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Review

Antibacterial modification of cotton using nanotechnology

Moustafa M.G. Fouda[a,b,*], E.S. Abdel-Halim[a,b], Salem S. Al-Deyab[a]

[a] Petrochemical Research Chair, Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia
[b] Textile Research Division, National Research Center, P.O. Box 12622, Dokki, Cairo, Giza 12522, Egypt

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ABSTRACT

This review article is undertaken with a view to survey important scientific research and developmental works pertaining to antibacterial modification of textiles using nanotechnology as a new means to achieve such textiles. Inevitably, conventional antimicrobial agents and their applications to textiles are reported. This is followed by a focus on inorganic nanostructured materials that acquire good antibacterial activity and application of these materials to the textiles. Evaluation of the antibacterial efficacy is described. An outlook which envisions the importance of using nanotechnology in the antibacterial finishing of textiles is also outlined.

Contents

* Corresponding author at: Petrochemical Research Chair, Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia.
E-mail addresses: m_gaballa@yahoo.com, mmfoudah@ksu.edu.sa (M.M.G. Fouda).

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1. History

During World War II, when cotton fabrics were used extensively for tentage, tarpaulins and truck covers, these fabrics needed to be protected from rotting caused by microbial attack. This was particularly a problem in the South Pacific campaigns, where much of the fighting took place under jungle like conditions. During the early 1940s, the US army Quartermaster Crops collected and compiled data on fungi, yeast and algae isolated from textiles in tropical and subtropical areas throughout the world. Cotton duck, webbing and other military fabrics were treated with mixtures of chlorinated waxes, copper and antimony salts that stiffened the fabrics and gave them a peculiar odor. At the time, potential polluting effects of the application of these materials and toxicity-related issue were not a major consideration.

After World War II, and as late as the mid-to-late 1950s fungicides used on cotton fabrics were compounds such as 8-hydroxygiunoline salts, copper naphthenate, copper ammonium fluoride and chlorinated phenols. As the government and industrial firms became more aware of the environmental and work place hazards these compounds caused. Alternative products were sought. A considerable amount of work was done by the Southern Regional Research Laboratory of the US Department of Agriculture, the Institute of Textile Technology (ITT) and some of the ITTs member mills to chemically modify cotton to improve its resistance to rotting and improve other properties by acetylation and cyanoethylation of cotton. These treatments had limited industry acceptance because of relatively high cost and loss of fabric strength in processing. In addition, the growing use of man-made fibers such as nylon, acrylics and polyester, which have inherent resistance to microbial decomposition, came into wider use to replace cotton in many industrial fabrics (Ramachandran, Rajendrakumar, & Rajendran, 2004).

2. Introduction

Clothing and textile materials are good media for growth of microorganisms such as bacteria and fungi. According to recent reports, microorganisms could survive on fabric materials for more than 90 days in a hospital environment. Such a high survival rate of pathogens on medically used textiles may contribute to transmissions of diseases in hospitals. As a means to reduce bacterial population in healthcare settings and possibly to cut pathogenic infections caused by the textile materials, utilization of antimicrobial textiles in healthcare facilities is considered to be a potential solution (Qian & Sun, 2003).

Textile surface modification provides a way to impart new and diverse properties to textiles while retaining comfort and mechanical strength. Currently, functional finishes on textile fabrics are of critical importance to improve textile products with multifunctional properties. Textile finishes can be divided into esthetic and functional finishes. Esthetic finishes are finishes used to modify the appearance or hand of a fiber or fabric. They can alter the texture, luster, or drape of a textile material. Mechanical and chemical processes may be used to impart an esthetic finish, this type of finishing with a greater emphasis being placed on mechanical processes. Many different chemicals and processes are used in the finishing of textile materials. Functional finishes that alter fiber or fabric performance, maintenance, durability, safety, and environmental resistance can be considered as functional finishes. Functional finishes are generally applied specifically to alter properties related to care, comfort, and durability. Most functional fabric properties are imparted by using chemical and wet processing methods (Hudson, Clapp, & Kness, 1993; Tomasino, 1992). Some common functional finishes are: antimicrobial, antistatic, durable press, flame resistant/retardant, soil release/resistant, water proof/repellent, UV protection, self-cleaning, and wrinkle recovery. This review article will focus on the antimicrobial finishes of textiles. The driving force behind the chemical finishing of cotton during the next 10 years is anticipated to comprise several factors. Of these factors, mention is made of the following: (i) chemical finishes which maximize the added value; (ii) chemical finishes which are friendly with the environment; (iii) methods which are convenient for application, and (iv) the need for better quality and minimum use of water and energy (Hashem, Refaie, & Hebeish, 2005).

In recent years, antimicrobial finishing of textiles has become extremely important in the production of protective, decorative and technical textile products. This has provided opportunities to expand the use of such textiles to different applications in the textile, pharmaceutical, medical, engineering, agricultural, and food industries (Simoncic & Tomsic, 2010). Antimicrobial finishing of textiles protects users from pathogenic or odor-generating microorganisms, which can cause medical and hygienic problems, and protects textiles from undesirable esthetic changes or damage caused by rotting, which can result in reduced functionality. As a consequence of their importance, the number of different antimicrobial agents suitable for textile application on the market has increased dramatically. These antimicrobial agents differ in their chemical structure, effectiveness, method of application, and influence on people and the environment as well as cost (Dring, 2003; Gao & Cranston, 2008; Mahltig, Haufe, & Böttcher, 2005; Schindler & Hauser, 2004; Vigo, 1983). In the literature (Dring, 2003; Schindler & Hauser, 2004; Vigo, 1983), there are several different classifications of antimicrobial agents according to efficiency, mechanism of antimicrobial activity and washing resistance. According to these studies, products can be divided into biocides and biostats, leaching and bound antimicrobials, controlled-release and barrier-forming agents, and agents of poor and of good washing resistance. In general, the activity of antimicrobial finishes can be biocide or biostatic. While the biocides (bactericides and fungicides) include agents that kill bacteria and fungi, the biostats (bacteriostats and fungistats) inhibit the microorganisms' growth. The mode of action is directly related to the concentration of the active substance in the textile. The minimum inhibitory concentration (MIC) is required for biostatic activity, but the minimum biocidal concentration (MBC) should be exceeded for biocidal activity.

The majority of antimicrobial agents in the textile industry utilize a controlled-release mechanism (Vigo, 1983). These agents, which are also called, leaching antimicrobials (Schindler & Hauser, 2004), are not chemically bound to the textile fibers and their antimicrobial activity is attributed to their gradual and persistent release from the textile into their surroundings in the presence of moisture, where they act as a poison to a wide spectrum of bacteria and fungi. The antimicrobial efficiency depends directly on the

concentration, which should not drop below the MIC. Owing to leaching of the agent into its surroundings, the concentration of the active substance in the textile decreases and gradually falls under the limit of effectiveness. This can induce resistance to these substances in microorganisms; in addition, leaching agents do not withstand repeated laundering. A controlled release mechanism can also be found in agents that are chemically incorporated into the fiber surface, but with an active substance that is leachable in water. The important advantage of these agents over other leaching antimicrobials is that they can be regenerated under appropriate conditions.

