Antimicrobial cellulosic textiles based on organic compounds

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Abstract

Healthy body is one of the principle requirements of human beings, but the highly rated growth of harmful pathogens has challenged researchers for investigation of antimicrobial reagents. Infection of textile materials is a result of microbial adherence on the surface, and it is one of the vital clinical complications, which causes a high rate of mortality. New challenges as well as new opportunities in manufacturing of antimicrobial cellulosic textiles are the future concerns for textile and apparel industry. The major applications of antimicrobial textile could be ascribed according consumer demands, represented in more comfort, easy care, health, and durable to laundering. Such numerous properties could be achieved by the development of innovative methodologies with various finishing agents. Thus, the current review introduced an overview for the application of recent organic antimicrobial reagents in cellulosic textile finishing. The organic reagents are classified into two main categories; natural (chitosan, cyclodextrins and natural dyes) and synthetic (quaternary ammonium salts, triclosan, halogenated phenols and metal organic frameworks). The interaction between cellulose and such reagents, biological action mechanisms and factors affecting biocidal actions are all presented. For improvement of the durability and mechanical properties, pre-activation of cellulosic textile or using of cross-linkers is properly performed.

Keywords Cellulosic textiles · Organic antimicrobial · Natural agents · Synthetic agents

Introduction

Since 1941; Textile industry had considered developing antimicrobial fibers, as people had realized that textile could act in protection of wearers against the spread of bacteria and diseases (Hirschmann and Robinson 1941). Therefore, textiles were designed to be widely used in various antimicrobial treatments and rapidly became a prerequisite to be used in hospitals, hotels, sports, and personal care industries. Textile antimicrobial finishing must not only kill undesirable microbes and inhibit the spreading of diseases, but also must realize three other basic requirements (Mao 2001); which could be pointed as follows; (1) safety: the product must be nontoxic to human and its application on textile materials must not result in skin allergy and irritation, (2) compatibility: the as-used antimicrobial finishing agent

should not result in negative effects for the textile properties or appearances and must be compatible with common textile industrialization, and (3) durability: the reagent must be capable of enduring laundry, drying, and leaching (Mao 2001; Hirschmann and Robinson 1941). Medical textiles are manufactured to be applied in hygiene, healthiness, and private care as well as surgical uses. The medical textiles could be produced in knitted, woven, and non-woven structures based on their applications. Antimicrobial textile as one of medical textiles act by protecting users from hygienic problems resulting from exposure to pathogenic or odor-generating microbes, where, the growth of microorganisms results in reduction of functionality by undesirable aesthetic changes or rotting damage. Consequently, marketing of different antimicrobial textile finishing agents has dramatically increased. These antimicrobial textile finishing agents are characterized by different chemical structures, cost effectiveness, method of processing, and their environmental impact (Gao and Cranston 2008; Schindler and Hauser 2004; Dring 2003; Mahltig et al. 2005; Vigo 1983).

Cellulose is known world wide as the most abundant, renewable, and an almost inexhaustible polymeric raw material with fascinating chemical structure and properties.

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Additionally, cellulose is ascribed as poly-disperse linear stiff-chain homopolymer, which is composed of regio- and enantio-selectively β -1, 4-glycoside-bonded D-glucopyranose monomeric units. Cellulose polymer with its hydroxyl groups and the oxygen atoms of both the pyranose ring and the glycosidic bond, ordered hydrogen bond systems and acts in formation of various types of supra-molecular semi-crystalline structures. Therefore, cellulosic polymer is characterized by its chirality, highly functionality, biodegradability, wide chemical modifying capacity, and its capability to form versatile semi-crystalline fibers (Klemm et al. 1998, 2005).

Marketing of cellulose fibers has extensively grown in the past few years, as the expense of raising demand from the textile industry. Hence, functionalization of cellulose-based textiles is of increasing interest and a broad range of cellulose fabric products with special function can be obtained. When it comes to functional cellulosic textiles in sports and casual clothing, consumers are not only seeking fashion, but ergonomics, especially comfort and health. It is now a common practice in industrialized countries to announce new functional cellulosic textiles on a regular basis. Functionalization of cellulosic textiles has been an active research field of particular interest including antibacterial against both type Gram-positive and Gram-negative and antifungal properties (Ilić et al. 2009; Lee et al. 2003; Ahmed et al. 2015, 2018; El-Rafie et al. 2014; Emam et al. 2013, 2014, 2015a, b, 2017a, b; Ahmed and Emam 2016; Zahran et al. 2014).

