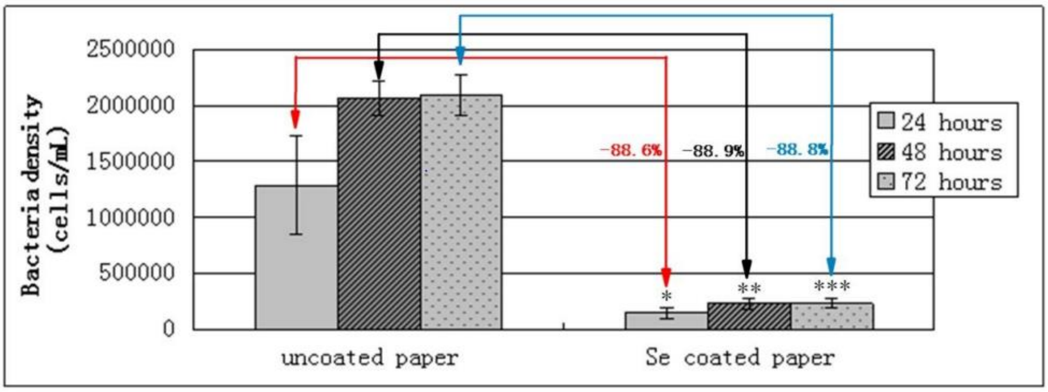

Figure 6: S. aureus density on both uncoated and coated paper towels after 24, 48 and 72 hours (Wang, 2015, p.88).

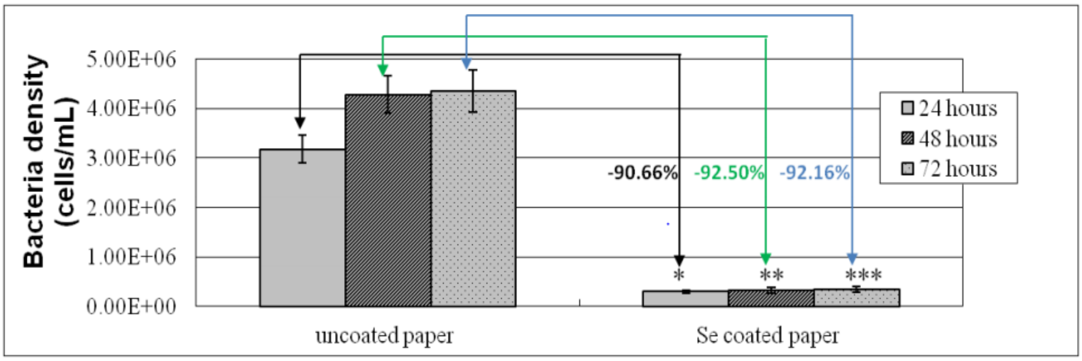

Figure 7: S. epidermidis density on both uncoated and coated paper towels after 24, 48 and 72 hours (Wang, 2015, p.89).

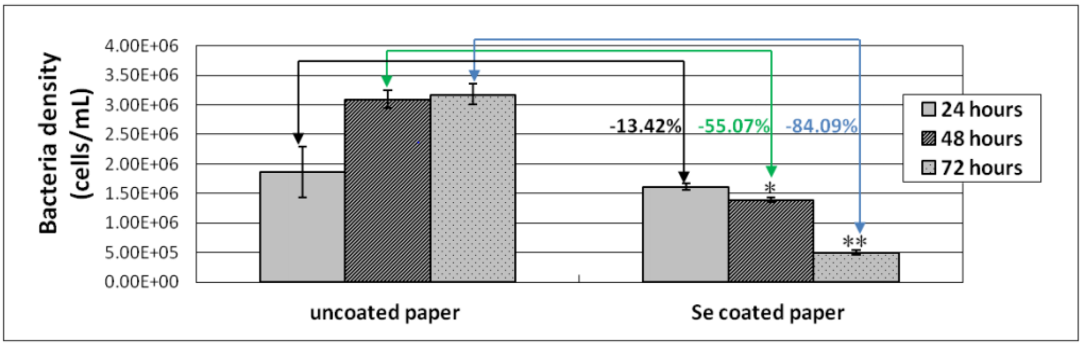

Figure 8: Pseudomonas aeruginosa density on both uncoated and coated paper towels after 24, 48 and 72 hours (Wang, 2015, p.91).

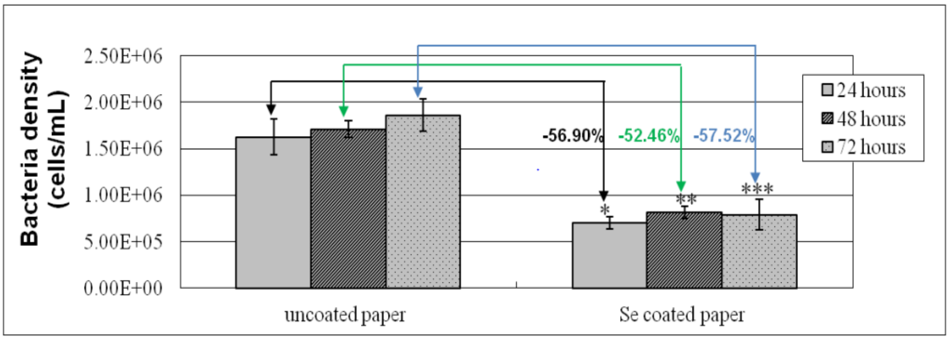

Figure 9: E. coli density on both uncoated and coated paper towels after 24, 48 and 72 hours (Wang, 2015, p.93).

These results imply that the application of SeNPs coatings onto paper towels could be implemented in public restrooms to highly reduce the presence of germs, and consequently decrease the probability of disease transmission and infections, typical of public environments.

