Sustainable antimicrobial finishes for Textiles from natural bio-extracts and conductive polymers

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Abstract: *Natural fibers Textiles such as cotton, silk wool, jute etc. are pronto microbial attack and therefore they are not suitable for various healthcare and hygienic applications including daily use. Many types of research have been conducted in many dimensions for the preparation of anti-microbial textiles for those applications. The conventional method of preparation of the anti-microbial textiles is treating textiles with some inorganic salts like CuCl2, quaternary ammonium salts, halamines etc. The recent approach is coating textiles with natural bio-extracts such as neem, aloe vera, tulshi, etc. which is a sustainable one. Most recently, coating the textiles with conductive polymers such as polypyrrole, polythiophene, polyaniline, etc. for the preparation of anti-microbial textiles is very successful and found to be the promising, sustainable and green approach.*

1. Introduction

Textile fabrics are a very suitable substrate for the growth of microorganisms when the basic requirements for their growth such as nutrients, oxygen, moisture, and appropriate temperature are present. The large specific surface area of textiles can promote the growth of microorganisms on the surface of the textile substrates. Natural fibers are more prone to microbial attack than synthetic fibers. Cellulosic fibers like cotton, jute, viscose, etc. themselves are not a direct source of nutrients for microorganisms but, under some appropriate conditions, few fungi secrete enzymes that convert cellulose into glucose which is a nutrient source for microorganisms[1]. In addition to that dust, soil, and a few textile finishes like size paste can be the source of nutrients. Synthetic antimicrobial agents are very effective against a wide range of microbes and give a durable effect on textile. There are a number of demerits of synthetic antimicrobial agents including poor wash fastness, leaching in water, and their toxiological effects. So, there is a huge demand for antimicrobial textiles based on the eco-friendly agent which not only can mitigate microbial growth on the surface of textile materials but also satisfy the requirements imposed by various recognized agencies towards sustainability and eco-friendliness[2]. Presently, in the era of eco-friendly operation, it has become vital for human beings also to live in a world of hygiene and a healthy atmosphere. The major obstacle that comes in their way is the microorganisms, which are responsible for deterioration, staining, odour and toxiological effects. Microbes cause harm to human beings by transmitting various diseases and infections. thus, it becomes very important to alter all the surface properties of all the garments with eco-friendly anti-microbial agents so that there is no chance of bacterial growth and they become safe for end-use.

2. Origin of the antimicrobial textiles

During the second World War, the cotton fabrics were extensively used for making tent, tarpaulins and truck covers. These fabrics are required to be protected from rotting due to microbial attacks. In the South Pacific campaigns it is a problem, where much of the fighting took place under jungle. Cotton duck, webbing, aprons and other military fabrics were treated with mixtures of chlorinated waxes, copper and antimony salts in early 1940's. These salts and finishes stiffened the fabrics and produce foul odour. After the second world war, the fungicides which are applied on cotton textiles are 8-hydroxygiunoline salts, copper ammonium fluoride, chlorinated phenols, etc. These agents are not eco-friendly. Now-a-days, various nations and industrial firms are more aware of the environmental and workplace hazards about these compounds, and recconding and seraching for alternative ecofriendly products [3].

3. Functions of antimicrobial textiles

1. To avoid cross infection by pathogenic micro-organisms.
2. To arrest metabolism in microbes in order to reduce the odour formation.
3. To control the infestation by microbes.
4. To protect the textile products from staining, discoloration and quality deterioration.

4. Purpose of antimicrobial finish

A. **Rot proofing** is an antimicrobial finish applied to givenmaterial for protection either long term or short term against physical deterioration.
B. **Hygiene finishes** are dealing with the control of infection and unwanted bacteria; aspecialized development is the prevention of dust mites.
C. **Aesthetic finishes** are used to control odour development and staining.