Generally, antimicrobial textile finishing reagents belong could be divided to two kinds; organic and inorganic compounds, where, the as-mentioned two kinds are mainly differing in the mechanism of inhibiting or killing bacteria (Kalyon and Olgun 2001; An et al. 1996; Taylor et al. 1998; Kim et al. 2002; Kawahara et al. 2000; Yi et al. 2003; Yu et al. 2003; Top and Ülkü 2004). According to literatures (Kalyon and Olgun 2001; An et al. 1996; Kim et al. 2002; Top and Ülkü 2004), inorganic antimicrobial reagents are found to require longer time rather than organic ones. Therefore, the represented review summarizes some of the recent organic antimicrobial finishing agents for revolutionizing the field of medical cellulosic textile (fibers/fabrics) in the upcoming years. The organic antimicrobial agents can be classified into natural in origins (e.g., chitosan, cyclodextrins, and natural dyes) and synthetic in origin (quaternary ammonium salts, triclosan, halogenated phenols, and metal organic frameworks).

Functionalization strategies

Most of the as-mentioned antimicrobial agents will be summarized in the following sections, which were basically classified into two main categories; naturally and synthetically

resourced functionalizing agents. Chemical formulas of some antimicrobial agents (naturally and synthetic) were presented in Fig. 1. Due to environmental awareness, the newly acquired properties not only ascribed as the intrinsic function and long service life of the antimicrobial textile but also a manufacturing process that must be considered as environment-friendly method. Therefore, research on environment-friendly antimicrobial agents based on natural resources for cellulosic textile finishing is considered world wide and is acquiring high popularity because of the inherent properties and applications (Joshi et al. 2009; Yusuf et al. 2012, 2016). On the other hand, use of natural resources as antimicrobial agents has some limitations represented in the cost effectiveness, lower efficiency, and giving limited functions. Therefore, the researchers started to overcome the aforementioned problems by synthesizing new organic antimicrobial agents or using already synthesized materials to impart microbial resistance for textiles, named synthetically resourced antimicrobial agents.

Naturally resourced antimicrobial agents

Chitosan

Chitosan is defined as the de-acetylated derivative of chitin, which is the second most abundant polysaccharide found worldwide after cellulose. Chitosan has found to exhibit various applications in different fields including pharmaceutical and medical purposes, paper production, waste water treatment, biotechnology, cosmetics, food processing, and agriculture, in addition to cellulosic textile finishing (Shabbir and Mohammad 2016; Lim and Hudson 2003). Chitosan is employed in textile finishing for functionalization, in enhancement of dyeability and physical characters, wrinkle resistance and bioactivity (Masri et al. 1978; Rippon 1984; Bhuiyan et al. 2017; Munna et al. 2017) as summarized in Table 1. The bactericidal action of chitosan biopolymer mainly relied on positive charge density, molecular weight, concentration, hydrophilic/hydrophobic property, chelating capacity, and the physical state of the biopolymer. In addition to, ionic strength in medium, pH, temperature, reactive time and type microbial strain are also ascribed to play a role in the biocidal activities of chitosan. Kong et al. (2010). Antimicrobial activity of chitosan as biopolymer with amphoteric nature is pH dependent, and it was reached the maximum activity in the acidic medium. This is due to the better solubility of chitosan in acidic forming poly-cation. On the other hand, there are no reports approving that, chitosan has any of antimicrobial effects under basic conditions (Lim and Hudson 2004). The treatment with chitosan can significantly enhance the antimicrobial activity and physical characteristics such as abrasion resistance and crease recovery property of treated fabric samples (Bhuiyan et al. 2017).

Fig. 1 Structures of naturally and synthetically resourced functionalizing agents for cellulosic textiles

However, a slight deterioration in strength, and elongation is observed, which is probably caused by acidic treatment during surface-coating with chitosan (Bhuiyan et al. 2017). Therefore, Munna et al., used citric acid as crosslinking agent to enhance the mechanical properties of cotton fabrics during the treatment with chitosan under gamma radiation (Munna et al. 2017).