The findings of the mentioned study are particularly interesting, as they can be replicated in other paper-involving applications, such as food packaging and water purification units.

Market Analysis

The development of new antibiotics has become too expensive and time consuming to keep up with the formation of new bacterial resistance mechanisms. Biswas et al. (2018) stated that the introduction of the latest classes of antibiotics dates back to 2003. For this reason, the market of non-drug antimicrobial coatings has been noticeably growing over the years, from an estimated figure of USD 1.5 Billion in 2014 to about the double in 2018. This market, as previously mentioned, is currently dominated by Silver, mostly in form of nanoparticles. Ag has been widely implemented as an antimicrobial agent in several fields, most extensively in medical and alimentary applications (Mishra, 2014). This trend however might change in the near future, considering the drawbacks that Silver and metals in general present. One of the main concerns when it comes to metals is their toxicity, which becomes a serious problem with excessive use.

Non-metal alternatives (e.g. Se) have a huge potential of becoming leaders in the antimicrobial market, as they possess similar functions to their metal counterpart, but carry only minimal toxicologic drawbacks and present several health benefits.

Selenium Manufacturers

The list of companies provided below has been retrieved by some recent market reports and is meant to give a general overview of the currently biggest Selenium manufacturers.

- *American Elements:* The company, based in California, offers an extremely broad catalogue with nearly every element and for a very large number of applications, making it one of the world's largest manufacturers in its field.
- *Hindalco Industries:* By producing mostly aluminium, copper and chemicals, the Indian company with presence in four continents manages to be considered one of the top selenium producer, earning a spot in this list.
- *Mitsubishi Materials Corporation:* The Japanese company, aside from selenium, specialises also in the production of cement and several metals.
- *Sumitomo Chemical:* Another Japanese company which produces chemicals for different applications (e.g. pharmaceutical, alimentary, energetic).
- *Behn Meyer:* The company was founded in 1940 in Singapore by two German men, and is now globally recognised as a major producer of chemicals.

These are just some of the globally recognised selenium manufacturers reported by the most recent market research reports on the topic. It can be noticed that Japan dominates the list with two spots out of five (The Market Reports, 2018; Arun, 2018; Rashmi, 2018; Technavio, 2017).

Chemical Coatings Producers

For what concerns chemical coatings, the market is led by American and European Companies, according to a report published by Business Wire in September 2017. The following companies represent the major competitors in this industry:

- *BASF:* A German company specialised in coatings and several other chemical products with sales for 64.5 billion euros in 2017.
- *Akzonobel:* A Dutch firm known for its paints, coatings and chemicals, which totalised 9.61 Billion euros in 2017.
- The American *DowDuPont* with 48.16 Billion USD in 2016.

- *PPG Industries:* Another American company specialised in coatings. Its revenues for 2015 amounted to 15.33 Billion USD.

Commercial interest

As anticipated, several are the industries that could benefit from antimicrobial coatings, considering the many application fields of these technologies. Among such industries, one of the most important in terms of size and financial capabilities is the *healthcare*, where antimicrobial coatings could represent a solution to inhibit the spreading of germs and bacteria and could be successfully implemented not only on surgical devices, catheters and prothesis, but also on hospitals' heating systems and highly touched surfaces.

Other public facilities such as *schools* and *airports* would also benefit from the implementation of coated heating systems in terms of safety and air purity (Martin, 2016).

The *food* industry is another huge stakeholder: as already discussed in this thesis, antimicrobial coatings can be found in food packaging or onto food surfaces to prevent the proliferation of microorganisms. Another possible use of antimicrobial coatings in this industry is onto the surfaces of restaurants' kitchens, which are very prone to develop biofilms and need to be constantly disinfected.

A smaller but growing industry that is likely to express commercial interest towards these types of coatings, in particular Selenium ones, is the *solar energy* industry. Selenium in form of quantum dots can in fact be coated onto the surfaces of photovoltaic systems to increase their efficiency (Wang, 2015).

Within this list of industries that would benefit from antimicrobial coatings and might consider their implementation, *footwear* is possibly the most bizarre but, given its global market size of about USD 230 Billion, should definitely not be excluded. Some studies have assessed the antimicrobial and antifungal effectiveness of coatings containing Silver nanoparticles applied on leather shoes. The tests performed showed that the implemented coatings highly reduced both fungal and microbial activity, representing a good solution to preserve shoes and cope with the challenging conditions they are exposed to, i.e. lack of ventilation and humid environment, ideal for microorganisms to live and propagate (Sánchez-Navarro - 2013).

Management Concepts

TQM

The Total Quality Management (TMQ) concept, as previously discussed, is characterized by several factors; all these factors emphasise on better relationships with both suppliers and customers, training of employees and superior quality (zero-defects mentality), as reported by Powell (1995), and so can be applied to the many of the aforementioned industries as well.

TQM focuses on continuously improving the offered product or service, by reviewing all the processes in the supply chain, prioritising the quality and focusing on the customers through statistical analysis and benchmarking. The final aim of this approach is a long-term success for the firm.

Some of the industries listed above as possible antimicrobial coatings users, especially the footwear and food industries, are likely to implement TQM to gain a competitive advantage over the industries that do not use it. The application of antimicrobial coatings integrates perfectly in a TQM approach, as discussed below.

In the *shoes industry*, the application of antimicrobial coatings can be seen as a TQM implementation because it leads to a better-quality product, characterised by a higher level of hygiene and a longer life. The focus on the customer, typical of a TQM approach, is in this case represented by the minimization of the discomfort experienced by the user.

In the *food industry*, similarly, TQM allows to achieve premium-quality groceries with a longer shelf life and better appearance. The focus on the customer consists in the better preservation of the food's nutritional values, while the environment is taken care of through the reduced food wastages, achieved thanks to slower decay processes, typical of coated groceries.