5. Types of bacteria and classification of antimicrobial agents

Microorganism are small living forms of life, which cannot be seen with the naked eye as shown in figure: 1

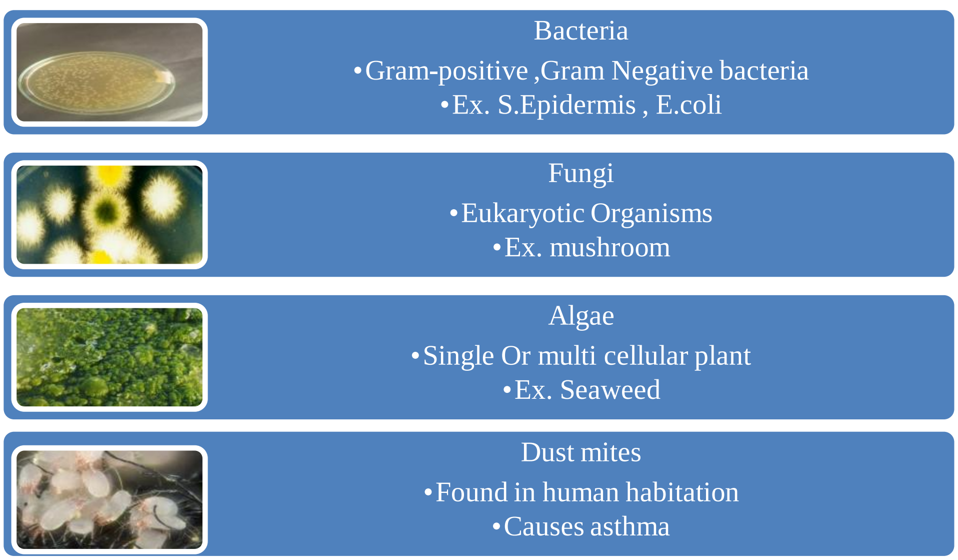

Figure 1. Various types of microorganism

The antimicrobial agents are classified broadly in two types viz. leaching types and non-leaching types.

5.1 Leaching type or conventional antimicrobials

These products diffuse from the garment to come in contact with microbe. They washed off the garments, forming a space of activity and any microbes coming into the space are destroyed. However, with time, the potential decreases and thus, it just attacks the microbes, giving them a chance to form a strain by mutation. The microbes are consumed by the antimicrobial agents as they act on them. The product share eventually used up by the bacteria and slowly loses their effectiveness.

5.2 Non leaching type

These agents are bound to the product and control the cation of the microorganisms. These products do not migrate off the garments, but, destroy the bacteria when it comes in contact with the surface of the garment. The microbes are not consumed by the antimicrobial agents. The antimicrobial agents destroy the bacteria by acting on thier cell membrane. The antimicrobial finishing is permanent type and will remain functional through the life cycle of the base fabric and can withstand more than 40 laundry washes.

6. Types of antimicrobial agents according to action against microorganism

There are two catgories of antibacterial agents such as: (a) Biostatic drugs that inhibit the growth of microorganisms; like bacteria, fungi and viruses[4]. (b) Biocidal drugs those kill microorganisms by producing hydroxyl radicals through a mechanism of common oxidative reaction and damage cellular death pathway involving alterations in central metabolism and iron metabolism [5]. The efficiency of killing of microorganisms by bactericidal agents is >99.9%. The aniti-microbial agents work on three fundamental mechanisms viz. inhibition of protein synthesis, inhibition of DNA replication and repair or inhibition of cell-wall turnover.

6.1 Inhibition of protein synthesis

There are three sequential phases viz. initiation, elongation and termination for mRNA involving the ribosome and a host of cytoplasmic accessory factors. The ribosome organelle is composed of two ribonucleo protein subunits, that organize (initiation phase) on the formation of a complex between an mRNA transcript. The broadest classes of antibiotics are the drugs that inhibit protein synthesis and they can be divided into two subclasses, viz: 50S inhibitors and 30S inhibitors[6].

6.2Inhibition of D.N.A. replication and repair

The antibiotic-induced cell death occus due to the formation of double-stranded DNA breaks following treatment with DNA gyrase inhibitors. These mechanims are performed by the synthetic quinolone class of antimicrobials, including the clinically-relevant fluoroquinolones, which target DNA-topoisomerase complexes. Quinolones are introduced in the 1960s as derivatives of nalidixic acid, which was discovered as a byproduct of chloroquine (quinine) synthesis and to treat urinary tract infections. Other first generation quinolones and nalidixic acid and (i.e. oxolinic acid) are rarely used now ad days owing to their toxicity. However, these bacteriostatic drugs predominantly inhibit ribosome function, targeting both the 30S (tetracycline family and amino cyclitol family) and 50S (macrolide family and chloramphenicol) ribosome subunits. The aminocyclitol group of 30S inhibitors are the bactericidal aminoglycoside family of drugs and the bacteriostatic drug spectinomycin; the aminoglycoside family, excluding spectinomycin, is the only class of ribosome inhibitors known tocause protein mistranslation. With respect to other classes of bactericidal antibiotics, quinolones target DNA replication and repair by binding DNA gyrase complexed with DNA, which drivesdouble-strand DNA break formation and cell death as shown in Figure 2.[5] [6].