It has been reported that, water-soluble chitosan derivatives prepared by saccharization, alkylation, acylation, quaternization and metallization were found to exhibit higher antimicrobial effect than the native one (Xie et al. 2007;

Ignatova et al. 2007). Chemical modification in the structural form of chitosan by incorporating certain groups with higher charge density, such as asparagine *N*-conjugated chitosan oligosaccharide and guanidinylated chitosan (Jeon et al. 2001; Hu et al. 2007a), was reported to acquire chitosan for higher antimicrobial action. In contrast to, *N*-carboxyethyl chitosan failed in showing any antimicrobial properties, which could be attributed to lacking free amino groups (Yancheva et al. 2007).

It is well known that, positive charge density shows enhanced electrostatic interaction of biopolymers with

Table 1 Antimicrobial cellulosic textiles using naturally resourced functionalizing agents

Functionalizing agents	Functions	References
Chitosan		
Chitosan	Antibacterial	Kong et al. (2010), Ignatova et al. (2007), Jeon et al. (2001), Hu et al. (2007a), Takahashi et al. (2008), Munna et al. (2017)
Chitosan	Antibacterial, enhancement of the dyeability and wrinkle resistance	Kong et al. (2010), Lim and Hudson (2004), Bhuiyan et al. (2017)
Nano-chitosan	Enhancement the dyeability	Chattopadhyay and Inamdar (2013)
Chitosan/poly(sodium-4-styrene sulfonate)	Antibacterial without affecting on breathability, flexibility or feel	Joshi et al. (2011)
Chitosan/poly(butyl acrylate) Chitosan/poly(Nisopropylamide)	Durable antibacterial	Ye et al. (2006)
Chitosan/ <i>N</i> -halamine	Durable antibacterial	Cheng et al. (2014)
Methoxypolyethylene glycol- <i>N</i> -chitosan	Durable antibacterial	Abdel-Mohsen et al. (2012)
Chitosan- <i>O</i> -polyethylene glycol	Antimicrobial, anti-crease with comfortable sensation	Aly et al. (2010)
Cyclodextrins		
Monochlorotriazine β -cyclodextrin	Enhance the release of essential oil	Bilia et al. (2014), Khanna and Chakraborty (2017)
β -Cyclodextrin	Capturing of organic pollutants	Alzate-Sánchez et al. (2016)
Cyclodextrin/triclosan	Antibacterial with control release	Cabrera et al. (2012)
β -Cyclodextrin/acrylic acid/AgNPs	Antibacterial	Hebeish et al. (2011)
Monochlorotriazinyl- β -cyclodextrin/acrylic acid	Antibacterial	Hebeish et al. (2014)
Natural dyes (plant extract)		
Food wastes	Coloration	Yusuf et al. (2016)
Timber wastes	Coloration	Bechtold et al. (2006)
Agricultural industries wastes	Coloration	Shahid and Mohammad (2013)
Walnut shell	Coloration	Tutak and Korkmaz (2012)
Horse chestnut	Coloration	Tutak and Korkmaz (2012)
Pomegranate peel	Coloration, antibacterial, UV-protection	Tutak and Korkmaz (2012), Gawish et al. (2017)
<i>Berberis vulgaris</i> root	Coloration	Tutak and Korkmaz (2012)
Thyme	Coloration	Tutak and Korkmaz (2012)
Sage tea	Coloration	Tutak and Korkmaz (2012)
Henna leaves	Coloration, UV-protection	Tutak and Korkmaz (2012), Hasan et al. (2015), Omer et al. (2015)
Madder root	Coloration, UV-protection	Tutak and Korkmaz (2012), Gawish et al. (2016)
<i>Aloe vera</i>	Coloration, antibacterial	Ammayappan and Moses (2009)
Curcumin	Coloration, antibacterial	Ammayappan and Moses (2009), Gawish et al. (2017)
Cutch	Coloration, antibacterial	Gawish et al. (2017)
Red onion peel	Coloration, UV-protection	Gawish et al. (2016, 2017)
Mediterranean flora	Coloration, UV-protection	Grifoni et al. (2014)
Chamomile	Coloration, UV-protection	Gawish et al. (2016)
Chitosan-curcumin	Antioxidant, antibacterial, coloration	Zemljič et al. (2014)

bacterial cells (Fig. 2a). Increment the degree of deacetylation for chitosan was found to increase the charge density for higher electrostatic interaction and thus enhanced biocidal activities (Takahashi et al. 2008). The interaction

between positively charged chitosan macromolecules and the negatively charged bacterial cell membranes results in the leakage of protein and other intracellular components. Such ascribed interaction is mainly dependent on pH. At a pH

Fig. 2 Interaction of quaternary ammonium salts with cellulose

less than pKa, the protonation of amino groups of chitosan takes a place which in turn results in electrostatic interaction between polymer and microbial cell wall. But at a pH higher than pKa, the hydrophobic interaction and chelation were reported to be responsible for chitosan antimicrobial activity (Hu et al. 2007b; Kong et al. 2008).