SWOT analysis

Some critical aspects need to be considered to have a complete overview of the analysed technologies. These are: strengths, weaknesses, opportunities and threats. This type of analysis is widely known as SWOT, and will be presented in this section of the project.

Strengths

Antimicrobial coatings have demonstrated to be highly effective in preventing the growth and propagation of bacteria onto surfaces. This is a strength per se, but what adds value to this strength is the fact that the use of these coating will reduce the need for antibiotics, which have been used extensively over the past decades, causing many bacteria to develop an antibiotic resistance and grow stronger.

When narrowing the analysis to Selenium coatings only, another strength emerges: their low toxicity. Selenium is in fact considered an essential trace element for the human body for its nutritional properties, and its moderate use is recommended by the FDA, as a too low assumption is usually associated with a decrease in the functionality of the immune system, reduced cognitive functions and can even lead to mortality in extreme cases.

Selenium has also been shown to be able to inhibit the growth of tumours, while simultaneously promoting the growth of healthy osteoblast cells (Tran et al., 2010).

Weaknesses

Silver coatings carry two main issues with them: their *cytotoxicity* to mammalian cells (Biswas et al., 2018) and their still obscure *interplay with bacteria and cells* (Wang, 2015). Toxicity problems are mostly attributed to metals, but it has been shown that heavy doses of non-metallic materials such as Selenium salts can be toxic as well.

Selenium's antimicrobial effectiveness, moreover, has not been proved on a wide spectrum of bacteria with different sizes and features yet. There is a possibility that some bacteria and viruses might be immune to Selenium, making the coatings ineffective in some applications. More *in vivo* research on a wider variety of microorganisms and bacteria is needed to confidently start implementing Selenium coatings in different areas.

Opportunities

Some of the external factors that represent opportunities for the antimicrobial coatings under analysis are: *device-related infections* and the phenomenon of *antibiotic resistance*. These coatings can in fact help reduce the number of post-operatory infections by inhibiting the proliferation of pathogens and the formation of biofilms onto medical protheses. This would lead to a significant decrease in both costs and mortality associated to such events.

In the U.S. alone, 88,000 people die every year because of surgical infections and the cost to deal with the during and post-surgery contamination is estimated between USD 35.7 billion and USD 45 billion (Wang, 2015). These figures only refer to the United States and would be significantly higher when considered worldwide. A global implementation of non-drug antimicrobial coatings in medical application would heavily impact hospitals and patients in a very positive way.

More studies still need to be carried out to assess the effectiveness of Selenium against different types of microorganisms, however, from the literature already available on the topic, Se coatings show huge potential and could represent the solution to the problem of bacteria resistance. Some Se compounds have been shown to have bacteria inhibitory effects very similar to the ones of penicillin, meaning that they could help reduce the use of this antibiotic and, consequently, the resistance phenomenon that some bacteria developed against it.

The fact that bacteria resistance develops more quickly than the introduction of new classes of antibiotics (Biswas et al., 2018) gives another huge opportunity to these technologies, as a solution to this problem will soon be needed.

Threats

One of the concerns of antibacterial Silver coatings is that their extensive implementation could cause the development of some sort of resistance, similarly to what happened to antibiotics. Negative environmental impacts are also one of Silver's potential threats and should be carefully considered when choosing the materials for the coatings (Molling, 2014).

Not only metals carry concerns in the antimicrobial field: Selenium coatings have not been studied appropriately over the long term and, even though their effectiveness and inertness is promising according to the scholars, it is necessary to point out that the studies that have been carried out on Selenium as an antimicrobial agent on medical applications only focus on the short term efficacy of these treatments, leaving an unknown regarding the possible events that could manifest after the implantation of the prothesis. One of the concerns that arises when considering a long-term use of these coatings is their potential cytotoxicity to some cells. (Tran & Webster, 2013).

All these grey areas represent *threats* for these technologies, in terms of both *reduced trust* towards them and potential *non-acceptance* from the healthcare system and some governments.

Management plan

This section contains a management plan ideated to provide guidance to *(i)* cope with the threats that the novel coatings under analysis must face and *(ii)* help promote their commercialization.

The following steps have been created by following solid management principles (e.g. Total Quality Management, Lean production and Supply chain analysis) and are thought to be a good starting point to achieve the desired outcome:

1. For these novel coatings to be implemented among various industries, it is necessary to *perform more studies* on the *long-term* effects, as pointed out by Tran et al. (2013). These long-term analyses should include both laboratory experiments (in vitro) and, most importantly, clinical trials (in vivo), in order to examine the effects of selenium coated implants in humans over the long-term.

2. Positive outcomes from these studies are expected, considering the promising results obtained in the many short-term in vitro studies already published. Hence, from a managerial point of view, the second step towards these coatings' commercialization in several industries would be to *activate campaigns* to raise awareness on the efficacy and safety of such technologies, promoting their acceptance.

3. Once the solution to commercialise has become publicly trusted and generally recognised as safe, the managerial department should start its *research of clients*. In other words, a *supply chain analysis* should be performed to find and attract the industries that might manifest interest towards antimicrobial Selenium coatings. The product should be promoted by emphasising on the social and economic benefits that would result as a consequence of its implementation. Here are some points to draw attention to, given as an example:

   - Medical system: reduction in the number of victims of device-related infections; reduced costs associated with the treatment of infections.

   - Food industry: increased safety associated with microorganism reduction; preservation of nutritional value; positive environmental effect due to reduced food waste.

4. The last step of the proposed management plan is to *maintain contact with such industries*, to receive feedback in order to improve the coatings and tailor them for every single industry. This way of managing the commercialization of these coatings, will allow to meet the needs of different clients.