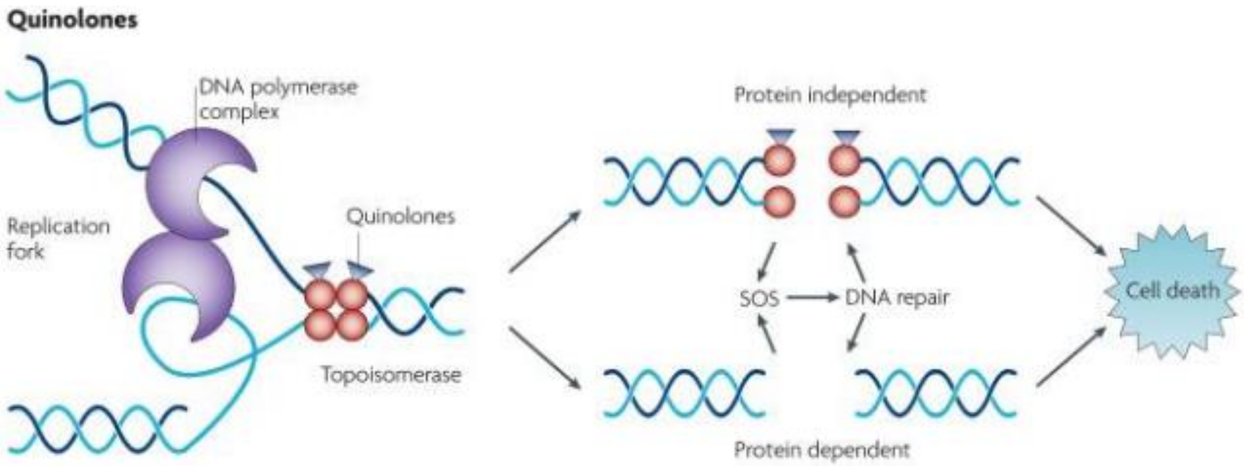

Figure 2. Mechanism of antimicrobial effect by inhibition of DNA replication and repair

6.3 Inhibition of cell wall synthesis

Blactams are the cell-wall synthesis inhibitors that interact with penicillin-binding proteins and glycopeptides interact with peptidoglycan building blocks and interfere with normal cell-wall synthesis. They induce lysis and cell death as shown in Figure 3. There will be change in cell shape and size after the treatment with a cell wall synthesis inhibitor that induce cellular stress responses, and culminate in cell lysis.

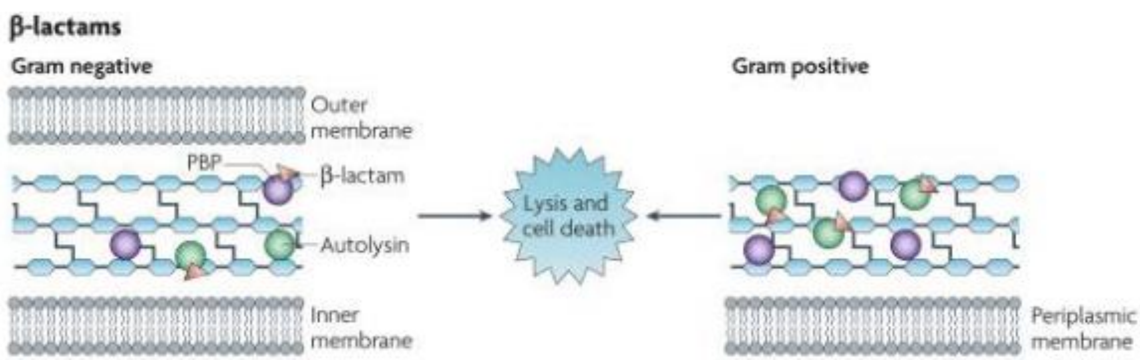

Figure 3. Mechanism of antimicrobial effect by inhibition of cell wall synthesis [6].