Cellulosic fabrics are characterized by being less susceptible for effective dyeing and this disadvantage was overcome using chitosan as finishing agent before dyeing

processing. Where, both cotton and chitosan are basically characterized by similar structures, and thus, their molecular backbones are bonded through Van der Waals forces and cross-linking by the formation of Schiff base between cellulosic reducing end groups and the amino groups of chitosan (Rippon 1984). Due to the cationic nature of chitosan in acidic conditions, it is found to exhibit ease of absorption with anionic dyes such as direct, acid, and reactive dyes through electrostatic attraction.

Additionally, wrinkle resistance as another function can be acquired by cellulosic textiles by chitosan treatment, where, wrinkle resistance can be effectively enhanced as durable press finishing in cellulosic fabrics (Younsook and Dong 1998). The mechanical properties of cotton fabrics are negatively affected by the treatment and are oppositely proportional with the molecular weight of chitosan (Younsook and Dong 1998). The shrinkage resistance is linearly proportional with the molecular weight of chitosan used in the treatment of cellulosic textiles (Julia et al. 1998). The most interesting property imparted to cellulosic textiles by treatment with chitosan macromolecules is the antimicrobial activities, as the chitosan-finished cellulosic textiles were found to be effectively applicable as medical textiles (Shin et al. 1999; Lee et al. 1999; Zhang et al. 2003; Joshi et al. 2011; Naebe et al. 2016). Chitosan was mixed with anionic polyelectrolyte of poly(sodium-4-styrene sulfonate) for layer-by-layer coating of cotton textile to impart antimicrobial properties without affecting textile breathability, flexibility or feel (Joshi et al. 2011). Naebe et al., pre-activated the cotton fabrics by atmospheric helium/oxygen plasma to increase the adsorption amount of chitosan (Naebe et al. 2016). Dye uptake, wash fastness and antibacterial potency for the cotton fabrics were all improved by treatment with nano-chitosan (Chattopadhyay and Inamdar 2013). The treatment with chitosan did not affect the mechanical properties of cotton fabric, while the finishing with nano-chitosan resulted in slight improvement in tenacity and observable decrement in elongation at break (Chattopadhyay and Inamdar 2013). For durable antibacterial finishing, chitosan-poly(butyl acrylate) and chitosan-poly(*N*-isopropylamide) in the form of core-shell particle was applied onto cotton fabrics using pad-dry-cure technique (Ye et al. 2006), while, modified chitosan by *N*-halamine was used (Cheng et al. 2014). Break tensile strength and elongation for fabrics are both improved after functionalization and use of crosslinkers resulted in further improvement in the mechanical properties (Ye et al. 2006), while using of chitosan/*N*-halamine led to decrease in the breaking strength (Cheng et al. 2014). Abdel-Mohsen et al., reported a method for biomedical functionalization of cotton fabrics based on use of methoxypolyethylene glycol-*N*-chitosan graft copolymer in the presence of citric acid (Abdel-Mohsen et al. 2012). Chitosan-*O*-polyethylene glycol/citric acid was used as multifunctional finishing agent (antimicrobial, anti-crease and comfortable sensation) for cotton fabrics (Aly et al. 2010). Due to use of citric acid as crosslinkers, the mechanical properties of cotton fabrics are improved after functionalization (Aly et al. 2010; Abdel-Mohsen et al. 2012).

Cyclodextrins

Cyclodextrins have internal lipophilic cavities and external hydrophilic surfaces and consequently, the main activity of cyclodextrins is basically related to their capacity for including various guest molecules (Bilia et al. 2014; Alzate-Sánchez et al. 2016). Cotton was grafted with monochlorotriazine β -cyclodextrin to improve the release properties of essential oils (Bilia et al. 2014; Khanna and Chakraborty 2017). The tensile strength of cotton fabrics was insignificantly changed by the grafting with monochlorotriazine β -cyclodextrin; however, the grafting yield exceeded 13% (Khanna and Chakraborty 2017). Porous β -cyclodextrin was covalently bonded with cotton fabric for capturing organic pollutants from the contaminated environment (water and air) (Alzate-Sánchez et al. 2016). The complexation or release of substances by fixed cyclodextrins can also be employed for medical purposes such as medical diagnostics by testing substrates from sweat of patients encapsulated via cyclodextrins (Buschmann et al. 2001). Interactive cyclodextrin derivatives, were found to intensively bond to cellulosic backbone of cotton textiles (Cabrera et al. 2012; Hebeish et al. 2011, 2014).