The bound antimicrobials (Schindler & Hauser, 2004) include finishes that are chemically bound to the surface of the textile fibers, where they act as a barrier and control microorganisms which come into contact with the fiber surface. Because these agents do not leach into the surroundings of the textile substrate, the probability of microorganisms developing resistance to them is small. Covalent binding of the agent to the textile surface can be ensured if there are enough reactive groups in the agent and the fibers, and if the application process is carried out under suitable conditions. Accordingly, when using bound antimicrobials, the mechanism of chemical binding to the textile surface and the conditions that initiate or catalyze the reaction should be known. Bound antimicrobials are much more resistant to repeated laundering in comparison to leaching agents. However, washing durability of the agent cannot assure its durability of antimicrobial function. The latter could decrease or even expire with the adsorption of dirt, deadly microorganisms or complex formation between the finish and the anionic detergent during laundering. For antimicrobial finishing in the textile industry, it is not only the antimicrobial efficiencies of the agents that are important, the environmental, health and safety aspects of their use must also be taken into account (Simoncic & Tomsic, 2010).

It should be stressed that the release of finishes from the textile into the surroundings could have negative impacts on living organisms in water because they can affect susceptible bacteria, thereby potentially selecting resistant bacteria. Fortunately, bound antimicrobials are environmentally friendly finishes with no leaching of toxic products into the surroundings. Taking these facts into account, much research has focused on the synthesis of novel antimicrobial agents where leaching antimicrobials have been replaced with bound antimicrobials. Some of the most important examples are presented in this review.

3. Conventional antimicrobial agents for textiles

3.1. Quaternary ammonium compounds

Cationic surface active agents (cationic surfactants), including particularly quaternary ammonium salts (QASs), are important biocides that for many years have been known to be effective antiseptic and disinfectant agents (Dring, 2003; Gao & Cranston, 2008; Purwar & Joshi, 2004; Schindler & Hauser, 2004; Vigo, 1983). As antimicrobial agents for textiles, monoammonium and "gemini" or "dimeric" ammonium surfactants (Fig. 1) with an alkyl, alkylaryl and perfluorinated hydrocarbon group are used (Massi, Guittard, Levy, & Gêribaldi, 2009; Murguia, Machuca, Lura, Cabrera, & Grau, 2008). These are active against a broad spectrum of microorganisms such as Gram-positive and Gram-negative bacteria, fungi and certain types of viruses (Ahlström, Chelminska-Bertilsson, Thompson, & Edebo, 1995). The antimicrobial activity of QASs depends on the length of the alkyl chain, the presence of the perfluorinated group and the number of cationic ammonium groups in the molecule. The antimicrobial function arises from attractive interactions between the cationic ammonium group of the QAS and the negatively

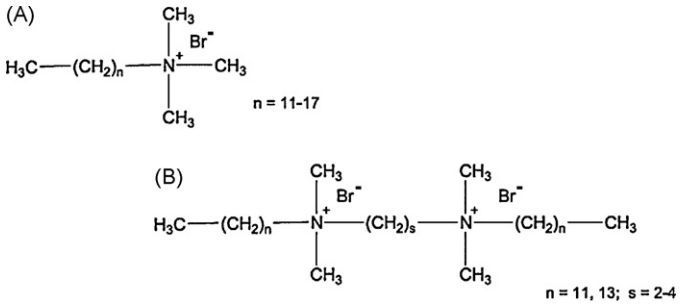

Fig. 1. Chemical structure of monoquaternary ammonium salt, alkyltrimethylammonium bromide (A) and diquaternary ammonium salt, alkanediyl-α,ω-bis(dimethylalkylammonium bromide) (B).

charged cell membrane of the microbe; these interactions consequently result in the formation of a surfactant–microbe complex. This in turn causes the interruption of all essential functions of the cell membrane and thus the interruption of protein activity (Gilbert & Moore, 2005). QASs also affect bacterial DNA, causing a loss of multiplication ability (Marini, Bondi, Iseppi, Toselli, & Pilati, 2007). If the long hydrocarbon chain is bonded to the cationic ammonium in the structure of the QAS, two types of interactions between the agent and the microorganism can occur: a polar interaction with the cationic nitrogen of the ammonium group and a non-polar interaction with the hydrophobic chain. Penetration of the hydrophobic group into the microorganism consequently occurs, enabling the alkylammonium group to physically interrupt all key cell functions.

Despite many positive properties, QASs have an inherent weakness: leaching from the textile. There are no reactive functional groups in the structure of the QAS to allow its chemical bonding to the fibers. Owing to the lack of physical bonding, leaching of the QAS occurs, resulting in a fast decrease in concentration to below the MIC. In addition, QASs have poor wash durability. To develop new, permanently bonded, non-leaching QAS biocidal groups for textile fibers, contemporary studies have synthesized polymerizable QASs (Caillier et al., 2009; Shao, Jiang, Meng, & Qing, 2003; Summers, Eastoe, & Richardson, 2003) with acrylate or methacrylate groups for incorporation in the structure (Fig. 2). Such QAS monomers have been named surfactant monomers or "surfmers". Under appropriate conditions, "surfmers" polymerize into a bulk polymer network with a polycationic structure, including side QAS groups chemically bonded to the main polyacrylate chain. The merit of fixed bonding to the textile surface is that the QAS groups can act as a biobarrier and kill microorganisms by contact. Furthermore, the formation of a polymer network on the surface of the fibers strongly increases the durability and wash resistance of the antimicrobial agent.

3.2. N-halamines

N-halamines are heterocyclic organic compounds containing one or two covalent bonds formed between nitrogen and a halogen (N—X), in which the latter is usually chlorine (Sun, Chen, Wheatley, & Worley, 1995). N—Cl bonds of different stability can be formed by the chlorination of amine, amide or imide groups in dilute sodium hypochlorite. N-halamines are biocides that are active for a broad spectrum of bacteria, fungi and viruses. Their antimicrobial properties are based on the electrophilic substitution of Cl in the N—Cl bond with H; this reaction can be carried out in the presence of water and results in the transfer of Cl+ ions that can bind to acceptor regions on microorganisms. This hinders enzymatic and metabolic processes, leading to the destruction of the microorganisms. As an N—H bond, which does not have antimicrobial properties, is formed in the substitution reaction, further exposure of the agent to dilute

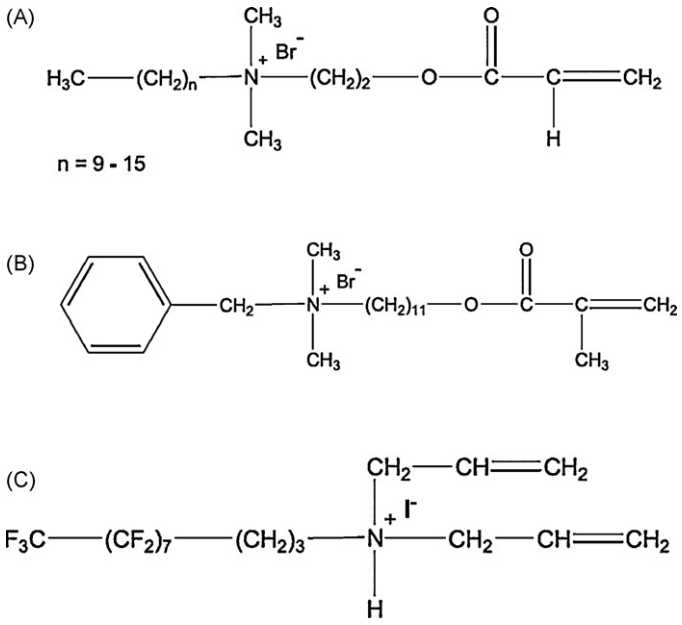

Fig. 2. Chemical structures of various "surfmers": alkyl(2-(acryloyloxy)ethyl)-dimethyl ammonium bromide (A) benzyl(11-(acryloyloxy)undecyl)dimethyl ammonium bromide (B), and N-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-heptadecafluoroundecyl)-N,N-diallylmethyl ammonium iodide (C).