7. Applications methods of antimicrobial agents onto textiles

There are various methods of applications of antimicrobial agents on to textile substartes. Most importantly, internal antimicrobial release is one of the method where antimicrobial agents are incorporated into the synthetic fibres during spinning. The fibre itself become intrinsically antimicrobial material that can release antimicrobial agent internally af this finish[7]. Another approach is **surface application of antimicrobial finish** that is universally applicable for all types of fibers. However, the durability to washing depends on the affinity of antimicrobials towards the fibre substrate. The durability of the finish depends on the bonding strength of the polymers with the textile surface. In case of some fibres like PAN, ionic charge could be another factor to consider for certain fibers,. The third approach is **Chemical bonding** which is theoretically the best way to achieve durability and it is suitable for cellulosic, wool and polyamide fibres. But, this method requires suitable reactive groups on the fibers to work effectively.

8. Natural and Ecofriendly antimicrobial agents

The conventional methods of preparation of anti-microbial textiles is the treating textiles with some inorganic agents like $CuCl_2$, quaternary ammonium salts, halamines etc. Theses processes are not ecofriendly and susuatainable. However, there are sustainable method by coating textiles with natural bio-extracts such as neem, aloe vera, tulshi etc. Recently, coating with conductive polymers like polypyrrole, polytgiophene, polyaniline etc. are found to be very promising as a sustainable and green approach for preparation of antimicrobial textiles.

8.1 Neem(*Azadiracta indica*)

Neem (*Azadirachta indica*) is called evergreen tree of India, and recognized as one of the most promising sources of compounds with insect control, medicinaland antimicrobial properties[8]. The antimicrobial ingredients of neem are found in all parts of the tree such as seed, bark, leaves and roots [9]. The ingredients are hence extracted from these parts of the plants. There are about 300 different types of active ingradients have been extracted from different parts of neem tree. Among them, the most important limonoids are azadirachtin, salannin and nimbin (Fig 4). The neem extracts have excellents pest repellent property and due to that they have been widely used in herbal pesticide formulation to inhibit growth of both Gram positive and Gram negative bacteria. A systematic reseach was conducted on integrating neem seed and bark extracts to cotton. Figure5 [10] shows the images of colony forming unit of *Bacillus subtilis* bacteria before and after the treatment of cotton/polyester blend fabric with neem seed extracts. Table 1.[11] shows effectiveness of various concentrations of neem extracts against killing bacteria on the surface of textiles.

