



Performance on Antibacterial Finishes for Textile Applications



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submission: 📅 May 05, 2018; **Published:** 📅 May 24, 2018

Abstract

Microorganisms are found everywhere in our world and most of them cause infectious diseases to human beings such as viruses, fungi, pathogenic bacteria etc. Suitable conditions like nutrients, warmth and humidity may accelerate the growth of these harmful microbes on textiles which not only increase the risk of spreading diseases but also cause some unwanted effects to textile products including loss of strength, decoloration and unpleasant smell. Antimicrobial agents are ultimate solution which inhibit and kill the microorganisms and are applied to textile products. Antimicrobial textiles are consumed continuously where fabric surface is expected to contact microorganisms. Much attentions have paid for development and finishing of these functional agents onto textiles. Various kinds of antimicrobial agents and finishes which provides superior safety, recharge ability, durability and excellent disinfection power are discussed in this article.

Keywords: Antimicrobial agents; Textile fabric; Antimicrobial activities; Mechanisms; Performances

Introduction

The discovery and applications of textile fabrics bearing antimicrobial functionalities has been one of most important and active research field in recent years. Antimicrobial finishes on textiles are anticipated to have resistance from spreading harmful microbes such as bacteria, fungi, spores, viruses etc. by killing them or inhibiting their growth. These finishes reduce the risk of spreading infectious diseases as well as minimize the hygienic issues. The antimicrobial finishes are mainly classified into biocidal and biostatic finishes. The textiles which can kill bacteria are called biocidal textiles while those which inhibit microbes are known as biostatic textiles. Odor control sportswear and conservation of textile artifacts require biostatic finishes but are not suitable to provide microbial protection for humans in their untreated form. Biostatic finishes are ultimate solution for human protections in medical applications which have ability to kill microbes rapidly as they contact the finished surface. Long term performance of antimicrobial finishes may achieve only by incorporation of limitless supply of agent in finish or customarily restore it on textiles, otherwise antimicrobial functionality will be lost on usage or exposure to air with the passage of time. Thus, durability of finish (especially storage and washing durability) on textile product is another challenge beside power of antimicrobial function. The practical methods for incorporation of antimicrobial agents include sol-gel technology, plasma treatments, microencapsulation, etc which could offer prolonged release of agents. Antimicrobial textiles

should not cause irritation to skin and sensitization reactions when they have intimate contact with human skin. This article provides development, performances and progress of novel antimicrobial finishes on to textile fabrics.

Action of antibacterial agents

The choice of antimicrobial agent is always depend upon its final usage, requirements and way of its antimicrobial action. They act in two ways.

- (1) The antimicrobial agent chemically bind on the surface of treated fabric and do not detach from surface by its own. Microbes kill by agent when become in contact with treated fabric.
- (2) The antimicrobial agent only physically attached with fibers and leaches or diffuses in environment and performs its action of killing microbes.

The former action losses the concentration of agent with the passage of time owing to its regular leaching and diffusion towards microbial environment and ultimately losses durability with usage and laundering. In later mechanism, although agent remain attached to fiber surface and do not leaches out but requires recharging of antimicrobial functionality as the reactive sites responsible for antimicrobial activity become consume during bacteria killing. Recently, third type of mechanism is observed to be adopted by

nano-metal oxides which act as photocatalysts. They remain bind on surface of fiber and do not leach or diffuse out. Advantageously, they do not require recharging of antimicrobial functionalities. Actually, they utilize light energy to perform redox reaction with compounds in environment forming reactive oxygen species which further execute antibacterial action. In the whole mechanism, photoactylasts act as catalyst and do not lose its concentration and utilizes renewable energy source.

Antimicrobial agents

N-halamines: N-halamines are investigated as one of the most important antimicrobial agents possessing strong antimicrobial activity and safety, durability and rechargeability [1,2]. N-halamines are characterized by one or multiple polar nitrogen-halogen (N-X) covalent group which exhibit strong antimicrobial power and inactivate microbes through oxidative halogen. Depending upon chemical linkage, imide N-halamine, amide N-halamine and amine N-halamine are further three types of N-halamine. Their antimicrobial activities and stabilities vary due to presence of electron-withdrawing and electron-donating groups in environment of N-X bond. The N-X bond is reduced during killing microbes by N-halamine agents with an advantage of reversibility of antimicrobial function. Halogenating agent like dilute solution of bleaching solution can recover the biocidal activity as illustrated in Figure 1; [3,4]. This pronounced recharging of antimicrobial functionality separate them from other classes