SECTION 3: Spray-coating

The materials chosen for the solution to be applied onto the implants, groceries or commodities in general, together with the selected coating method, influence the performance of the films obtained. Coatings exist of different types and can be realised in many ways. Common coating methods include: dipping, foam application and spray coating. This last is in general preferred in applications where thinner layers are required, but it does not guarantee the same level of homogeneity as the other techniques. Nevertheless, studies found that spray-obtained coatings, even though less homogeneous and thinner, presented antimicrobial capabilities comparable to the ones obtained with the other methods. With spray coating, it is also possible to reduce cross-contamination (Andrade, 2012). For these reasons, spray coating has been selected over the other coating techniques and will be dealt with in this project.

Spray coating – working principle

Spray coating, unlike the other mentioned methods, allows to choose the thickness of the layer to depose and is suitable for large surfaces. If the coating must be performed on more than one side of the same product, however, it is necessary to perform a second operation, after having coated and dried the first surface.

The image below represents the structure of an industrial spray system for coating applications.

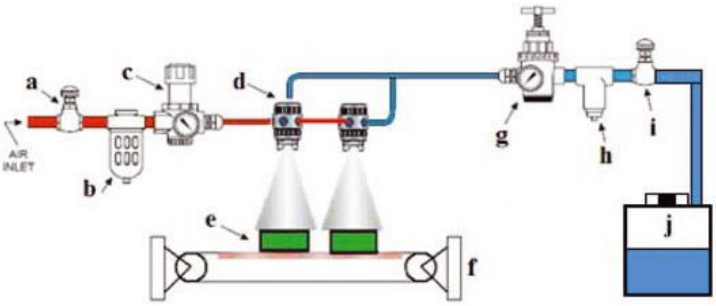

Figure 10: Sketch of industrial spray system, comprising shut-off valves for both air and liquid, air filter, gauges, nozzles, a conveyor belt and a tank (Andrade, 2012, p.330).

The presented working principle allows to use less solution compared to other coating technologies (Baldwin, 2011). According to Turton (1999), the dual-fluid atomiser is the most widely used in coating applications. In this system, the solution (1^{st} fluid) is atomised, either internally or externally, by the pressurised gas (2^{nd} fluid).

Temperature and pressure of the fluids are constantly controlled, as they influence the quality of the spray, as summarised in the table below.

Spray characteristics	Increase in operating pressure	Increase in specific gravity	Increase in viscosity	Increase in fluid temperature	Increase in surface tension
Pattern quality	Improves	Negligible	Deteriorates	Improves	Negligible
Droplet size	Decreases	Negligible	Increases	Decreases	Increases
Spray angle	Increases then decreases	Negligible	Decreases	Increases	Decreases
Capacity	Increases	Decreases	Full/hollow cone – increases Flat – decreases	Depends on fluid sprayed and nozzle used	No effect
Impact	Increases	Negligible	Decreases	Increases	Negligible
Velocity	Increases	Decreases	Decreases	Increases	Negligible
Wear	Increases	Negligible	Decreases	Depends on fluid sprayed and nozzle used	No effect

Table 2: Influence of different parameters on spray (Andrade, 2012, p.330).

Spray nozzles

It is possible to choose from a number of nozzles to realise the coatings. A first classification divides the atomisers into two categories:

- Hydraulic nozzles
- Pneumatic nozzles

Hydraulic nozzles

Hydraulic nozzles have four pattern types to choose from:

Hollow cone

In this configuration, the produced aerosols are present only in the outer surface of the conical spray shape, giving origin, as the name suggests, to a hollow cone. This spray shape guarantees the smallest droplet size possible (Schick, 2008), but, to guarantee sufficient coverage, up to four nozzles are necessary (Hall, 2012).

Full cone

Droplets are homogeneously distributed throughout the volume of the cone generated by the atomiser. This pattern type allows to cover large surfaces and is largely used in the food industry, because of its homogeneity.

Flat spray

This spray shape, being a sort of 2D layer, produces a line on the surface it is applied onto. This pattern is ideal in applications where the commodity moves relative to the nozzle and a high impact is required (Hagers, 1997).

Solid stream

This pattern consists in a stream of solution, which starts breaking into aerosols only after leaving the atomiser.

The four types of hydraulic nozzles are represented in the image below.

Figure 11: Spray patterns. (a) Hollow-cone; (b) Full-cone; (c) Flat-spray; (d) Solid stream (Andrade, 2012, p.331).

Pneumatic nozzles

This second classification of atomisers consists in pneumatic nozzles. In these, a high-pressure gas (usually in the range 4 to 5.5 bars) is used to atomise a solution and depose it onto a surface. Depending on the nozzle design, the mixing solution-gas can be realised either internally or externally to the atomiser, as shown in Figure 12.

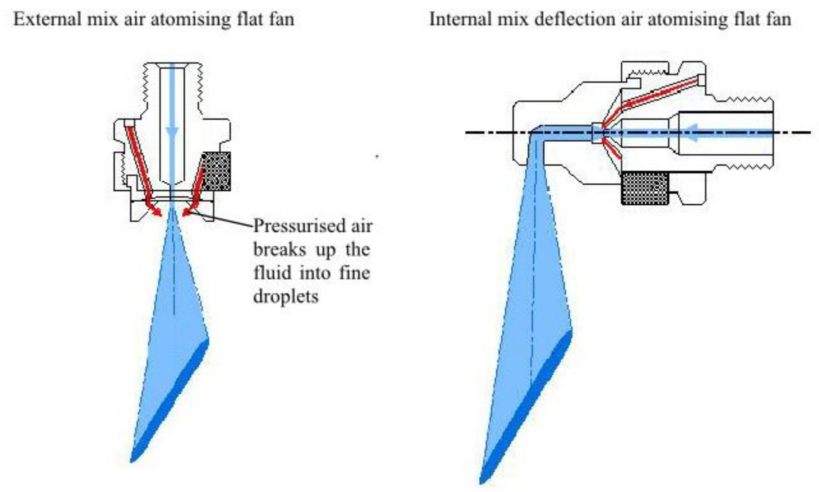

Figure 12: External (left) vs internal (right) mixing nozzles (SNP the Spray Nozzle People, retrievable at: http://www.spray-nozzle.co.uk/spray-nozzles/air-atomising-nozzles/external-mix-variant).