Inclusion substrates like cyclodextrins were reported to be successively grafted to cotton textiles, followed by inclusion of triclosan as antimicrobial agent to control its release capabilities, and the treated cotton was found to exhibit excellent action (Cabrera et al. 2012). Durable antibacterial cotton fabrics were performed by Hebeish et al., via applying a β -cyclodextrin-containing composite (Hebeish et al. 2011, 2014). β -cyclodextrin-grafted poly acrylic acid copolymer was used in preparation of nanosilver and the composite was applied onto fabrics (Hebeish et al. 2011), while cotton fabrics were pretreated with reactive copolymer of monochlorotriazinyl- β -cyclodextrin-grafted acrylic acid or β -cyclodextrin grafted acrylic acid prior to in situ reduction of nanosilver (Hebeish et al. 2014).

Natural dyes

Dyes have been applied before the progression of textile functionalization industry to prepare finished textiles with simultaneous coloration. Color shading of textile materials by synthetic dyes is necessary for the textile industry. However, the discharge of these dyes from textile industry in wastewater was found to be greatly dangerous to the aquatic flora and fauna due to their toxicity, non-biodegradability and their carcinogenic effects. Therefore, dyes extracted from natural origin like plants gained a high popularity over synthetic ones (Shabbir and Mohammad 2016; Yusuf et al. 2012; Ghaheh et al. 2014). These materials were mainly advantageous with lower cost effectiveness, giving a new generation of textile dyes and add new functions such as

antimicrobial activities (Table 1). Additionally, the application of by-products and wastes from food, timber and agricultural industries can be expressed to be good alternatives for synthetic dyes (Bechtold et al. 2006; Shahid and Mohammad 2013; Yusuf et al. 2016).

Cellulosic textiles could be dyed by natural dyes through the coordination bonding of cellulose molecules with the aid of various metal ions. Most of the natural dyes require the use of a mordant (e.g., copper sulphate, ferric sulphate, potassium aluminum sulphate), to have a coloring power on cellulosic textiles (Tutak and Korkmaz 2012; Hasan et al. 2015). Pre- and post-mordanting could be performed to improve the fastness properties (Tutak and Korkmaz 2012; Hasan et al. 2015). By changing the applied extract or mordant, different resulted colors could be obtained. Furthermore, the finished cellulosic textiles were reported to exhibit antimicrobial potency (Ammayappan and Moses 2009; Gawish et al. 2017). Cotton fabrics treated with *Aloe vera* as a natural colorant, exhibited antibacterial activity higher than that treated with chitosan (Ammayappan and Moses 2009). Extracts of chamomile, red onion peel, madder, Mediterranean flora and henna leaves were used for coloring the cotton fabrics by imparting UV-protective and/or antibacterial properties (Gawish et al. 2016, 2017; Grifoni et al. 2014; Omer et al. 2015). Beside coloration, the effect of mordant on the added functions (antimicrobial activity and UV-protection) was studied for different dyed fabrics including cotton (Gawish et al. 2017). By incorporation of chitosan–curcumin, antioxidant, and antibacterial functionalized viscose fabrics were produced (Zemljic et al. 2014).

Synthetically resourced functionalizing agents

Quaternary ammonium salts

Quaternary ammonium salts as a type of functionalizing agent with molecular formula of nitrogen in cationic form, are ascribed as active reagents against different species of microorganisms. The biological activities of quaternary ammonium salts are principally affected by the length of the alkyl chain, the presence of the per-halogenated group and the number of cationic ammonium groups in the molecule (Shabbir and Mohammad 2016; Simoncic and Tomsic 2010). According to the literature (Gilbert and Moore 2005) quaternary ammonium salts with alkyl chain composed of 12–14 of alkyl groups were found to exhibit excellent bactericidal action against Gram-positive bacterial strains. While, alkyl chain with 14–16 alkyl groups showed better biocidal action against Gram-negative bacteria. Initial interaction between quaternary ammonium salts and bacterial wall is reported to be a result of electrostatic interaction between positively charged quaternary ammonium salt and the negatively charged microbial membranes (Fig. 2b). This

is followed by the integration of quaternary ammonium salt hydrophobic tail into the bacterial hydrophobic membrane core, where it acts in denaturation of structural proteins and enzymes. Additionally, quaternary ammonium salts were found to induce dose- and time-dependent ultra-structural changes in antibiotic-resistant *Escherichia coli* (*E. coli*) (Ioannou et al. 2007). On the other hand, counter ion which is strongly bonded to quaternary ammonium salts was found to cause lower biocidal action, which could be due to slow and lower release of free ions into the surrounding medium (Chen et al. 2000).