of biocidal agents. N-halamines attracted attention of researcher from both academic and industry after investigated them as water disinfectant with excellent water disinfectant abilities [5-8]. In this respect, 1,3-dimethylol-5,5-dimethyl-hydantoin (DMDMH) based N-halamine was synthesized and utilized to fabricate antimicrobial textiles with rechargeable and durable functionalities [9]. DMDMH serves as crosslinker between N-halamine and fabric. However, this agent showed some decreased functionality during wearing [10]. Moreover, DMDMH releases formaldehyde which causes health hazards. Polycarboxylic acids were found good alternatives for crosslinking N-halamines with advantage of better water solubility and free from formaldehyde residues [11,12]. Later one, a large number of stable N-halamine agents were investigated which showed better performance during usage of finished textiles such as polymeric N-halamines [13-19], unsaturated N-halamines [20-23], reactive N-halamines [24-28], N-halamine based imidazolidones [29] and siloxane based N-halamines [30-35]. A combination of N-halamines with other biocidal agents such as quaternary ammonium salts [36-41], titanium dioxide [42] and triclosan [43] are also found potential way regarding stability, durability and antimicrobial power. These coatings are applied both physically and chemically. However, N-halamine antimicrobial agents may also be incorporated prior to extrusion process for textile fiber production [44-47]. Synthesis route of antimicrobial cotton finished with N-halamine based methylene-bis-acrylamide is depicted in Figure 2.

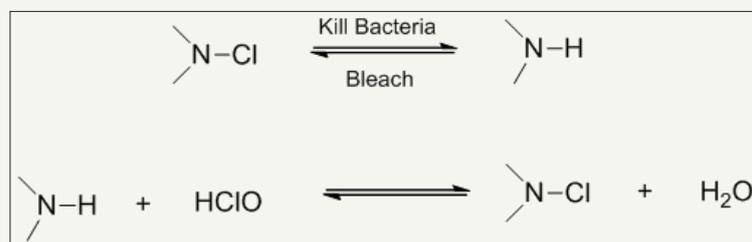


Figure 1: Reduction of N-halamine during microbes killing and its recharging via bleaching.

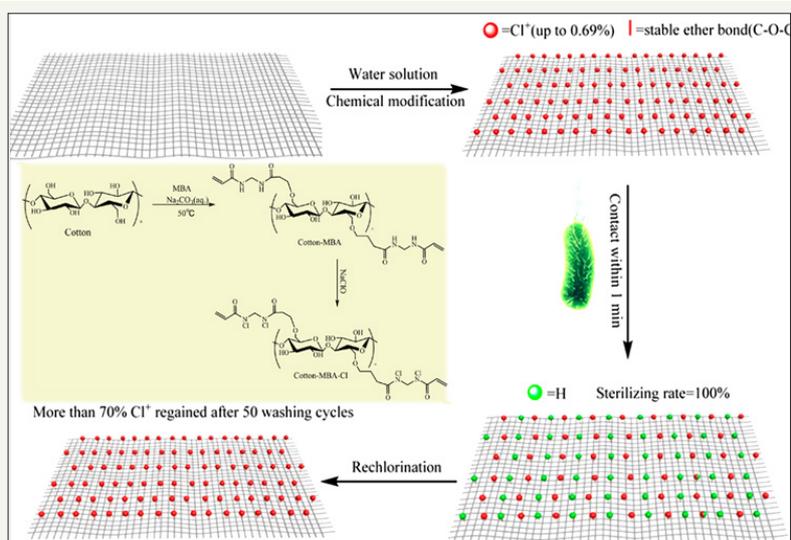


Figure 2: Synthesis route of antimicrobial cotton finished with N-halamine based methylene-bis-acrylamide [4].