Between the two atomiser types, internal mixing nozzles usually generate the smallest aerosol sizes. External mixing nozzles, on the other hand, by generating the droplets externally, are less subject to clogging. For this reason, they are more suitable for thick solutions (Hagers, 1997; Hede et al., 2008). Pneumatic nozzles are more expensive to operate compared to their hydraulic counterparts, due to the energy and to the equipment required for the compressed gas. They are also more complex to control automatically and to maintain (Andrade, 2012).

Other spray systems are currently being studied to increase the performances of the coatings. Details about their features, however, are out of the scope of this project.

Coverage area

This section is meant to define a relation between the coverage area (the surface covered by the solution sprayed from the nozzle) and other parameters of the spray system, such as: distance between nozzle and surface, nozzle size, spray aperture angle, etc.

Spray shape

First, to make assessments about the coverage area, it is important to point out that atomizing nozzles can generate different spray shapes, as described in the previous section. The three most common ones are shown again in the image below.

Figure 13: Full cone, flat fan and hollow cone. Respectively from left to right.

Aperture angle

Besides the shape of the spray, it is essential to know its aperture angle. Note that it is assumed to have the nozzle positioned vertically, perpendicular to the surface to coat, not tilted (by referring to the real model built in the laboratory). The only angle to be considered is therefore the spray aperture angle.
This angle depends on the type of nozzle, on the gas pressure and on some features of the solution to spray. It can be found in the literature that, for *common atomizing nozzles*, the aforementioned angle ranges between 20° and 60°.

If it is necessary to have a higher flexibility in the system, for example to be able to cover different surface sizes, a *hydraulic nozzle* should be employed. These nozzles in fact have a much wider range of spray angles, which goes from 15° to 110°. However, the only shape they allow is the flat fan.

A third type of nozzle, which is one of the most used because of its versatility, is the *swirl nozzle*. It can be used in several fields, such as cleaning, cooling, washing and chemical applications.
The typical shape of the spray in these nozzles is conical, either full or hollow.
In full cone-shaped spray systems, swirling is used to help make uniform the distribution of mist inside the cone. While in the hollow cone-shaped sprays, very thin layers of fluid form inside the nozzle chamber, thanks to the centrifugal force generated by the swirling motion; subsequently, these layers exit the nozzle as fine droplets with the shape of a hollow cone.
Swirling nozzles can have different designs. Here are the two main configurations:

- *Axial flow*: the fluid enters the nozzle with a direction parallel to the cone;
- *Tangential flow*: the fluid enters the nozzle with a direction perpendicular to the cone.

The droplet size is bigger in this last configuration, while the cone angle is more stable.
In the axial flow configuration, the spray aperture angle is variable and shows weak fluctuations, but it is never higher than 90°.

Calculation of the coverage area

For the final calculation of the coverage area, some assumption will be made in order to make this theoretical model as close as possible to the real system used for the experiments.

For this reason, a standard atomizing nozzle has been selected, with a constant size in the range 1 to 3 mm and a full cone-shaped spray which will cover a circular area (fig.13, picture on the left). The aperture angle of the cone in this type of nozzles, as previously seen, ranges between 20° and 60°. We will assume a 60° aperture for this analysis (30° on each side of the vertical line), which is the closest to the one represented in fig.13 for the full cone (again on the left).

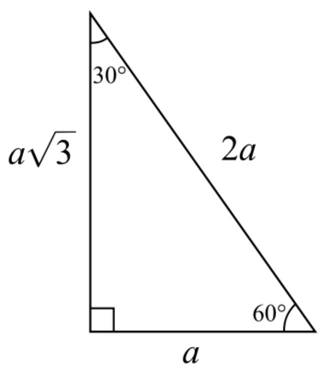

Figure 14: Spray aperture angle, one side. Note that the nozzle is supposed to be at the top of the triangle, and that the real spray shape will be the cone obtained by revolving the above image around its vertical axis.

It is also assumed to have an average distance of 15 cm between the nozzle and the substrate (indicated as $a\sqrt{3}$ in fig.14), since it normally varies in the range 10-20 cm.

The following list summarises all the assumptions made:

- Nozzle type: standard atomizing nozzle
- Nozzle size: 1 to 3 mm
- Spray shape: full cone
- Spray aperture angle: 60°
- Distance nozzle-substrate: 15 cm

The coverage area can now be calculated:

As already mentioned, the shape of the deposed atomized solution on the substrate is circular, since we have a conical spray shape. This means that the surface is simply measured as:

$$S = \pi * a^2$$

Where:

- *S*: surface
- *a*: radius of the circle

Since π is a constant known coefficient, the only unknown to be found is the radius a, which can be visualised in fig.14 as the base of the depicted triangle.

To find a, it is necessary to go back to the previously assumed distances and dimensions and find the distance nozzle-substrate, which is 15 cm. By referring again to fig.14, we can see that this height is equal to $a\sqrt{3}$, for the given setup and angles. So, we have:

$$a\sqrt{3} = 15\ cm$$

$$a = \frac{15}{\sqrt{3}}\ cm$$

$$a = 8.66\ cm$$

Now that the radius has been calculated, the surface calculation is straightforward:

$$S = \pi * a^2 = 235.61\ cm^2$$

Influence of height variation on coverage area

If a different coverage area is required, it's sufficient to slightly change the distance between the nozzle and the plate, since the covered surface is proportional to the square of such height. This implies that a consistent change can be obtained with a small variation in this distance. Some different set-ups are given below:

Let's start by reducing the distance nozzle-substrate of 5 cm.; this means that our parameter $a\sqrt{3}$ will now measure 10 cm.