Many research works interested in the functionalization of cellulosic textiles were focused on modification of cellulose by different quaternary ammonium salts (Table 2). Figure 3 shows the interaction between cellulose and quaternary ammonium salts. Due to the loss of the physical bonding and leaching of these salts, the treated textiles with quaternary ammonium salts have poor washing durability (Simoncic and Tomsic 2010). Polymerizable quaternary ammonium salts with acrylate or methacrylate groups were carried out and sol–gel method for uploading/fixing on textile surfaces was reported (Owusu-Adom and Guymon 2008; Caillier et al. 2009). A more recent report on a novel environmentally friendly antimicrobial cotton fabrics finished with reactive siloxane sulfopropyl-betaine was studied to extend the research of quaternary ammonium salts (Chen et al. 2011). The results showed that the finished cotton fabrics exhibit good biological activity against bacteria and fungi, being nontoxic to animals and also does not induce skin stimulation. In addition to antibacterial activity and enhancement the hydrophobicity, the finishing with siloxane sulfopropyl-betaine is accompanied by large improvement in tensile strength of cotton textiles (Chen et al. 2011). Moreover, quaternary ammonium salts were used to cationize the cellulosic textile to easily dye with anionic dyes. A 3-chloro-2-hydroxypropyl trimethylammonium chloride, polyamino chlorohydrin quaternary ammonium, 2,3-epoxypropyl trimethyl ammonium chloride and glycidyltrimethyl ammonium chloride were used to modify cotton fabrics to improve its dyeing with salt-free reactive dye to overcome the problem of salt usage (Hauser and Tabba 2001; Hashem et al. 2003; Acharya et al. 2014; Arivithamani and Dev 2017a, b; Ramasamy and Kandasaamy 2005; Ma et al. 2017; Kamel et al. 2009, 2011).

Triclosan

Production of biologically active reagents including triclosan or halogenated phenols is motivated by increment in consumer requirement. Triclosan (2, 4, 4'-trichloro-2'-hydroxydiphenyl ether) is a highly effective biological reagent against most of the bacterial species (Fig. 2c); however, it has poor antifungal properties. Triclosan and its

Table 2 Antimicrobial cellulosic textiles based on synthetically resourced functionalizing agents

Functionalizing agents	Functions	References
Quaternary ammonium salts		
Quaternary ammonium surfactant/poly acrylate/clay	Antibacterial	Owusu-Adom and Guymon (2008)
Quaternary ammonium group/methacrylic acid	Antibacterial	Caillier et al. (2009)
Siloxane sulfopropyl-betaine	Antimicrobial, enhancement of hydrophobicity and tensile strength	Chen et al. (2011)
2,3-Epoxypropyl trimethyl ammonium chloride	Enhancement the dyeability	Hauser and Tabba (2001)
3-Chloro-2-hydroxypropyl trimethylammonium chloride	Enhancement the dyeability	Hashem et al. (2003), Acharya et al. (2014), Arivithamani and Dev (2017a, b), Ramasamy and Kandasaamy (2005), kamel et al. (2011)
Polyamino chlorohydrin quaternary ammonium	Enhancement the dyeability	Ramasamy and Kandasaamy (2005), Kame et al. (2009)
Glycidyl trimethyl ammonium chloride	Enhancement the dyeability	Ma et al. (2017)
Triclosan		
Triclosan/Ag	Antimicrobial	Dhiman and Chakraborty (2015)
Triclosan/methyl ester-containing silicon	Antimicrobial and hydrophobic	O'Lenick (2002)
Triclosan/dimethyl dihydroxy ethylene urea	Antibacterial, anti-crease, enhanced surface softness	Ibrahim et al. (2010)
Triclosan/butan tetracarboxylic acid or citric acid	Durable antibacterial	Orhan et al. (2009)
Triclosan/ β -cyclodextrin	Durable antimicrobial	Peila et al. 2013
Triclosan/poly lactide microspheres	Antibacterial	Goetzendorf-Grabowska et al. (2004)
Triclosan/melamine-formaldehyde	Antimicrobial	Ocepek et al. (2012)
Triclosan/AgNPs-PVP/microwave curing	Antimicrobial and coloration	Ibrahim et al. (2013a)
Triclosan/chitosan/ <i>Aloe vera</i> /TiO ₂ -NPs/silicone softener	Antimicrobial, UV-protection, soft-handle, water repellent	Ibrahim et al. (2013b)
N-halamines		
Methylol-5,5-dimethylhydantoin	Antimicrobial	Schindler and Hauser (2004), Vigo (2001)
Polybiguanides		
Poly(hexamethylene biguanide)	Antimicrobial	Zhao and Chen (2016), Gao and Cranston (2008), Blackburn et al. (2006)
Polyethyleneimine		
N-Alkyl-polyethyleneimine	Antimicrobial, antibiotic	Milović et al. (2005), Lin et al. (2003)
Metal organic frameworks		
Copper-benzene tri-carboxylic acid (Cu-BTC)	Antibacterial	Rodríguez et al. (2014), Wang et al. (2015)