Reactive N-halamines possess the reactive sites which are able to covalently attach on fibers surface. In this way, fabric provides durable antimicrobial functionality even after laundering. The chlorine loading lasts after 50 wash cycle which can be recover via bleaching. Examples are coated polyester [48] and cotton [24,25,49,50]. Polymeric N-halamines are such a antimicrobial polymers whose polymer back bone contains (i) one type of monomer exhibiting reactive group like epoxy ring which is able to covalently crosslinked onto cotton fabric and (ii) other monomer is a kind of N-halamine repeat unit capable of performing antimicrobial activity [12,17]. Figure 3 depicts the chemical structure of important epoxides based cyclic N-halamines. Hydroxyl and amine functionalized reactive reagents like 2,4,6-trichloro-s-triazine (chemical structure Figure 4) not only bound on cellulose fibers at low temperature but also prevents the fabric mechanical and physical damage under high temperature owing to its good thermal stability [27,51,52]. Moreover, N-halamines with higher hydrophilicity kill microbes more rapidly as compared to lower hydrophilic or strong hydrophobic ones [50]. A series of 2,4,6-trichloro-s-triazine based N-halamines has fabricated and investigated [26,53-55].

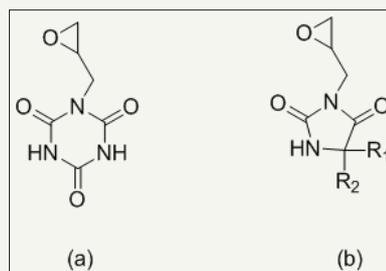


Figure 3: chemical structures of epoxides based cyclic N-halamine, (a) 1-glycidyl-s-triazine-2,4,6-trione and (b) 3-glycidyl-5,5-dialkylhydantoin.

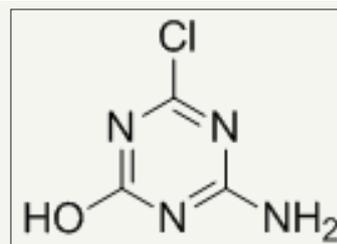


Figure 4: Chemical structure of hydroxyl and amine functionalized reactive reagent, 2,4,6-trichloro-s-triazine.