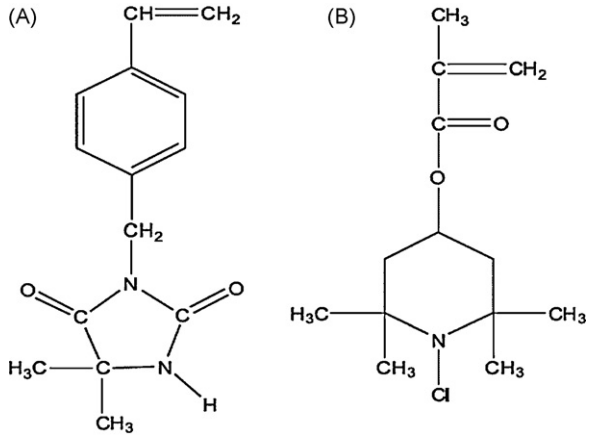

Fig. 3. Chemical structures of 3-(4′-vinylbenzyl)-5,5-dimethylhydantoin (A) and N-chloro-2,2,6,6-tetramethyl-4-piperidinyl methacrylate (B).

sodium hypochlorite is needed for regeneration of its antimicrobial activity (Barnes et al., 2006; Qian & Sun, 2005).

N-halamines can be applied to various textile surfaces including cellulose (Barnes et al., 2006, 2007; Ren, Kocer, Worley, Broughton, & Huang, 2009), polyamide (Lin, Cammarata, & Worley, 2001) and polyester (Ren, Kocer, et al., 2008) fibers. To increase their effectiveness and the durability of the antimicrobial finish (Barnes et al., 2006), research has been oriented toward synthesis of N-halamide monomers with an incorporated vinyl reactive group (Fig. 3) (Ahmed, Hay, Bushell, Wardell, & Cavalli, 2008; Ren, Kou, et al., 2008) that can polymerize on cellulose fibers under appropriate conditions to form a coating with excellent durability after washing (Ren, Kou, et al., 2008).

3.3. Chitosan

Chitosan is a deacetylated derivate of chitin, which is a natural polysaccharide mainly derived from the shells of shrimps and other sea crustaceans. Chemically, it can be designated as poly-β-(1 → 4)-D-glucosamine or poly-(1,4)-2-amido-deoxy-β-D-glucose (Fig. 4) (Fahmy & Fouda, 2008; Fouda, El Shafei, Sharaf, & Hebeish, 2009; Fouda, Wittke, Knittel, & Schollmeyer, 2009). In addition to its antimicrobial activity, chitosan has some important advantages such as non-toxicity, biocompatibility and biodegradability.

To provide antimicrobial effect for textiles, chitosan can be used as an additive when spinning antimicrobial fibers (Fan et al., 2006) and also as a finishing agent (Fouda, El Shafei, et al., 2009) for surface modification, mainly of cellulose, cellulose/polyester and wool fibers. Chitosan is positively charged and soluble in acidic to neutral solutions because the amino groups in chitosan have a pK_a of ~6.5. Its antimicrobial function arises from its polycationic nature, which is caused by protonation of the amino groups at the C-2 atoms of the glucosamine units; such antimicrobial function is very similar to that determined for QAS. Positively charged amino groups can bind to the negatively charged bacterial surface, resulting in the disruption of the cell membrane and an increase in its permeability. Chitosan can also interact with the DNA of microorganisms to prevent protein synthesis.

The antimicrobial efficiency of chitosan depends on its average molecular weight, degree of deacetylation and the ratio between protonated and unprotonated amino groups in the structure (Fouda, El Shafei, et al., 2009). It is believed that chitosan of a low molecular weight is more antimicrobially active than chitosan oligomers (Fouda, El Shafei, et al., 2009). The efficiency also increases with increased deacetylation, which can exceed 90%. An important disadvantage of chitosan is its weak adhesion to cellulose fibers, resulting in a gradual leaching from the fiber surface with repetitive washing. To enable chitosan to bind strongly to cellulose fibers, various crosslinking agents are used, including mostly polycarboxylic acids (1,2,3,4-butantetracarboxylic and citric acids) (Fouda, El Shafei, et al., 2009; Fouda, Wittke, et al., 2009) and derivates of imidazolidinone (Huang, Wu, Chen, & Lian, 2008). In the presence of a crosslinking agent, hydroxyl groups of chitosan and cellulose can form covalent bonds with carboxyl groups of polycarboxylic acid in an esterification reaction or with hydroxyl groups of imidazolidinone in an etherification reaction, thus leading to the formation of a crosslink between chitosan and cellulose. This greatly improves durability and wash resistance. In addition, the reactivity of quaternized chitosan has been improved by introducing functional acrylamidomethyl groups to the primary alcohol groups (C-6), which can form covalent bonds with cellulose in alkaline conditions (Fig. 5) (Lim & Hudson, 2004).

The chemical binding of chitosan to cellulose fibers can also be achieved by oxidation of cellulose fibers with potassium periodate

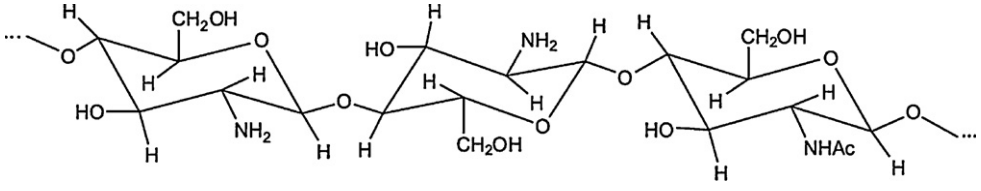

Fig. 4. Chemical structure of chitosan.

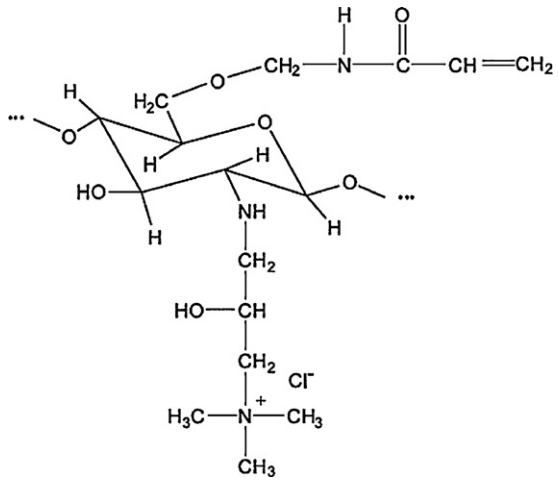

Fig. 5. Chemical structure of reactive *O*-acrylamidomethyl-N-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride.