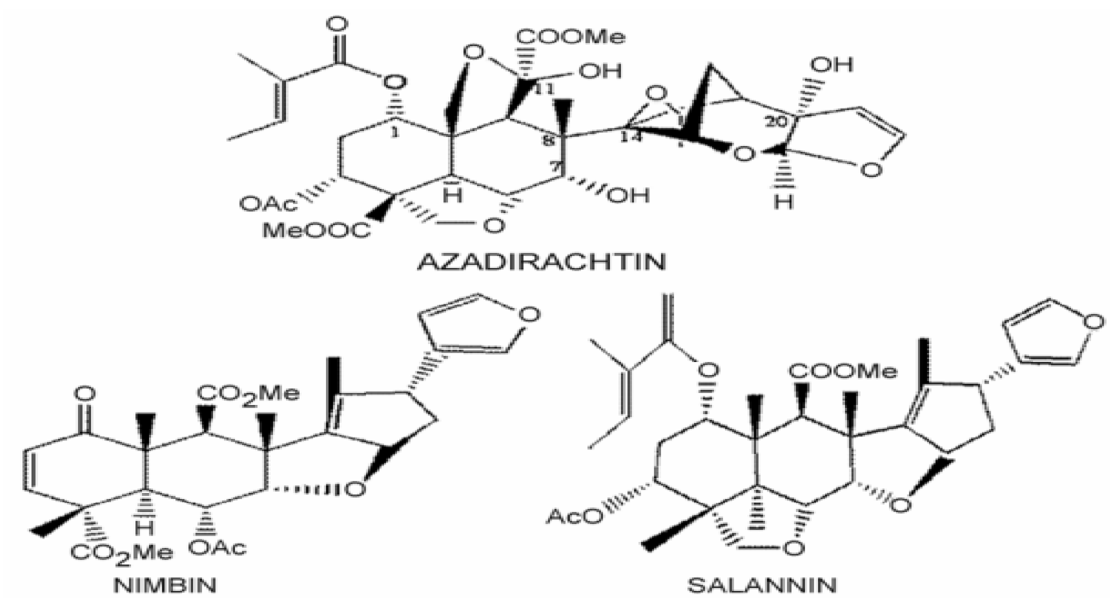

Figure 4. Active limonoids in neem extract

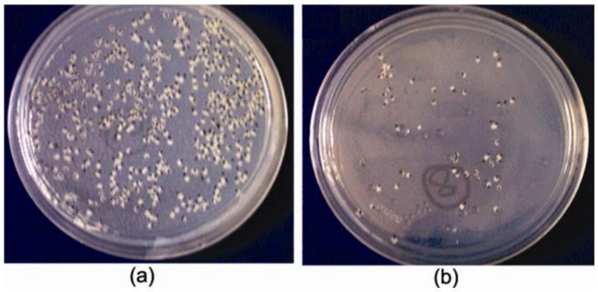

Figure 5.Photographs of (a) untreated and (b) neem seed extract (5%w/v) treated cotton (against *B. Subtilis* bacteria).

Table 1. Effectiveness of neem leaves extract coated fabric for antimicrobial effects

	Escherichia Coli		Bacillus	
SAMPLE	3% neem extract finish	5% neem extract finish	3% neem extract finish	5% neem extract finish
Without Wash	30.66	39.77	31.55	41.89
1st wash	11.93	15.49	20.86	25.92
2nd wash	10.48	15.01	18.04	20.91
3rd wash	10.21	13.75	11.18	13.31
4thwash	9.51	11.28	11.02	8.32
5thwash	9.02	11.92	5.93	8.49

8.2 Aloe Vera

Aloe vera (*Aloe barbadensis*, Miller) has been used in Ayurveda as a skin care product for more than 2000 years. In recent times, it has been observed that the Aloe leaf contains more than 75 nutrients and about 200 active ingredients, including 20 minerals, 18 amino acids and 12 vitamins[12]. Aloe vera possesses antibacterial and antifungal properties, which can be exploited for medical textile applications, such as wound dressing, suture, bioactive textiles.

There are various polysaccharides avaialble in Aloe vera. Examples are glucomannan, acetylated glucomannan, glucogalactomannan with different composition, galactogalacturan, acelylated mannan or acemannan. Acemannan a long chain polymer consisting of randomly acetylated linear D-mannopyranosyl units has immunomodulation, antibacterial, antifungal and antitumor properties.

Aloe vera extract at various concentrations (5, 10, 15, 20 and 25 gpl) was applied on cotton fabric in presence of ecofriendly cross-linking agent glyoxal (100gpl) by a pad-dry-cure technique. Qualitative (AATCC-147- 1998) and quantitative (AATCC-100-1998) evaluations were conducted to evaluate antibacterial efficassy of the Aloe vera treated cotton fabric. It was observed that the absorbance of the sample is directly proportional to the concentration of the cells in the sample. The untreated and treated samples were compared in terms of their absorbance values at 600 nm (Table 2)[13]. With the increase in aloe vera concentration absorption value decreases which signifies less number of bacteria cell present in the solution.

Table 2. Estimation of antimicrobial effect by absorbance test at 600 nm wavelength

S.no	Sample	absorbance value
1	Untreated	1.02
2	5% gel treated	0.94
3	75%gel treated	0.93
4	100%gel treated	0.89
5	Commercial gel treated	0.97

8.3 Tea tree

Tea tree (*Melaleuca alternifolia*) is native to the Himalayan zone. The oil of tea tree possesses more than 100 different compounds and which is known as a natural medicinal ingredient. It has antiseptic (five times better than the usual household disinfectants), dermatological (prevents dry skin), and anti-fungal properties and can also be used to fight infections/ infestations [14]. Its oil is found to have some of the best natural antifungal / antiseptic properties. The oil works against a wide varaeties of bacteria, such as *Escherichia coli, Proteus vulgaris, Propioibacteriumacnes, Pseudomonas aeruginosa,Staphylococcus aureus, Salmonellatyphimurium, Proteus mirabilis, Helicobacterpylori, Streptococcus pyogenes*, etc.

8.4 Tulsi leave

Tulasi or basil (Ocimum sanctum L.) is a sacred plant and its various medicinal properties have been recognised since ancient times and in Ayurveda. Different parts of this plant are used for treatment of various ailments. The essential oil which is obtained from fresh and dried leaves differ greatly in terms of chemical constituents. Therfore, it surely differ in biological activities towards many ailments. The activity of essential oils obtained from fresh and dried leaves of tulsi against dissmissing enteric bacteria i.e., Escherichia coli, Shigella sp., Salmonella typhi, yeast (Candida albicans) etc. are experimentally proved. The major bio-ingredients that are responsible for antimicrobial effect are reported in table 3 [15].