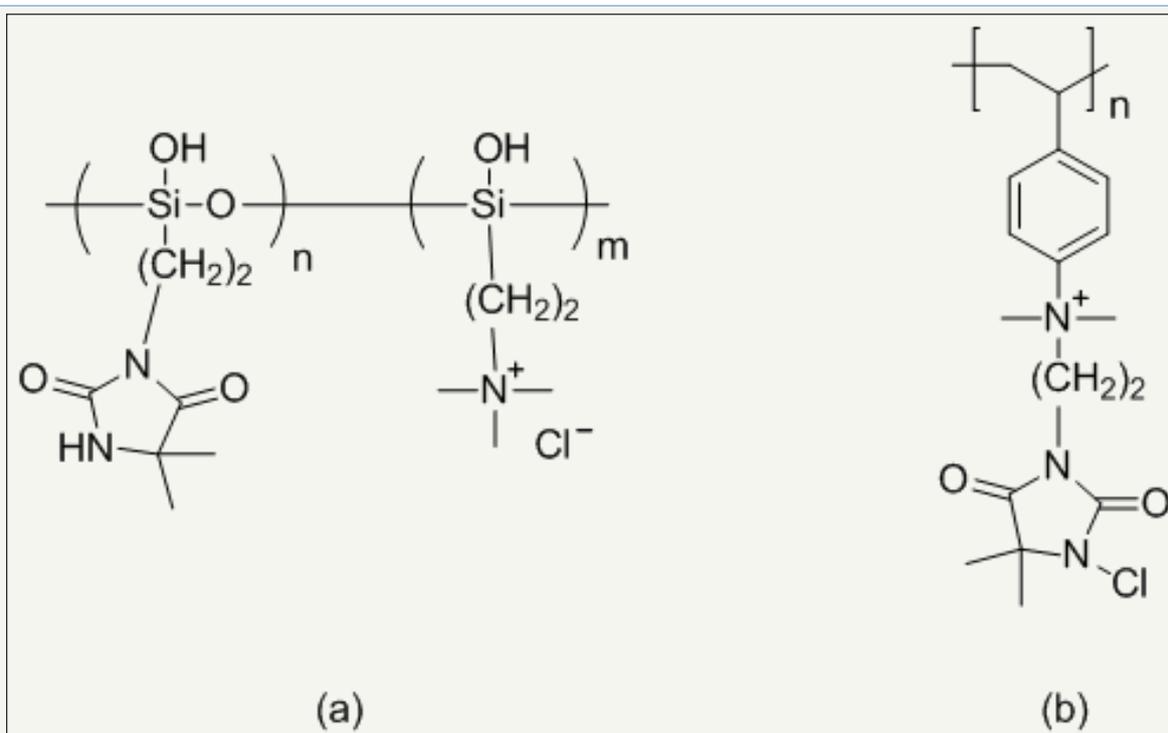


Figure 5: Chemical structures of (a) poly(3-(5,5-dimethylhydantoinylpropyl)siloxane-co-3 dimethyldodecylammonium propylsiloxane chloride) and (b) poly(1-chloro-5,5-dimethylhydantoinyl-3-ethyl-p-ethenylphenylmethyldimethylammonium chloride).

Another way to finish N-halamines on fiber surface is graft polymerization of fabric. Vinyl functionalized N-halamines can be grafted on fiber using free radical initiator. They are classified acyclic and cyclic N-halamines. Examples are 4-vinylbenzyl chloride [56], methacrylate chloride [57], acryloyl chloride [58], hydroxyl ethylmethacrylate [19] and allyl bromide [20] based N-halamines. Quaternary ammonium salt based N-halamines further promote

antimicrobial activity of N-halamines and exhibit excellent water solubility and ultimately ease of their application during fabric finishing [37,59,60]. Figure 5 shows the chemical structures of quaternary ammonium salt based N-halamines while Figure 6 show schematic of grafted cotton by quaternary ammonium salt based N-halamines.

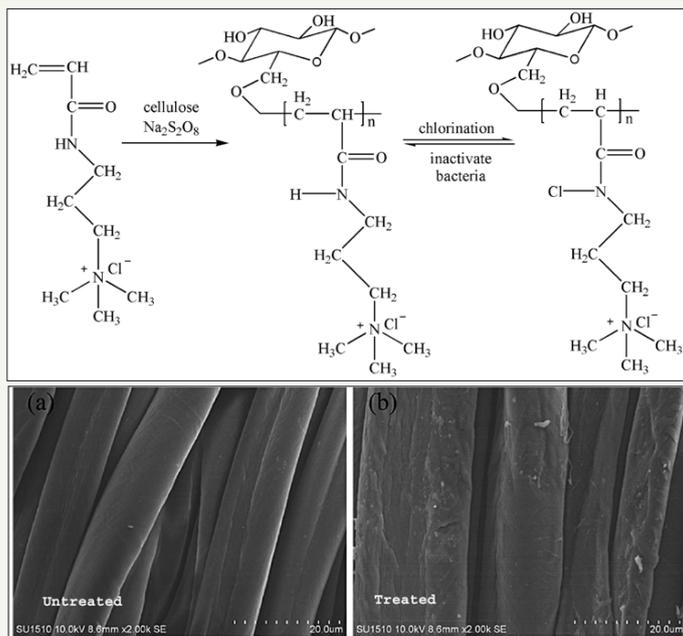


Figure 6: schematic of grafted cotton by quaternary ammonium salt based N-halamines and their scanning electron microscopy (SEM) images [59].

Halogenated phenols: Halogenation of phenols imparts improved antibacterial functionality to phenols. Para halogenated phenols have greater potential as compared to other halogenated phenols, however, with decreased water solubility. A number of halogenated products of phenols are depicted in Figure 7. Triclosan is most important bactericidal among halogenated phenols and exhibit good antimicrobial power against a broad spectrum of microbes and antibiotic-resistant bacteria. It is used in antibacterial household textiles, cleaning wipes, towels, socks, shoe-socks, for protection of transport and industrial filter [61-63]. Triclosan block the lipid biosynthesis of microbes and ultimately inhibit the fatty acid biosynthesis. Beside this, it also inhibits growth of microbes by reacting with amino-acids of active enzyme's sites

[64]. Halogenated phenols are not able to form strong bond with fiber surface, so they perform their activity through leaching mechanism. 6% Triclosan solution applied to cotton fabric retain its antibacterial up to 50 laundering washing cycles [64]. The agent leaches slowly and kills microbes in its environment [65]. However, these agents lose their concentration on usage with passage of time and become effective less. Recently, new strategies are investigated where halogenated phenolic antimicrobial agents are tried to bind on the fiber surface chemical by using suitable cross linkers. This method is however increasing the durability of antimicrobial functionality of halogenated phenols. The binding mechanism of triclosan on cellulose fiber is illustrated in Figure 8.