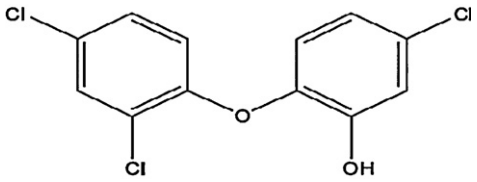

Fig. 6. Chemical structure of triclosan.

under acidic conditions to form aldehyde groups, which are allowed to react with the amino groups of chitosan and form a Schiff base (C=N double bond) (Kitkulnumchai, Ajavakom, & Sukwattanasinitt, 2008). Following the model of N-halamine halogenation, some of the amino groups in chitosan have been transformed into an —NHCl structure in the presence of sodium hypochlorite (Cao & Sun, 2007). It has been found that chlorination significantly improves the antimicrobial activity of chitosan.

3.4. Halogenated phenols

Among halogenated phenols, triclosan 5-chloro-2-(2,4-dichlorophenoxy) phenol (Fig. 6) (Yazdankhah et al., 2006) is the most widely used biocide; it is present in many contemporary consumer and personal health-care products, detergents and household objects, including textiles and plastics.

At bactericidal concentration, triclosan is very effective against a broad range of microorganisms, including antibiotic-resistant

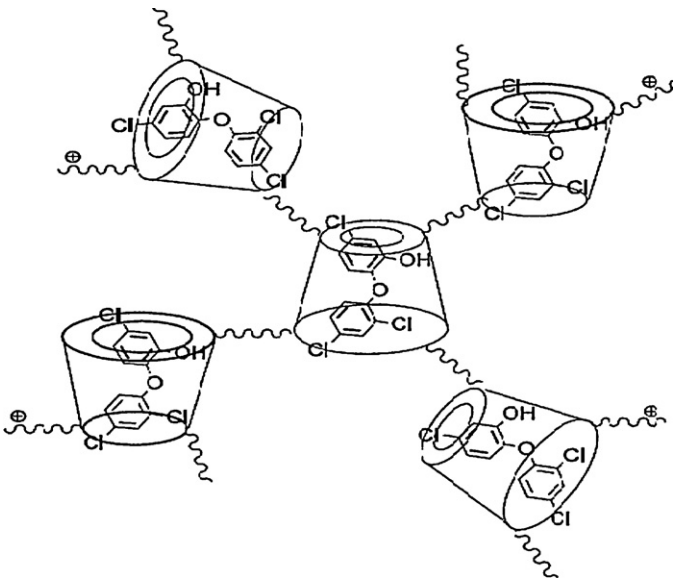

Fig. 7. Schematic presentation of host–guest complexes between cationic β-cyclodextrin and triclosan.

bacteria. As the widespread use of triclosan could represent a potential risk in terms of the development of resistant microorganisms (Yazdankhah et al., 2006) strong binding to solid surfaces with subsequent controlled release is important. Triclosan has therefore been applied to cellulose fibers in combination with polycarboxylic acids as crosslinking agents (Orhan, Kut, & Gunesoglu, 2009). The application of polycarboxylic acid to fibers previously finished with triclosan enhances the washing durability of the antimicrobial coating.

Novel host–guest complexes including triclosan molecules have been prepared with the use of cationic β-cyclodextrins (Fig. 7), which are torus-shaped cyclic oligosaccharides containing six to eight glucose units linked by α-1,4 bonds (Qian et al., 2009). Water solubility, stability and antimicrobial activity have been determined for the host–guest complexes. Owing to strong electrostatic attraction, the complexes are adsorbed to the surface of cellulose fibers almost completely. Triclosan has also been encapsulated in biodegradable polylactide as a carrier and used for finishing nonwoven textiles (Goetzendorf-Grabowska et al., 2008).

3.5. Polybiguanides

Polybiguanides are polymeric polycationic amines that include cationic biguanide repeat units separated by hydrocarbon chain

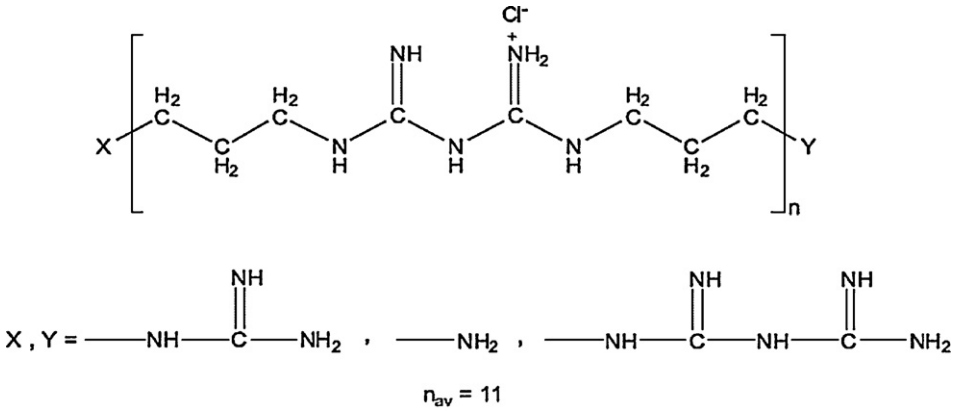

Fig. 8. Chemical structure of poly (hexamethylenebiguanide). Here nav is the average number of repeat units.

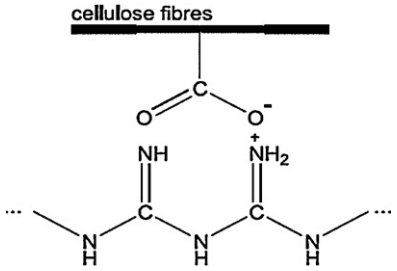

Fig. 9. Binding of poly (hexamethylenebiguanide) to the carboxylic group of cellulose.

linkers of identical or dissimilar length. One of the most important antimicrobial agents among them is poly (hexamethylenebiguanide) (PHMB) with an average of 11 biguanide units (Fig. 8) (Kawabata & Taylor, 2007); PHMB exhibits much greater antimicrobial activity than corresponding monomeric or dimeric biguanides. PHMB is widely used in medicine as an antiseptic agent, especially for preventing wound infection by antibiotic-resistant bacteria (Moore & Gray, 2007). Owing to its high biocidal activity and low toxicity, it has also attracted attention for the antimicrobial finishing of textiles, mainly for the protection of cellulose fibers (Kawabata & Taylor, 2007).

The literature (Blackburn, Harvey, Kettle, Payne, & Russell, 2006) indicates that PHMB can bind to the anionic carboxylic groups of cellulose (Fig. 9), which are formed through oxidation of glucose rings during pre-treatment processes such as bleaching and mercerizing. At lower concentrations, electrostatic interactions between PHMB and carboxylic groups in the cellulose dominate; however, hydrogen bonding of PHMB with cellulose resulting in multilayer adsorption becomes increasingly dominant as the concentration of PHMB increases. The adsorption of PHMB increases if cellulose fibers are previously dyed with anionic reactive dyes, which provide sulfonic acid sites with which the PHMB can react. However, strong PHMG–dye interactions cause a reduction in the antimicrobial activity of PHMB, which is undesirable.