derivatives are highly preferable for textile finishing due to its low skin toxicity, in addition to its antimicrobial action (Gao and Cranston 2008). Therefore, triclosan was applied in household materials for antimicrobial action and in cellulosic textile finishing also simultaneously for the same purpose as presented in Table 2. Dhiman and Chakraborty, studied the usage of triclosan, triclosan with Ag-dispersed metal and triclosan-chitosan composite in functionalization of cotton fabrics via pad-dry-cure method (Dhiman and Chakraborty 2015). The best antimicrobial results were detected for the fabrics treated with triclosan/Ag-dispersed metal and the mechanical properties of the finished cotton

fabrics are inconsiderably affected, whatever the antimicrobial agent applied (Dhiman and Chakraborty 2015). Triclosan as a finishing agent is found to exhibit low durability to washing because it is highly volatile at high temperatures and highly soluble at high pH (O'Lenick 2002). Triclosan was employed for manufacturing silicone-functionalized antimicrobial compounds, through the reaction with certain methyl ester-containing silicone compounds, where the final product was found to be greater in washing durability and have long-lasting antimicrobial finish (O'Lenick 2002). The as-mentioned compounds could be successively used in personal care and textile functionalization, with greater

Fig. 3 Schematic diagram illustrated the antibacterial action mechanism of the organic antimicrobial agents used in finishing of cellulosic textiles

long-lasting durable antimicrobial, germicidal, and fungicidal actions (Li 2001). Treatment of cotton fabrics with triclosan in combination with dimethyl dihydroxy ethylene urea produced finished fabrics with superior antibacterial and anti-crease activities, and the fabric softness was enhanced (Ibrahim et al. 2010). A study for the application of triclosan was reported for durable antibacterial finishing of cotton/polyester blended fabrics through pad-dry-cure method (Ibrahim et al. 2010).

The addition of butane tetracarboxylic acid and citric acid enhanced the durability of the antimicrobial coating against laundering (Orhan et al. 2009). The treatment with polycarboxylic acid alone exhibited decrement in mechanical properties of cotton fabrics with increment in acid concentration. However, the treatment with triclosan/polycarboxylic acid does not significantly affect the mechanical properties of fabrics (Orhan et al. 2009). Peila's et al., reported using two different ways of making antimicrobial cotton fabrics through adding triclosan into β -cyclodextrin cavity (Peila et al. 2013). The β -cyclodextrin-treated cotton fabrics followed by finishing with triclosan to produce fabrics with durable antimicrobial properties. Non-woven viscose fabrics

were finished with triclosan encapsulated in biodegradable polylactide as a carrier (Goetzendorf-Grabowska et al. 2004). Good antimicrobial cotton fabrics without substantially changing in its properties, were obtained via treatment with melamine–formaldehyde polymer micro-capsulated with triclosan using screen printing (Ocepek et al. 2012). Due to use of melamine–formaldehyde, the mechanical properties of cotton fabrics are not substantially changed by treatment (Ocepek et al. 2012). For cellulosic fabrics' pigmentation with acquiring antimicrobial activity, triclosan was first incorporated to the fabrics and then followed by microwave curing (Ibrahim et al. 2013a). Moreover, print paste including chitosan, *Aloe vera*, triclosan, TiO_2 -NPs and silicone softener was applied onto cotton/wool and viscose/wool-blended fabrics followed by microwave activation (Ibrahim et al. 2013b). The produced fabrics showed multi-functional properties represented in antimicrobial activity, UV-protection, soft-handle and water-repellent property.