Here is the new setup:

$$a\sqrt{3} = 10\ cm$$

$$a = \frac{10}{\sqrt{3}}\ cm$$

$$a = 5.77\ cm$$

For the surface, we obtain:

$$S = \pi * a^2 = 104.72\ cm^2$$

It can be noted how a 1/3 decrease in height more than halves the coverage area.

Let’s now see the effect of a change in the opposite direction, the distance nozzle-plate will now be increased by 5 cm. compared to the initial setup.

Setup 3:

$$a\sqrt{3} = 20\ cm$$

$$a = \frac{20}{\sqrt{3}}\ cm$$

$$a = 11.55\ cm$$

Leading to:

$$S = \pi * a^2 = 418.88\ cm^2$$

In this case, a 1/3 increase in height almost doubled the surface.

It is worth pointing out that these calculations give as a result the theoretical coverage area, not the actual one. In fact, in real systems, the covered area deviates from the theoretical values (real surfaces are smaller than calculated ones), especially when the nozzle is far from the substrate. This phenomenon is represented in the figure below.

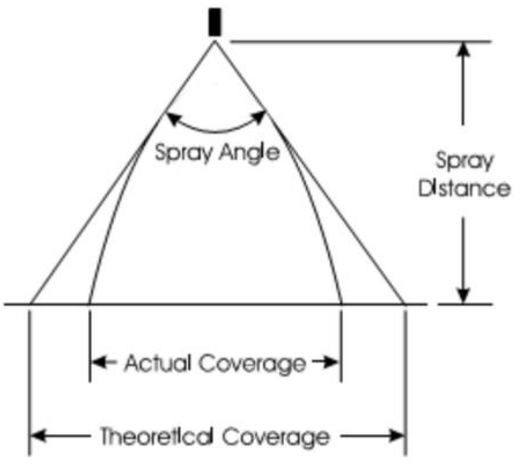

Figure 15: Actual vs theoretical coverage area (Relab Spray & Purification Technology Ltd.).

SECTION 4: Experimental component

Real prototype

A real spray-coating system for the application of the studied antimicrobial coatings was developed in the laboratory throughout this project. The prototype is composed by a nozzle having two inlet ports: one for the pressurized gas and the other for the solution to be sprayed. This nozzle was connected to the solution tank and to the gas through hoses, valves and adaptors, as described more in detail in the following sections. The limited availability of tools and equipment, however, limited the quality of the prototype, which needed constant modification and improvements.

This practical component of the project focused on *(i)* the assembling the system, *(ii)* performing experiments, *(iii)* improving the prototype and *(iv)* solving of the few problems encountered in the laboratory, such as:

- Lack of support for the atomiser
- Water leakages from the nozzle orifice
- Decoupling of the pressurised gas hose from the connector with high pressures

All these problems were successfully addressed, but, as expected, other minor issues emerged (e.g. air leakages), as discussed later on in this paper.

This practical section was accompanied by adequate research to find the suppliers, select the right components to use for the assembling of the system and to get a glimpse of other prototypes to emulate and use as a reference. Data was collected through tests and experiments, and successively compared to the theoretical results calculated in the previous section. The setup of the physical prototype is described below.

Fastening of the nozzle

A threaded rod was used to attach the nozzle to the top of the chamber (after drilling a hole on this last) and to keep it in the correct position during the spraying operations. A picture of this section is shown below.

Figure 16: Threaded rod and nozzle used in the prototype.

Positioning of the solution reservoir

Several trials were done to find the most suitable elevation for the water tank, in order avoid leakages or other issues. The best solution was found by replacing the pressure hose and mounting a clamping system for such hose; this avoided the decoupling of the hose when high gas pressures were used. The adoption of such solution made it possible to increase the air pressure up to values high enough to suck the water from the reservoir, which was finally positioned below the nozzle level: this eliminated the leakages from the nozzle orifice, which were due to the continuous gravity-driven water flow.

Replacement of the gas hose

The hose for the pressurised gas was replaced with a 13mm clear flexible vinyl tube. The chosen tube was thicker than the previous ones used for the trials, this guaranteed a better fitting with the connectors and allowed the use of hose clamps to reinforce the couplings hose/adaptors. Such tube was connected to the pressurized air source on one end and the to the nozzle air inlet port on the other.

Mounting of a pressure meter

A *JFlex* indicator for the pressure (shown in the pictures below) was connected to the gas hose, to be aware of the pressure used during the experiments. To do this, a T-connector was attached to the hose on two ports and to the pressure meter on the third one, so that the pressure inside the vinyl tube could be read on the indicator. 304 grade stainless steel hose clamps were also used, to ensure strong connections.

Figure 17: Pressure meter sub-assembly.

Another similar tube with a slightly smaller diameter (the one connected to the right port of the nozzle, reported in figure 18) was used to drive the solution (water, in the tests done in the laboratory) to the nozzle liquid inlet port. It was connected to such port on one end to go directly to the solution tank. The system, does not use a pumping mechanism to carry the solution to the nozzle: the water is in fact sucked towards it by means of the pressured air entering the nozzle from the opposite port.

Figure 18: Spraying System Co. Air atomising nozzle used for the experiments.

Note the hose clamp (on the left), mounted to prevent a decoupling of the 13mm air hose from the brass connector. A clamping system was, on the contrary, not needed for the solution hose: high pressures are never reached there and a tight fitting with the adaptor is always guaranteed, being the hose 7mm wide.