4. Nanotechnology

In recent years nanotechnology has become one of the most important and exciting forefront fields in physics, chemistry, engineering and biology. It shows great promise for providing us in the near future with many breakthroughs that will change the direction of technological advances in wide range of applications. The prefix nano in the word nanotechnology means one billionth of a meter (1×10^{-9}). Nanotechnology deals with various structures of matter having the dimension of the order of a billionth of a meter. Structures on this scale have been shown to have unique and novel functional properties. Based on that principle, many applications of nanotechnology from the simple to the complex have been done. One of these applications is to prepare antimicrobial textiles based on heavy metals in their nanoscale.

Particles at the nanoscale are below the wave length of visible light and therefore, cannot be seen. Consequently they can impart new properties. For example, Ti-nanoparticles are applied for the textile materials in order to develop textile products with UV-protection and self-cleaning property. Also silver nanoparticles are used as antimicrobial agent for wound dressing materials as well as for wound healing. In addition, the production of fibers with diameter less than 100 nm is now feasible with the invention of electrospinning process. Electrospinning is a manufacturing new technology capable of producing thin, solid polymer strands from solution by applying a strong electric field to a spinneret with a small capillary orifice. The spun, polymer based nanofibers, can be loaded with different additives which could be metal nanoparticles like silver, drugs or catalysts depending on the required applications. The resulted nanofibers are collected and bundled. These electrospun fibers have high surface area and porous structure, where more than one drug can be encapsulated directly into the fiber. The resulted matrix can be used extensively for medical textiles production with multifunctional properties.

The intersecting fields of study that create this domain of science and engineering perfectly typify the rapid, multidisciplinary advancement of contemporary science and technology. Inorganic materials such as metal and metal oxides have attracted lots of attention over the past decade due to their ability to withstand harsh process conditions. The use of nanoparticles of silver, gold and zinc oxide has been seen as a viable solution to stop infectious diseases due to the antimicrobial properties of these nanoparticles. In view of the textile industry's innovative history, it is no wonder that nanotechnology has found its way into this sector so quickly. Nanotechnology is forecasted as the second industrial evolution in the world. The novel properties and low material consumption amount has attracted global interest across disciplines and industries. The textile sector is no exception.

As stated by the "European Technological Platform for Textiles and Fashion", the textile industry to thrive must improve and reduce the costs of the processes, offer innovative products for traditional markets, develop new products for new markets (Rajendran et al., 2010). Nanotechnology can have an important role to achieve these goals and, in effect, all over the world public and private research institutions and private enterprises are actively engaged in nanotechnology research aimed at applications in the textiles sector. With growth in world population and the spread of disease, the number of antibiotic resistant microorganisms is rising along with the occurrence of infections from these microorganisms. With this increase in health awareness, many people focused their attention on educating and protecting themselves against harmful pathogens. It soon became more important for antimicrobial finished textiles to protect the wearer from bacteria than it was to simply protect the garment from fiber degradation. The need for antimicrobial textiles goes hand-in-hand with the rise in resistant strains of microorganisms. Functional textiles include everything from antimicrobial finished textiles, to durable, or permanent press finished garments, to textiles with self-cleaning properties, and also textiles with nanotechnology (Rajendran et al., 2010).

5. Antibacterial modification of textiles using sol–gel technology

The sol–gel process is known as chemical solution deposition, it is a wet-chemical technique widely used in the fields of material science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (or *sol*) that acts as the precursor for an integrated network (or *gel*) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal chlorides, which undergo various forms of hydrolysis and polycondensation reactions. In this chemical procedure, the 'sol' (or solution) gradually evolves toward the formation of a gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks. In the case of the colloid, the volume fraction of particles (or particle density) may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation

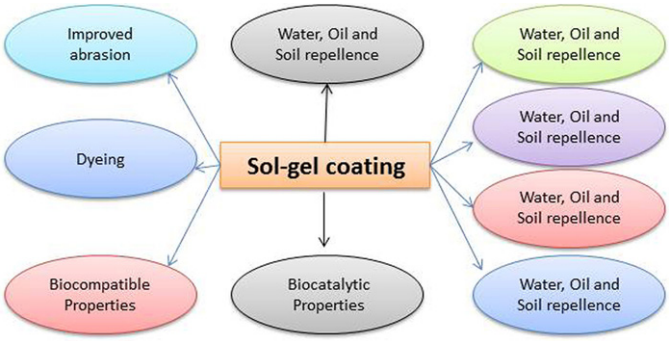

Fig. 10. Different applications of sol–gel coating on textiles (Mahltig & Bottcher, 2003).

to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation. Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes imposed upon the structural template during this phase of processing (Brinker & Scherer, 1990).

The precursor sol can be either deposited on a substrate to form a film (e.g., by dip coating or spin coating), cast into a suitable container with the desired shape (e.g., to obtain monolithic ceramics, glasses, fibers, membranes, aerogels), or used to synthesize powders (e.g., microspheres, nanospheres) (Brinker & Scherer, 1990). The sol–gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Sol–gel derived materials have diverse applications in optics, electronics, energy, space, (bio)sensors, medicine (e.g., controlled drug release), reactive material and separation (e.g., chromatography) technology and in the production of antimicrobial textiles.

Recently, investigations have been conducted to improve properties of textile fabrics by embedding various finishes in sol–gel coating to enhance fabric performance. The following section will focus on different sol–gel applications that create new functional properties in textile fabrics. Textiles coated with sol–gel are reported to impart many important properties, as shown in Fig. 10.

Antimicrobial finishing of cotton textile based on water glass by sol–gel method was investigated by Xing, Yang, and Dai (2007). They prepared the silica sol by acidifying water glass solution with 0.05 M H_2SO_4 solution to pH 11. Antimicrobial treatment was performed by impregnating cotton textile in silica sols and then treated with silver nitrate solution. The antimicrobial activity of the treated cotton fabrics was determined according to AATCC Test method 100-1999. The anti-microbial activity is evaluated by determining the percentage reduction of bacteria count on the sample after exposing the treated fabric to the bacteria.

This result was compared to an untreated control sample by exposing to a bacterial lawn. This antibacterial activity was measured by washing the samples several times after sol–gel treatment. Mahltig et al.'s (2005) results exhibited that antimicrobial durability of the treated samples increased with increase in water glass content. For the samples without water glass, bacterial reduction % was zero only after 10 washing cycles. But with a water glass content of 2% and 5%, higher silver ions were retained that resulted in more than 99% bacterial 25 reduction even after 20 and 50 cycles of washing. The bacterial reduction % also increases with increase in silver content as well.

Mahltig, Fiedler, and Bottcher (2004) investigated antibacterial effect by embedding the biocides in silica coatings. Biocides used in this study were silver nitrate, colloidal Ag, (cetyltrimethylammoniumbromide) CTAB, and octenidine. Silica sol solution was prepared from tetraethoxysilane (TEOS) and 3-glycidyloxypropyltriethoxysilane (GOPTS) (Mahltig et al., 2004). Properties such as antibacterial efficacy wash-out and long-term behavior were analyzed. Their results showed biocidal additives octenidine and CTAB exhibit high inhibition rate of more than 90% against the fungi *Aspergillus niger* after 4 h of leaching, whereas colloidal Ag treated samples without sol–gel have the lowest inhibition.