. Table 3. Major chemical constituents of the essential oil of *Tulsi* used in antimicrobial study.

Major constituents	% in Fresh leaves oil	% in Dried leaves oil
Eugenol	57.94	6.34
Beta-Caryophyllene	15.32	18.20
Beta-elemene	7.57	11.38
GermacreneD	9.10	3.24
Caryophyllene oxide	3.20	29.36

8.5 Other natural Bio-extracts

Clove oil (eugenol) is a primary product of Syzygiumaromaticum. Bioactivity of clove oil was evaluated in size paste as well as finishing agent for pteparation of antimicrobial cotton textiles.

The washing fastness of the treated fabric was significaltly improved by using dimethylol dihydroxyethylene urea based inbuilt catalyst (KVSI)[16]. In a study, Sarkar et al demonstrated that clove oil with 0.5% conc. has 17 mm of zone of inhibition using Staphylococcus aureus and Klebsiella pneumonia, but, cotton textiles treated with 1% clove oil (along with KVSI) results 47 mm inhibition zone against Staphylococcusaureus (Gram positive) bacteria. The antimicrobial effects of five different solvent extracts of four Indian nutraceutical plants viz. Psidium guajava L., Manilkara zapota (L.) var. Royen., Punica granatum L. and Syzygium cumini L. leaves against 14 pathogenic microorganisms was reported[17]. The antimicrobial activity was tested by agar by well diffusion method. Among them, P. guajava leaves showed the best and durable antimicrobial effect, denoting the possibilities of its potential use for the natural remedies for the treatment of infections.

9. Conductive polymer coated textiles for anti-microbial efficacy

Seshadri and Bhat are pioneer to conduct reseach and to report antibacterial activity of π-conjugated polymers such as polypyrrole, polyaniline etc. It is a novel approach of developing antimicrobial textiles by coating textiles with conjugated polymers like polypyrrole, polyaniline, polythiophene etc. which are found to be very promising as a sustainable approach.The mechanism of antimicrobial activities is suggested to be a due attack on the cell wall of the bacteria by the charged nitrogen and chloride ions of polypyrrole.

Polypyrrole coated cotton fabric showed a 65% reduction of gram-positive bacteria and 59% for gram-negative bacteria and 73% for a fungal culture which is boosted by the addition of another antimicrobial agent viz., $CuCl_2$ as shown in Table 4[18].

Table 4. Anti-microbial properties of PPy treated cotton fabrics.

Sample	**Microbial Reduction (%)**		
	Staphylococcus Aureus	Escherichia Coli	Candida Albicans
Cotton +PPy	64.86	59.14	73.07
Cotton +PPy+$CuCl_2$	92.53	97.60	100.00

Unlike quaternary ammonium salt and halamines, the merit of polypyrrole is that it is insoluble in water. More over, it is biocompatible and non-toxic in nature. Very good antibacterial efficassy against S. aureus and E. coli bacteria has been observed by polypyrrole-coated cotton fabrics.

10. Global scenario for the antimicrobial textiles

The highest consumption of antimicrobial agents by application is in the market, including interior and exterior coatings which are developed to provide protection against the growth of microbes and mildews. Other markets which are expected to see the growth for antimicrobial finish such as hospitals, daycares, nursing homes, and other medical applications where high standards of hygiene and protection are required [19]. It has been observed that the disinfectant and antimicrobial chemical market in USA are gowing 5% annually from 2009 based on the concerns about bacterial and pathogenic threats. Among them, nitrogen compounds, phenolic compounds, and organometallics will reside over as the top products.