Experiments and Analysis of the results

After the system was set up and worked correctly, some experiments were carried out to test the prototype and to compare the actual results with the theoretical ones, previously calculated.

Experiment 1: Air pressure vs solution flow rate

Due to the lack of a pumping system, the solution flow rate in the system is strictly related to the pressure of the gas pumped in the nozzle: the water is sucked out from the reservoir, thanks to the void created inside the solution hose by the pressurised air flowing in the nozzle.

What can be expected from this experiment is a variation of such flow rate as a reaction to a variation in the air pressure. Several measurements were done to verify this hypothesis and analyse such relationship, as reported below in the *results* section.

Results and Analysis

It was found that the fastest flow rate obtainable for the water, flowing on a vertical pipe with a diameter of 7mm, corresponds to an air pressure of 0.6 bars, which resulted to be also the minimum required to start driving the liquid out of the reservoir for the given hose size.

By slowly increasing such pressure up to 0.95 bars, the fluid inside the hose was still driven to the atomising unit, but its speed decreased proportionally to such increase in pressure.

At 0.95 bars, an interruption in the upwards motion was registered and the solution stayed in equilibrium inside the vertical hose. With a further increase in the air pressure, the water motion started to revert, driving the solution back to the tank. This happened for any pressure in the range 0.95 to 2.8 bars (as tested in the lab).

Pressures above 2.8 bars lead to excessive air leakages from the seals in the T-connector (as explained in the *issues* chapter) and have been avoided for safety reasons and because they are outside the scope of this experiment: the aim was in fact to analyse the relation between the air pressure and the suction rate of the solution; the two most critical pressure resulted to be 0.6 bars and 0.95 bars: considerably lower than the 2.8 bar threshold.

Obviously, as the water tank is elevated and the liquid hose is inclined from the vertical position, the suction process worked better: the less vertical distance the water has to travel, the more rapidly it flows inside the hose; since the energy that needs to be spent to face the gravity force and drive the solution to the nozzle becomes lower and lower.

Experiment 2: aperture area vs distance nozzle-substrate

Different *"area vs distance"* measurements were taken in order to detect a possible bias from the theoretical values. To do this, the nozzle was positioned at different heights (10, 12.5, 15, 20 and 25 cm) above a sheet of paper, laid on a plane surface. The sheet of paper, replaced after each test, was used to measure the diameter of the circle generated by the sprayed solution. Through the diameters, the coverage areas were successively computed.

Theoretically, the radius of the circle formed by the sprayed solution can be calculated by simply applying a trigonometric equation: it is in fact equal to the distance nozzle-substrate multiplied by the tangent of half the spray angle, as explained in the picture below.

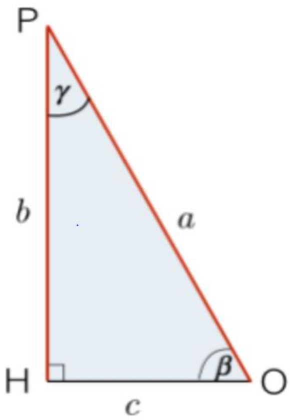

Figure 19: Rectangle triangle (Ricci, 2016. I triangoli rettangoli).

The angle γ in the picture indicates the semi-angle of the spray, as the above rectangle triangle represents only half of the cone; the base c (segment <u>*HO*</u>) is the radius of the circle whose area we want to measure, while the side b (segment <u>*PH*</u>) is the distance between the nozzle and the substrate.

By knowing γ and b it is possible to calculate c through the following formula:

$$c = b * tan(\gamma)$$

(Relazioni fra elementi di un triangolo rettangolo dipendenti dalla tangente. Retrieved from: http://www.ripmat.it/mate/i/id/idcc.html)

Figure 20 shows how, in real applications, the shape of the spray deviates slightly from a perfect cone, mainly due to the gravity force acting on the droplets.

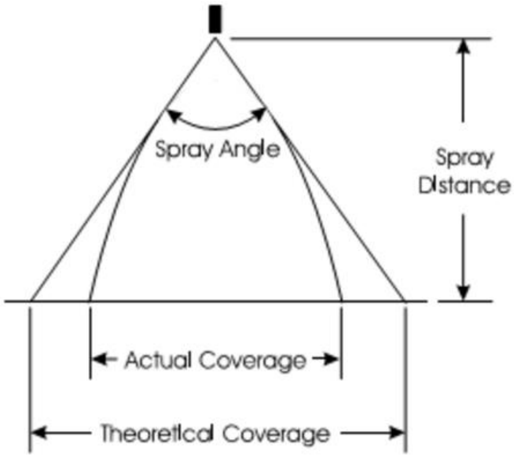

Figure 20: Actual vs theoretical coverage area (Relab Spray & Purification Technology Ltd.).

Results and Analysis

For the reason explained above, a perfect match between experimental and theoretical values is not achievable. In order to highlight such deviation, the numbers obtained experimentally have been compared to theoretical ones and reported in the table below. The diameters and areas measured in the lab are expected to be smaller than the theoretical ones, due to a reduced coverage area.

Distance nozzle-substrate (cm)	***Theoretical diameter (cm)***	***Measured diameter (cm)***	***Correspondent aperture angle for an ideal case (degrees)***	***Theoretical area (cm^2)***	***Area calculated from measured diameter (cm^2)***
10	6.3	5.3	29.6°	31.2	22.1
12.5	7.9	7	31.2°	49	38.5
15	9.5	8.5	31.6°	70.9	56.7
20	12.6	11.2	31.4°	124.7	98.5
25	15.8	14	31.2°	196	153.9

Table 3: Theoretical vs experimental values.