Daoud, Xin, and Zhang (2005) coated the cellulosic fibers with titanium oxide nanoparticles, which were obtained from aqueous titania sol. Titanium isopropoxide was hydrolysed and condensed in water to obtain the titania sol coating at low temperature. The stability of titania coating and the antibacterial activity of the coating was analyzed (Daoud et al., 2005). Treatment with sodium carbonates solutions showed less leaching behavior, which indicated that titania sols were strongly bonded with the cellulosic substrate. They confirmed the same with the help of FESEM images, which shows uniform distribution of the titania sols. The treated fabrics exhibited good antibacterial activity because of the formation of TiO_2 surface on the cellulose substrate which prevented the formation of a protective biofilm of adsorbed bacteria.

To fix a QAS on textile fibers, sol–gel technology has also been used in antimicrobial textiles. This enables the formation of a nanocomposite polymer network with an organic–inorganic hybrid structure (Nalwa, 2003; Novak, 1993). Colloidal solutions (sols) have been prepared for this purpose, consisting of mixtures of tetraalkoxysilane (Si(OR)4) and QASs with different structures (Wang & Wang, 2009) or organic–inorganic hybrids, including alkyltrialkoxysilanes (Rx-Si(OR)3), with incorporated quaternary ammonium groups (Fig. 11) (Li, Lee, Sheng, Cohen, & Rubner, 2006; Yu, Gu, Meng, & Qing, 2007). Alkoxysilanes are sol–gel precursors with alkoxy groups that can hydrolyze in the presence of a catalyst to form silanol (—SiOH) groups, which further condense among each other or with the hydroxyl (—OH) groups of the fibers. The formation of covalent bonds between —SiOH groups of the precursor and —OH groups of the fibers provides increased durability and wash resistance for the nanocomposite network on the finished fibers.

Quaternary ammonium functionalized polyhedral *oligomeric* silsesquioxanes (Q-POSS) are also used as sol–gel precursors with antimicrobial properties. These have a cage-like structure of (R*x*–SiO1.5)*n* ($n = 6, 8, 10, 12, \ldots$), where R*x* is a QAS group (Chojnowski et al., 2006; Majumdar et al., 2009). The most often used POSS precursors are octasilsesquioxanes ($n = 8$), which have a cubic form with QAS groups bound to silicon atoms. Accordingly, up to eight QAS groups can be incorporated into each molecule (Fig. 12), thus enhancing antimicrobial properties. Because Q-POSSs possess a polysiloxane core compatible with the siloxane matrix, they can be used as additives to the polysiloxane coating in combination with polydimethylsiloxane.

Substituted polycationic polysiloxanes with a pendant QAS (Fig. 13A) or imidazolium salt groups (Fig. 13B) are also important (Majumdar et al., 2008; Mizerska et al., 2009) as bacteriostats on textile fibers. These are mostly copolymers consisting of polydimethylsiloxane, polymethylhydrosiloxane and QAS- or imidazolium-modified polysiloxanes in different molar ratios.

6. Synthesis of nanoparticles

There are two methods for the production of nanoparticles which is summarized below.

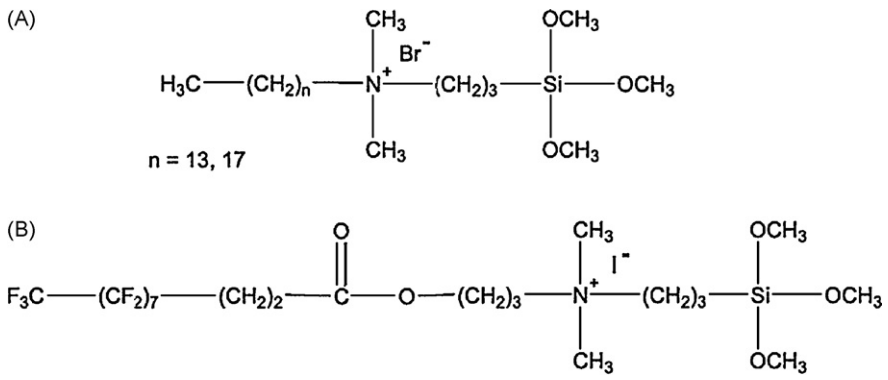

Fig. 11. Chemical structures of alkyltrialkoxysilanes with incorporated quaternary ammonium groups: alkyl-dimethyl-(3-(trimethoxysilyl)-propyl) ammonium bromide (A) and perfluorooctylated quaternary ammonium silane coupling agent (B).

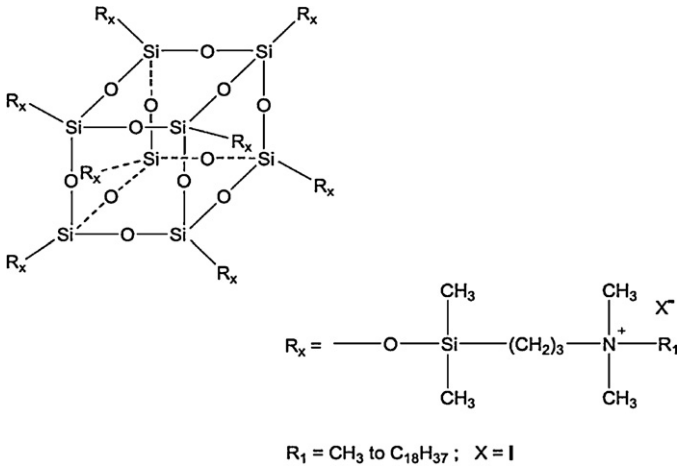

Fig. 12. Schematic presentation of idealized structure of totally quaternized quaternary ammonium functionalized polyhedral oligomeric silsesquioxanes.

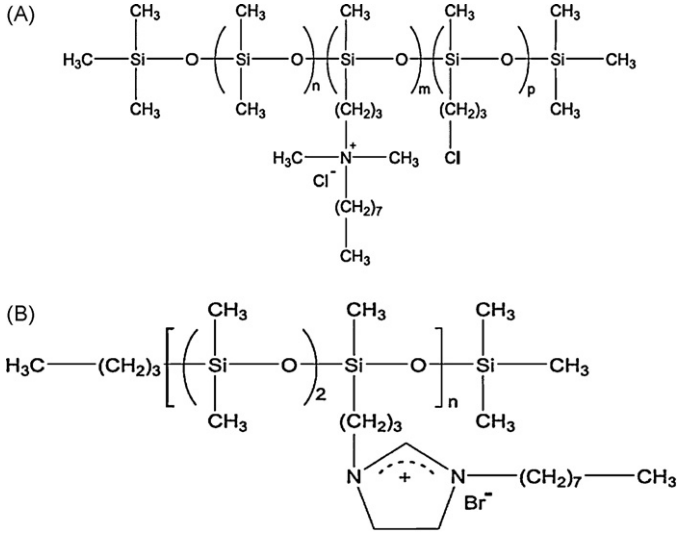

Fig. 13. Substituted polycationic polysiloxane with pendant QAS (A) and imidazolium salt (B) groups.