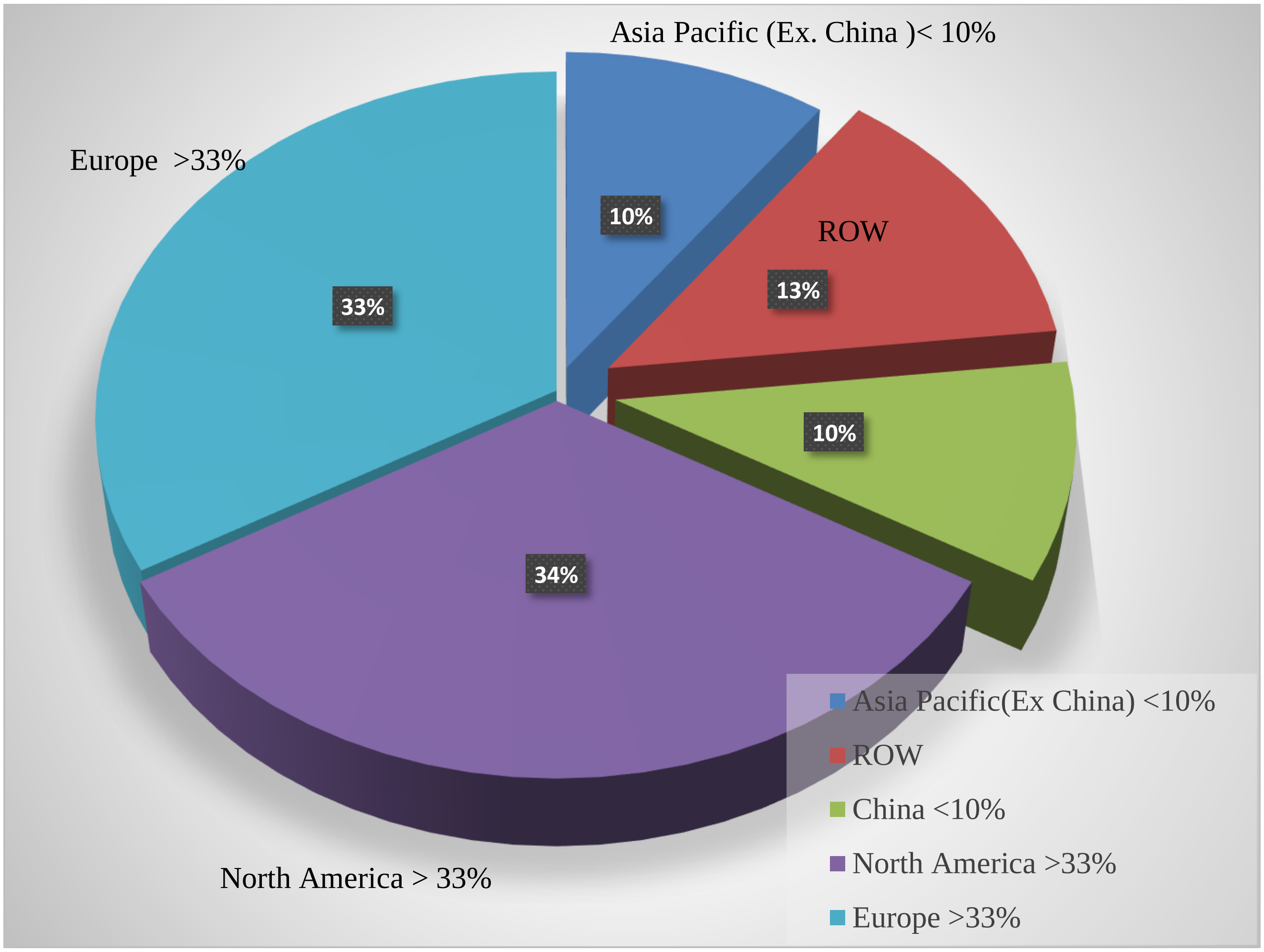

Figure 6. Market size of Biocides

11. Conclusions

There is a wide variety and huge resource of natural antimicrobial agents available in nature. They can be used for imparting useful antimicrobial property to textile substrates. The main challenge of applications of the natural antimicrobial agents onto textile substrate is that the most of these biomaterials are complex in nature with a mixtures of several active compounds and also their composition varies in different species of the same plant. Based on their geographical location, age and method of extraction their activity and composition are very inconsistent. It is a big challenge to get availability of these products in bulk quantities, their extraction, isolation and purification to get standardized products. The durability of finish over textile surafce, shelf life and sustainable antimicrobial efficiency in comparison to synthetic agents are other challenging aspects, which need to be taken care of. However, due to their ecofriendly and non-toxic nature, they are still promising candidates for niche applications such as medical and health care textiles. Electro-conductive polymers such as polypyrrole, polyaniline are also explored as antimicrobial agents and successfully applied or coated over textile substrates for getting antimicrobial effects and recent researches have been proved that this may be an alternative sustainable approach of preparation of durable antibacterial textiles.