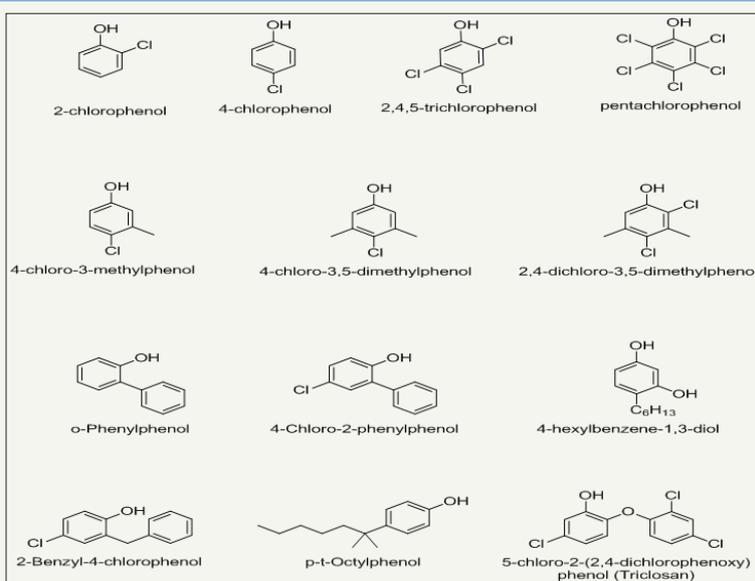


Figure 7: Chemical structures of various halogenated products of phenols.

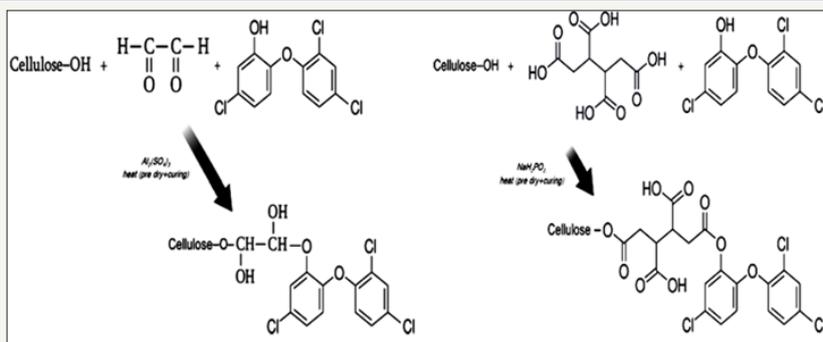


Figure 8: Binding mechanism of triclosan on to cellulose fiber using diacid a crosslinker [66].

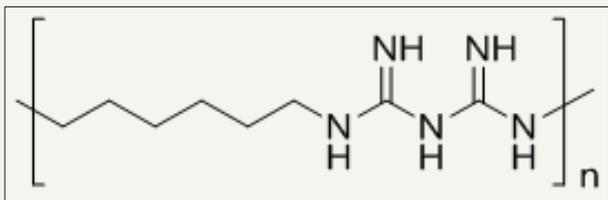


Figure 9: Chemical structure of polybiguanide from hexamethylene biguanide monomer, repeating using n=15-20, Molecular weight ~ 3000.

Polybiguanides: Polybiguanides are water soluble polymers of repeating unit alkyl biguanides. Polyhexamethylene biguanides are polymer of “hexamethylene biguanides” (HMB) repeat unit with degree of polymerization [15-20]. Figure 9 presents the chemical structure of PHMB. Polybiguanides are specially utilized as cleansing agents in food industry with 20% aqueous solution [66]. Their concentration between 5-25mg/ml is required to inhibition of bacteria but a concentration up to 250mg/ml may also require some bacteria like *Pseudomonas vulgaris* and *Paeruginosa*. PHMB is expected to inhibit gram positive bacteria in a way by which it activate outer membrane of lipopolysaccharide which then displaces cation via self-promotion mechanism [67-71]. Polybiguanides not only possess good antimicrobial activity but also have strong affinity to attach on surface of cotton fabric. The electrostatic interactions between negatively charged bacteria cell wall and positively charged biguanide repeat unit are responsible to kill bacteria. Advantageously, positively charged biguanide

groups are able to bind with negatively charged group’s especially carboxylic group in cellulosic fabrics via electrostatic interactions [72]. Moreover, its applicability becomes easier in exhaustion and padding processes due to its water soluble nature.