6.1. Top-down technique

The principle behind the top-down approach is to take a bulk piece of the material and then modify it into the wanted nanostructure and subsequent stabilization of the resulting nanosized metal nanoparticles by the addition of colloidal protecting agents. Cutting, grinding and etching are typical fabrication techniques, which have been developed to work on the nano scale. The sizes of the nanostructures which can be produced with top-down techniques are between 10 and 100 nm.

6.2. Bottom-up technique

Bottom-up or self-assembly refers to construction of a structure atom by-atom, molecule-by-molecule or cluster-by-cluster. Colloidal dispersion used in the synthesis of nanoparticles is a good example of a bottom-up approach. An advantage of the bottom-up approach is the better possibilities to obtain nanostructures with less defects and more homogeneous chemical compositions.

7. Stabilization of nanoparticles

There are two general kinds of stabilization procedures: electrostatic stabilization by the surface adsorbed anions and steric stabilization by the presence of bulky groups.

7.1. Steric stabilization

Steric stabilization can be achieved by the adsorption of large molecules, i.e. polymers, at the surface of the particles (Dutta & Hofmann, 2003).

7.2. Electrostatic stabilization

Electrostatic stabilization involves the creation of an electrical double layer arising from ions adsorbed on the surface and associated counter ions that surround the particle (Dutta & Hofmann, 2003). Recently, increasing public concern about hygiene has been driving many investigations for anti-microbial modification of textiles. However, using many anti-microbial agents has been avoided because of their possible harmful or toxic effects. Application of inorganic nano-particles and their nanocomposites would be a good alternative (Chen, Shen, & Gao, 2006) and consequently, they can open up a new opportunity for anti-microbial and multifunctional modification of textiles.

8. Classification of inorganic based nano materials

Nano-structured materials on the basis of inorganic active agents having good potential for anti-microbial activity on textile materials can be categorized in two main groups:

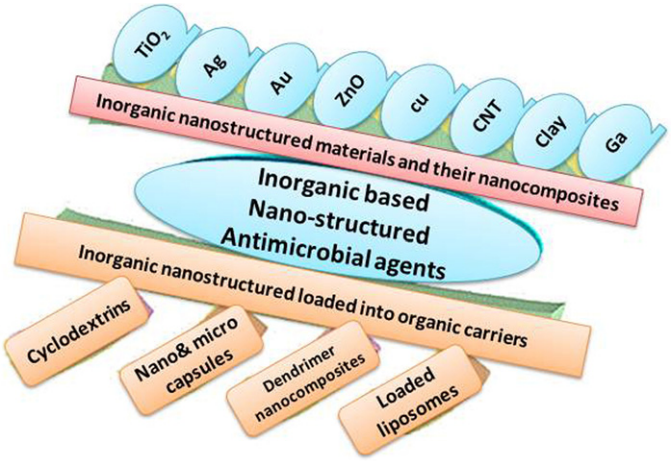

Fig. 14. Classification of inorganic based nano-structured anti-microbial agents.

(1) Inorganic nano-structured materials and their nanocomposites (Fig. 14).
(2) Inorganic nano-structured loaded organic carriers (Fig. 14).

The inorganic nano-structured materials include titanium dioxide, silver, zinc oxide, copper, gallium, gold nano-particles, carbon nanotubes, nano-layered clay, and their nano-composites. The inorganic nano-structured loaded in organic materials include cyclodextrin loaded with inorganic materials, nano- and micro-capsules having inorganic nano-particles, metallic dendrimer nano-composites and inorganic nano-particles loaded in liposomes. Note that categories such as loaded cyclodextrins, metallic dendrimers nano-composites and loaded liposome can be included in nano-capsules. However, each one has an especial concept, history, architecture and properties. This review focuses on the inorganic nano-structured materials with good antimicrobial activity potential for textile modification (Dastjerdi & Montazer, 2010).

8.1. TiO_2 nanoparticles

Currently, TiO_2 nanoparticles have created a new approach for remarkable applications as an attractive multi-functional material. TiO_2 nanoparticles have unique properties such as higher stability, long lasting, safe and broad-spectrum antibiosis. This makes TiO_2 nanoparticles applicable in many fields such as self-cleaning, anti-bacterial agent and UV protecting agent.

8.1.1. Mechanism of action

Titanium dioxide irradiation by light with more energy compared to its band gaps generates electron–hole pairs that induce redox reactions at the surface of the titanium dioxide. Consequently, electrons in TiO_2 jump from the valence band to the conduction band, and the electron (e^-) and electric hole (h^+) pairs are formed on the surface of the photo-catalyst. The created negative electrons and oxygen will combine into $O_2^{\bullet -}$, the positive electric holes and water will generate hydroxyl radicals. Ultimately, various highly active oxygen species can oxidize organic compounds of cell to carbon dioxide (CO_2) and water (H_2O). Thus, titanium dioxide can decompose common organic matters in the air such as odor molecules, bacteria and viruses (Fig. 15).

8.2. ZnO nanoparticles

Recently, ZnO has been found highly attractive because of its remarkable application potential in solar cells, sensors, displays, gas sensors, sun-screens, UV absorbers, antireflection coatings, antibacterial, and photo-catalysis. ZnO nano-particles have some advantages, compared to silver nano-particle, such as lower cost, white appearance, and UV-blocking property.

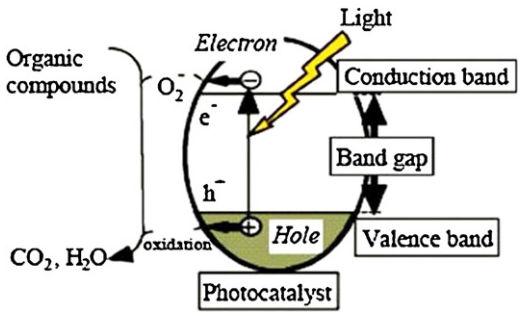

Fig. 15. Photocatalysis mechanism of TiO_2.

8.3. Silver nanoparticles

Since ancient times among various anti-microbial agents, silver has been most extensively studied and used to fight against infections and prevent spoilage. At present, many researchers have focused on anti-bacterial and multifunctional properties of silver nanoparticles (El-Rafie et al., 2011; Hebeish, El-Naggar, et al., 2011; Hebeish, El-Rafie, Ramadan, & El-Naggar, in press; Hebeish, Ramadan, El-Naggar, & El-Rafie, 2011b). Silver is a safer anti-microbial agent in comparison with some organic anti-microbial agents that have been avoided because of the risk of their harmful effects on the human body. Silver has been described as being 'oligodynamic' because of its ability to exert a bactericidal effect on products containing silver, principally due to its anti-microbial activities and low toxicity to human cells (Textor, Fouda, & Mahltig, 2010). Its therapeutic property has been proven against a broad range of micro-organisms, over 650 disease-causing organisms in the body even at low concentrations.

8.3.1. Mechanism of action

The brief explanation of its antimicrobial mechanism can be explained as follows.