Reference

1. Patel, B. H., & Tandel, M. G. (2005). Antimicrobial finish to cotton fabric by natural extracts. *MAN MADE TEXTILES IN INDIA*, *48*(12), 473.
2. Ammayappan, L., & Jose, S. (2015). Functional aspects, ecotesting, and environmental impact of natural dyes. In *Handbook of sustainable apparel production* (Vol. 333, No. 350, pp. 333-350). ROUTLEDGE in association with GSE Research.
3. Landage, S. M., & Wasif, A. I. (2012). Nanosilver—an effective antimicrobial agent for finishing of textiles. *International Journal of Engineering Sciences & Emerging Technologies*, *4*(1), 66-78.
4. Melrose et al "BIOSTATIC AND BIOCIDAL COMPOSTIONS" US005290894A,United States Patent and Trademark Office,Mar.1,1994.
5. Kohanski, M. A., Dwyer, D. J., Hayete, B., Lawrence, C. A., & Collins, J. J. (2007). A common mechanism of cellular death induced by bactericidal antibiotics. *Cell*, *130*(5), 797-810.
6. Kohanski, M. A., Dwyer, D. J., & Collins, J. J. (2010). How antibiotics kill bacteria: from targets to networks. *Nature Reviews Microbiology*, *8*(6), 423-435.
7. Han, D., Sherman, S., Filocamo, S., & Steckl, A. J. (2017). Long-term antimicrobial effect of nisin released from electrospun triaxial fiber membranes. *Acta biomaterialia*, *53*, 242-249.
8. Bagle, A. V., Jadhav, R. S., Gite, V. V., Hundiwale, D. G., & Mahulikar, P. P. (2013). Controlled release study of phenol formaldehyde microcapsules containing neem oil as an insecticide. *International Journal of Polymeric Materials and Polymeric Biomaterials*, *62*(8), 421-425.
9. Anonymous, https://www.discoverneem.com/neem-tree.html. Accessed on 12th March 2020.
10. Joshi, M., Ali, S. W., & Rajendran, S. (2007). Antibacterial finishing of polyester/cotton blend fabrics using neem (Azadirachta indica): a natural bioactive agent. *Journal of Applied Polymer Science*, *106*(2), 793-800.
11. Mahesh, S., Manjunatha, A. H., Reddy, V., & Kumar, G. (2011, December). Studies on antimicrobial textile finish using certain plant natural products. In *International Conference on Advances in Biotechnology and Pharmaceutical Sciences (ICABPS'2011) Bangkok Dec*.
12. Khurshid, M. F., Ayyoob, M., Asad, M., & Shah, S. N. H. (2015). Assessment of eco-friendly natural antimicrobial textile finish extracted from aloe vera and neem plants. *Fibres & Textiles in Eastern Europe*.
13. Anonymous http:// www.fibre2fashion.com/ industry-article/ textileindustry-articles/ an-eco-friendly-herbal-antimicrobial-finish/an-eco-friendly-herbal-antimicrobial-finish1.asp (accessed on 14th march 2020).
14. ABDEL-MAKSOUD, G., EL-AMIN, A. R., & AFIFI, F. (2013). THE INSECTICIDAL ACTIVITY OF TEA TREE OIL (MELALEUCA ALTERNIFOLIA) AGAINST THE COMMON PEST IN MUMMIES (DERMESTES MACULATUS). *International Journal of Conservation Science*, *4*(3).
15. Mirdha, B. R., Naik, S. N., & Mahapatra, S. C. (2007, March). Antimicrobial activities of essential oils obtained from fresh and dried leaves of Ocimum sanctum (L.) against enteric bacteria and yeast. In *International Symposium on Medicinal and Nutraceutical Plants 756* (pp. 267-270).

16. Sarkar, R. K., De, P., & Chauhan, P. D. (2003). Bacteria-resist finish on cotton fabrics using natural herbal extracts.
17. Chanda, S., & Kaneria, M. (2011). Indian nutraceutical plant leaves as a potential source of natural antimicrobial agents. *Science against microbial pathogens: communicating current research and technological advances*, *2*, 1251-1259.
18. Seshadri, D. T., & Bhat, N. V. (2005). Synthesis and properties of cotton fabrics modified with polypyrrole. *Sen'i Gakkaishi*, *61*(4), 103-108.
19. Anonymous https://www.freedoniagroup.com/(accessed on 17th march 2020).