Polybiguanides do not leach out and remain chemically bound to fiber surface where they act as barrier against microbes which come in contact with treated fiber and show good durability [72,73].

Natural products as antimicrobial agents

Natural products from secondary metabolites of plants have well known to human beings for cure of human diseases as they exhibit various biological activities on other organisms. These natural products are now also utilizing in commercial drugs and medicines. They also are being consumed in beverages, foods, flavoring, dyes, fibers and fragrances. Owing to their low toxicity, biocompatibility and biological activities, they have raised the interest of textiles engineers to utilize them for fabrication various functional textiles. They are investigated for evaluating various properties for textile products such as insecticidal effects, antimicrobial effects, vitalizing and energizing effects, promotion of comfort, health and fitness, UV protection and pleasant odor.

Synthetic antimicrobial agent although show good antibacterial power and durability, but toxic nature of some synthetic agents and their non-degradability in environment has shifted the trend of their utilization towards natural products as competitive alternatives. A small fraction of natural products have studied among 50000 known plant species.

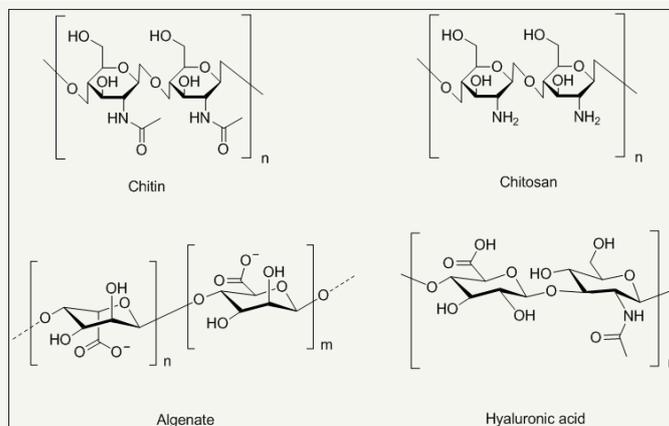


Figure 10: Chemical structures of some important natural antibacterial agents for antimicrobial finish of textiles.

The investigated natural product based antimicrobial agents for textile finishing are phenols, polyphenols, quinones, flavonoids, tannins, coumarins, terpenoids, natural polymers like chitin,

chitosan, alginate, gelatin and hyaluronic acid [74-83]. The chemical structures of some of natural products are depicted in Figure 10.

Photoactive antimicrobial agents

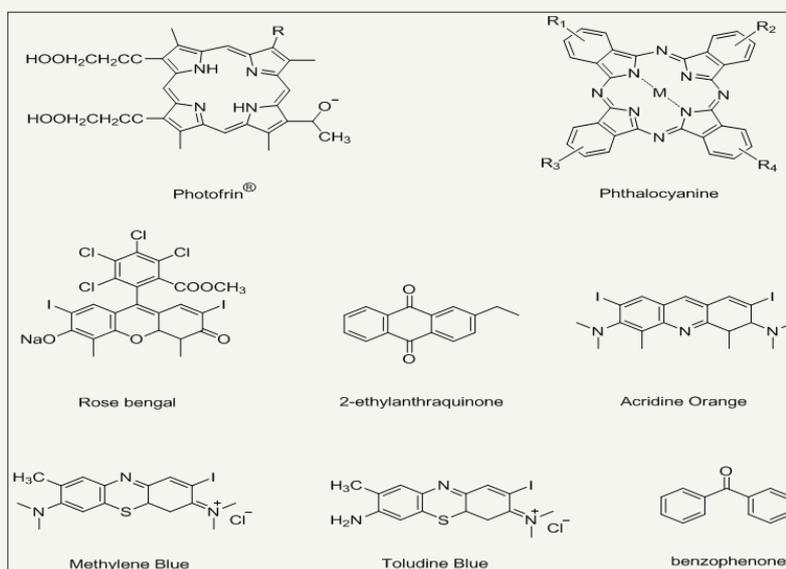


Figure 11: Chemical structures of some organic photosensitizers.