Generally, metal ions destroy or pass through the cell membrane and bond to the —SH group of cellular enzymes. The consequent critical decrease of enzymatic activity causes micro-organism metabolisms change and inhibits their growth, up to the cell's death. The metal ions also catalyze the production of oxygen radicals that oxidize molecular structure of bacteria. The formation of active oxygen occurs according to chemical reaction:

$$H_2O + 1/2O_2 \overset{\text{Metal ion}}{\longrightarrow} H_2O_2 \rightarrow H_2O + (O)$$

Such a mechanism does not need any direct contact between antimicrobial agent and bacteria, because the produced active oxygen diffuses from fiber to the surrounding environment. Silver ions can lead to denaturing of protein and cell death because of their reaction with nucleophilic amino acid residues in proteins, and attach to sulfhydryl, amino, imidazole, phosphate and carboxyl groups of membrane or enzyme proteins. Respiration blocking and cell death also may be caused by forming R—S—S—R bonds (Fig. 16).

8.4. Gold nanoparticles

Gold nanoparticles are known as a novel biomedical application. Their potent antibacterial effectiveness against acne or scurf and no tolerance to the antibiotic have caused their commercial usage in soap and cosmetic industries. They can remove waste materials from the skin and control sebum.

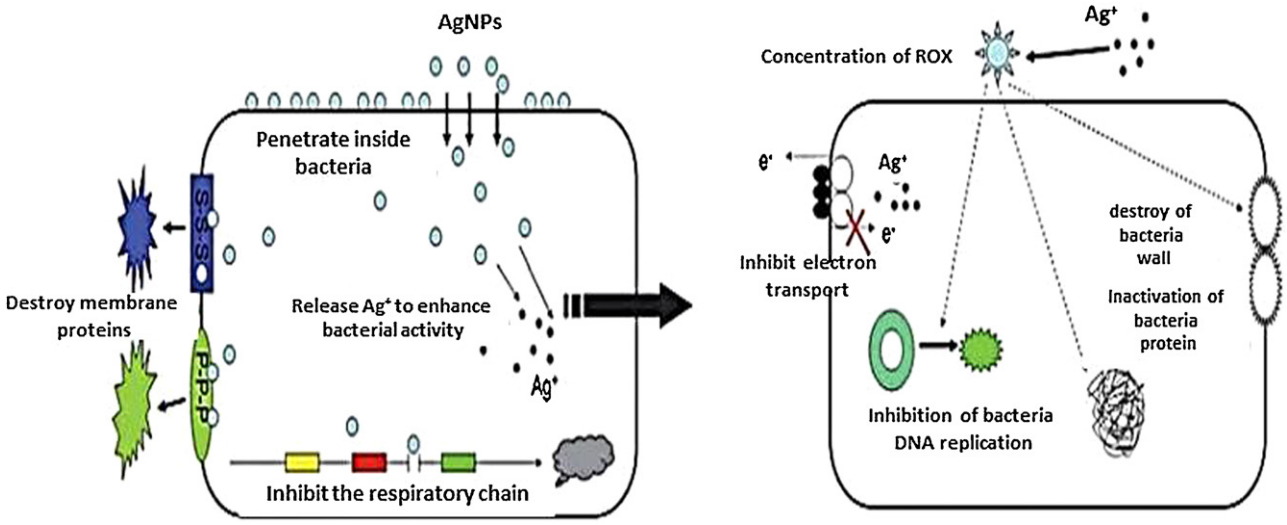

Fig. 16. Antimicrobial mechanism of silver nanoparticles.

9. Evaluation of antimicrobial efficacy

A number of test methods have been developed to determine the efficacy of antimicrobial textiles (Hofer, 2006). These methods generally fall into two categories: the agar diffusion test and suspension test.

9.1. Agar diffusion test

Agar diffusion test is a preliminary test to detect the diffusive antimicrobial finish. It is not suitable for non-diffusive finishes and textile materials other than fabrics (Gao & Cranston, 2010). The agar diffusion tests include AATCC 147-2004 (American Association of Textile Chemists and Colorists), JIS L 1902-2002 (Japanese Industrial Standards) and SN 195920-1992 (Swiss Norm). They are only qualitative, but are simple to perform and are most suitable when a large number of samples are to be screened for the presence of antimicrobial activity. In these tests, bacterial cells are inoculated on nutrient agar plates over which textile samples are laid for intimate contact. The plates are then incubated at 37 °C for 18–24 h and examined for growth of bacteria directly underneath the fabrics and immediately around the edges of the fabrics (zone of inhibition). No bacterial growth directly underneath the fabric sample indicates the presence of antimicrobial activity. The zone of inhibition should not be expected if the antimicrobial agent is firmly attached to the textile (e.g., covalently) which prevents its diffusion into the agar. If the antimicrobial agent can diffuse into the agar, a zone of inhibition becomes apparent and its size provides some indication of the potency of the antimicrobial activity or the release rate of the active agent (Gao & Cranston, 2010).

9.2. Suspension test

This type of test is exemplified by AATCC 100-2004, JIS L 1902-2002 and SN 195924-1992. These methods provide quantitative values on the antimicrobial finishing, but are more time-consuming than agar diffusion tests. Typically, a small volume (e.g., 1 ml) of bacterial inoculums in a growth media is fully absorbed into fabric samples of appropriate size without leaving any free liquid. This ensures intimate contact between the fabric and the bacteria. After incubating the inoculated fabrics in sealed jars at 37 °C or 27 °C for up to 24 h, the bacteria in the fabric are eluted and the total number is determined by serial dilution and plating on nutrient agar plates. Antimicrobial activity, expressed as percentage of reduction, is calculated by comparing the size of the initial population with that following the incubation. Appropriate controls, e.g., samples that have gone through the same processing except the antimicrobial finishing, should be included in each experiment to ascertain that the observed decrease in bacterial number is truly due to the antimicrobial finishing.

It should be noted that suspension tests are often performed under artificial conditions that promote bacterial growth (e.g., rich nutrients in the inoculum and saturating moisture in the testing fabrics). The moisture in the tests is also essential for the action of the biocide. As a result, dramatic results are often produced (e.g., >99% bacterial cells are killed during the assays), leading to an overwhelming impression of the efficacy of the antimicrobial ability. However, such conditions are rarely found during the normal use of a textile product. To date, very few studies have examined the antimicrobial effects under normal wearing conditions. To more closely mimic the real-life situation, the JIS L 1902-2002 method recommends the use of bacterial cells suspended in heavily diluted nutrient media to limit nutrient levels.

The ISO (International Organization for Standardization) has developed a test method (ISO 20743) in which bacteria is “printed” onto the surface of textiles without them being in an aqueous suspension. The printed samples are then incubated under humid conditions at 20 °C for a specified time (18–24 h) following which the surviving cells are counted. Antimicrobial tests only assess the antimicrobial effectiveness of the treated textiles. Before marketing, the textile products have to pass biocompatibility tests which involve three separate assays: cytotoxicity, sensitization and irritation. These assays are outside the scope of this review but are discussed elsewhere (Hofer, 2006).

10. Remarks and outlooks

Inorganic and metallic-based nanostructure materials have created a new interesting fields in all sciences for the continuous investigations due to their undeniably unique properties. Their applications have already led to the development of new practical productions. Considering the indubitable role of textiles in human life, these new fields in textile industry have been increasingly welcomed. However, designing new applicable and affordable techniques for manufacturing scale-up production will not only create a new field of study, but meet the expanding human requirements.

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