Notes:

- The theoretical diameter was calculated with the trigonometric formula previously discussed and readapted for this specific case:

$$d = 2 * r = 2 * [distance * \tan(17.5°)]$$

  Where the argument of the tangent (17.5°) represents the semi-aperture angle. The total spray angle is in fact considered to be 35° (based on the experimental parameters, which, being smaller and relatively close to this angle, lead to hypothesise such conclusion).

- The *"Correspondent aperture angle for an ideal case"* is the spray aperture angle an *ideal nozzle* would need to have, *in ideal conditions*, to generate circles with the measured diameters. It has been calculated (to estimate the real angle) by using the same trigonometric formula used for the diameter computation, knowing the distance and the radius.

Issues

Solution suction process

The spray coming out from the orifice of the nozzle is intermittent. This issue can be entirely attributed to the *discontinuous flow rate of the solution*, rather than on the nozzle itself.

To assure a constant flow rate to the nozzle and consequently a continuous spray, it is necessary to either:

a) Add some components to improve the current suction process

b) Change the mechanism used to drive the water from the tank to the liquid inlet gateway

The two proposed solutions to the problem are explained below:

a) It could be considered to switch to a gravity-fed system. In this way, the flow will be continuous, as it would solely rely on gravity (obviously constant) and to the presence of solution in the tank.

To avoid leakages of the solution from the nozzle orifice, however, it would be necessary to be able to stop the water feeding as soon as the spray is no longer required. To cope with this, an *automatically controlled valve* should be applied to the solution hose, this would allow to stop and control the flow when needed. The valve should be mounted as close as possible to the nozzle liquid port, to prevent creating a vacuum condition and having solution left in the second part of the hose (between the valve and the liquid inlet port).

A schematic of the proposed system has been drawn with *Paint* and is shown below.

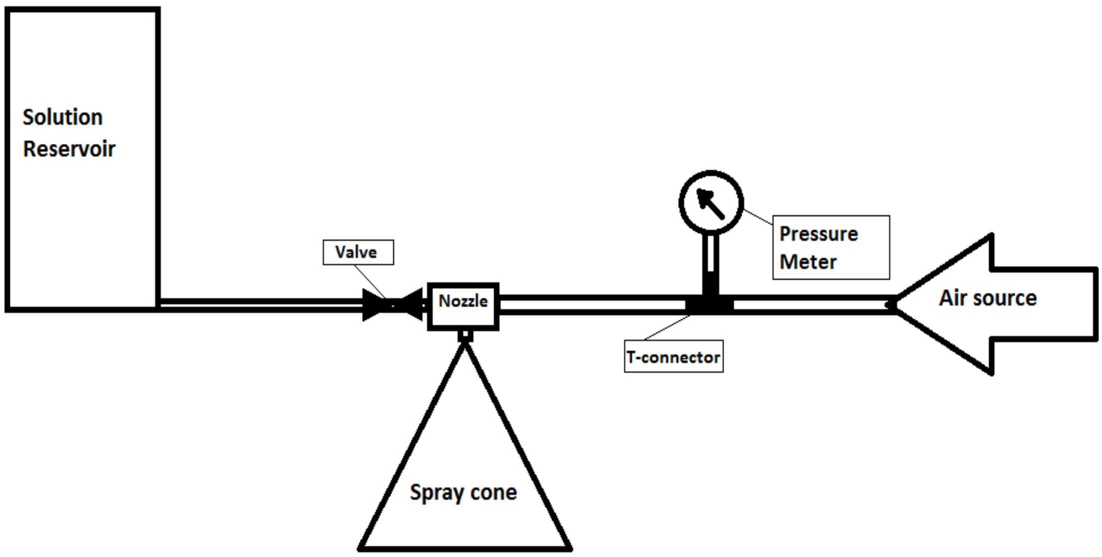

Figure 21: Schematic of the gravity-fed spray coating prototype.

Note that the pressurised air hose has been intentionally drawn with a diameter larger than the solution one, to have a more accurate representation of the actual system.

b) Another possible solution is to install a pump to deliver a certain flow rate for a certain time interval, meeting the requirements of the particular application of interest.

Air leakages from the T-connector junctions

During the experiment concerning the variation of the air pressure and the flow rate of the solution, a problem emerged: air leakages were registered in the area where the T-connector (used to attach the pressure meter to the pressurised air hose) is mounted. This issue doesn't influence the correct functioning of the system, as air still flows into the nozzle with a pressure high enough to nebulise the liquid and it is still possible to read such pressure on the indicator. However, it is a problem that should be addressed, because it may generate serious consequences if a gas other than air is used: it could be toxic and dangerous for the people in contact with the system, or simply too expensive to justify such a waste.

The reason why air leaks is because the hose clamps used in the prototype to attach the plastic hoses to the T-connector are not sufficient to have a perfect sealing. The most straightforward and viable solution to have a better fastening is to weld the ends of the plastic hoses to the connector ports, in order to close all the gaps that the pressurised air leaks from. As a further safety precaution, it would be advisable not to remove the stainless-steel hose clamps already mounted.

Conclusions

The novel antimicrobial coatings analysed in this paper present one of the most viable solutions to the issues that the food industry, the medical system, and many other industries are currently going through. They have in fact been proved effective in most fields by a large number of studies.

Before being extensively implemented, however, these solutions and all the potential consequences of their implementation would need to be studied more thoroughly over the long run.

Once both their safety and efficacy have been confidently established, it will be necessary to execute a management plan, like the one provided in one of the earlier sections, in order to promote their commercialization.

Lastly, it can be concluded that the edible bio-coatings and novel non-drug antimicrobials here presented will likely represent the future of the food industry and of the healthcare, respectively. Moreover, their implementation is expected to grow over time and across a variety of other industries, as the trust towards them increases.

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