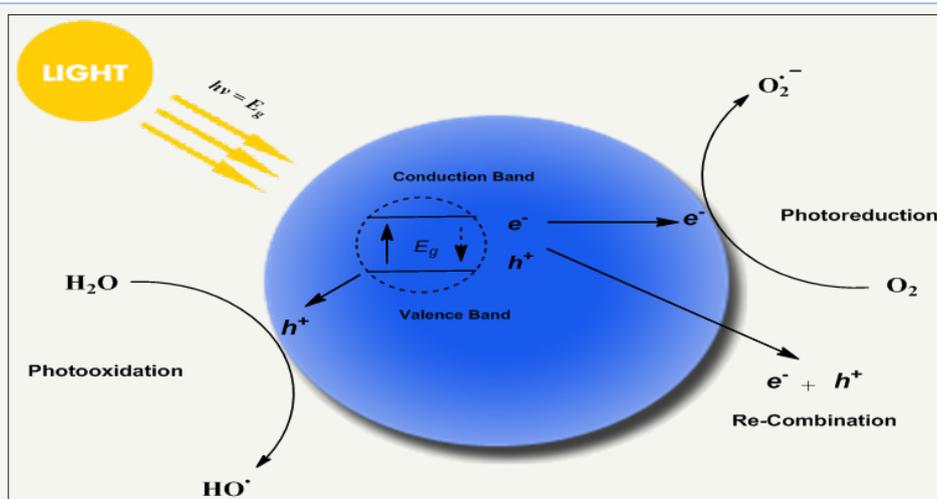


Figure 12: schematic redox mechanism of photocatalyst via photoexcitation and de-excitation producing reactive oxygen species by performing redox reaction with compounds in its environment, highly reactive oxygen species have potential to kill a broad spectrum of microorganism non-selectively with the advantage of good durability.

Photo-antimicrobial agents are light activated antimicrobial agents which trigger their antimicrobial activity upon light irradiation and cease in absence of light. The microbial resistance of light activated antimicrobial agents is purely dependent on exposure time, irradiation distance, light intensity and light source as well. Photoactive antimicrobial agents may either organic photosensitizer dyes or inorganic photocatalysts. Organic photosensitizers may be synthetic or natural such as phenothiazinium, rose Bengal, porphyrins etc (Figure 11). Inorganic photocatalysts are mostly metal oxide nanoparticles (NPs), for example, TiO_2 , ZnS , ZnO , Fe_2O_3 and SnO_2 based semiconductors [84-95]. Actually, a photochemical reaction occur when these agents absorb light and as a result they

continuously emit reactive oxygen species under light irradiation in visible (350-700nm) or UVA range. The generated reactive oxygen species may be hydrogen peroxide (H_2O_2), hydroxyl radical ($\text{HO}\cdot$), singlet oxygen ($^1\text{O}_2$) etc. Such species are able to inactivate a broad range of microbes including *Pseudomonas aeruginosa*, *Candida albicans*, *C. difficile*, *Escherichia coli*, *S. aureus*, etc. Photoactive antimicrobial agent possess excellent antimicrobial activities under light irradiation with durability. There is no need to supply agents regularly as those halogenated phenols require. They remain attach on fiber surface, however, wearing may cause the loss of agent from fabric surface. The schematic redox mechanism via photoexcitation and de-excitation is presented in Figure 12. Photocatalysts possess

band structure rather than continuous electronic states like metals. Excitation of electron from valence band to conduction band occur which is assisted by absorption of photons from light source ($h\nu > \Delta E_g$) [96,97]. Such excitation result in formation of hole-electron pair where a hole (h^+) bearing positive charge produce in valence band and active electron (e^-) produce in conduction band. Here, there may two chances of happenings. One is that the excited electron may come back to valence band by releasing heat. Secondly, here in excited state, a redox reaction may happen with absorbed compounds from nearby environment, for example, molecular oxygen, water or hydroxyl groups [98]. As a result of such redox reactions, various reactive oxygen species formed depending upon the absorbed compound. These extremely active oxygen species

then kill the bacterial non-selectively and perform their strong antibacterial activity. Most interestingly, photoactive antimicrobial agents act as catalyst and eventually go back to its original form via excitation/de-excitation process during redox reaction and impart durability to treated fabric. Thus photocatalysts do not lose their concentrations, no need to recharging of functionality, and thus ultimately they present excellent durability and antimicrobial activity.

Organic photosensitizers go in their excited state by absorbing particular amount of energy and produce reactive oxygen species via two photochemical methods [99-103]. These mechanisms are illustrated in Figure 13. The synthesis route and bacterial resistance of photo-antimicrobial cotton is presented in Figure 14.

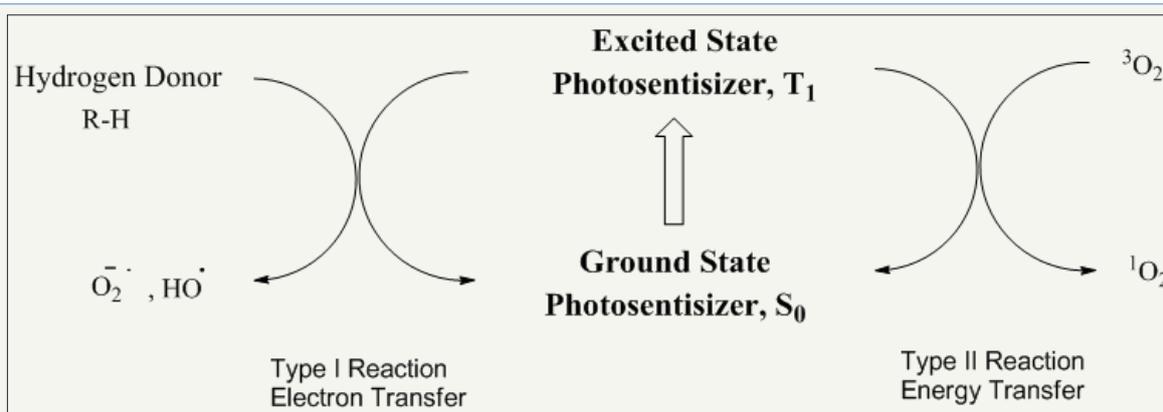


Figure 13: Mechanism of producing reactive oxygen species of photosensitizers via photosensitization process.

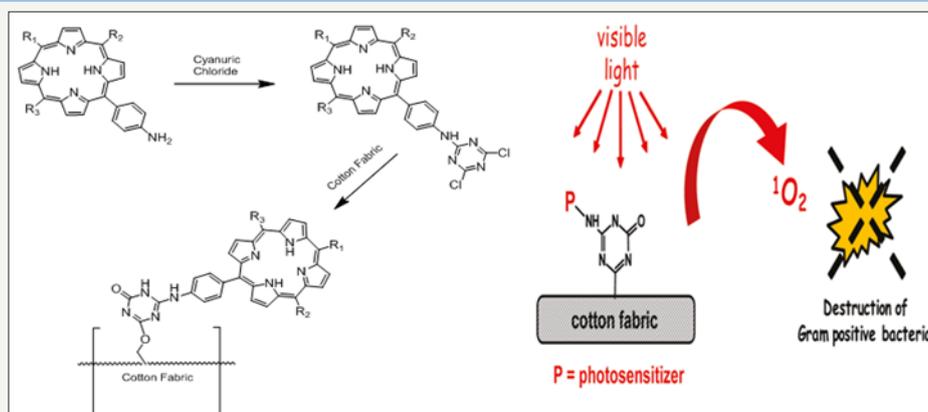


Figure 14: Synthesis route and bacterial resistance of photo-antimicrobial cotton [103].

Conclusion

Antimicrobial finishes are applied to textile products for a number of advantage regarding human health issues such as, inhibiting microbes from spreading, control of infections, control of odor, healing of wound, etc. antimicrobial textile should meet a number of key requirements including excellent resistance towards microbes, durability, should be safe to human skin and body. antimicrobial activities, durability, mechanisms and performances of various classes of antimicrobial agents is discussed. The major classes of antimicrobial agents for textile finishing applications are

N-halamines, halogenated phenols, polybiguanides, plant based natural products, and photoactive antimicrobial agents. In future, development of antimicrobial finishes with precised long term antimicrobial power, durability and actual wearing and laundering conditions should be practice out.

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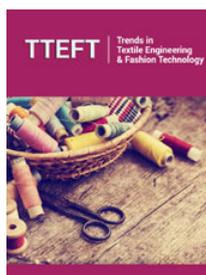
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