N-halamines

N-halamines are well defined as heterocyclic compounds which contain, in the main skeleton, one or two covalent bonds between nitrogen and a halide, where the halide is usually chloride. N-halamines were reported to be characterized by biocidal activities against a broad spectra of bacteria, fungi, and viruses (Worley et al. 1988; Sun et al. 1995; Shabbir and Mohammad 2017). The antimicrobial action of such referred class of organic finishing agents is correlated to the halogen atom as presented in Fig. 2c. These oxidizing halogens act in direct transferring of and dissociation to give free halogen in aqueous media, where, these reactive free halogens play the role of inhibiting or inactivating the bacterial cell (Denyer and Stewart 1998). Due to the as-explained biocidal action of N-halamines, such compounds were successively applied as powerful antimicrobial functionalizing agent for cellulosic textile finishing (Table 2). Certain compounds were incorporated to improve the washing durability. Schindler and Hauser reported that, antimicrobial cellulosic textiles were produced by treatment with methylol-5,5-dimethylhydantoin in the presence of hypochlorite, results in the formation of chloramines on the fiber surface (Schindler and Hauser 2004). However, high concentration of chloramines was deposited on cellulosic surface, gave problems of fabric yellowness and strength-loss (Vigo 2001).

Polybiguanides

Polybiguanides as polymeric polycationic amines, is mainly composed of cationic biguanide repeating units with hydrocarbon chain linkers of identical or dissimilar length. Compared to N-halamines, polybiguanides exhibited much greater antimicrobial properties (Zanoaga and

Tanasa 2014). Polyguanidines and polybiguanides are well known as a vital class of biocidal polymers, due to its high hydrophilicity, excellent biocidal efficiency against wide microbial spectrum and non-toxicity. It was reported that, when acrylate monomers were associated with biguanide groups, it exhibited good antibacterial action, owing to the electrostatic interaction with microbial cell membranes as schematic in Fig. 2a. Additionally, it displayed higher antimicrobial activity against Gram-positive bacteria rather than Gram-negative bacteria; this could be attributed to less complicated structure of Gram-positive bacteria, which facilitate the penetration of high molecular-weighted biocidal polymer (Ikeda et al. 1984). Therefore, recent approach has studied their application as new generation of antimicrobial finishing agents for textile functionalization. Cationic biguanide-interactive groups can bind with the negatively charged groups (COOH) of cellulose. One of the most applicable biguanide-based polymers is poly(hexamethylenebiguanide) (PHMB), because of its low toxicity and water solubility. Hence, padding and exhaustion as conventional application methods were used for applying PHMB onto cellulosic textile to imply antimicrobial potency (Zhao and Chen 2016; Gao and Cranston 2008; Blackburn et al. 2006) (Table 2).

Polyethyleneimine

Polyethyleneimine (PEI) is well known as a non-biodegradable, cationic and synthetic polymer containing primary, secondary, and tertiary amino functional groups. It is manufactured in both branched and linear-shaped polymer via acid-catalyzed polymerization of aziridine and ring opening polymerization of 2-ethyl-2-oxazoline followed by hydrolysis (Brissault et al. 2003; Samal et al. 2012). Due to the presence of amino groups in the backbone of polyethyleneimine, it has been widely exposed to chemical modifications for acquiring some of desirable physicochemical properties. It was reported that, the un-substituted polyethyleneimine did not exhibit any of antimicrobial activities. However, it was realized that hydrophobicity and positive charge density are vital requirements for antimicrobial activity. Therefore, polyethyleneimine was modified to be incorporated with alkyl groups to potentiate both of these requirements (Lin et al. 2002). Different researches studied certain methods for incorporation of *N*-alkyl-polyethyleneimine in all commercial plastics, textiles, and glass, for acquiring these immobilized surfaces complete inactivation of bacteria (both waterborne and airborne bacteria), and fungi (including pathogenic and antibiotic-resistant strains), where, the biocidal action was interoperated via cell-membrane rupturing (Milović et al. 2005). *N*-alkylated polyethyleneimine was also reported to be immobilized over woven cotton textiles (Table 2), and the modified textiles were found to exhibit strong antimicrobial properties against numerous airborne

Gram-positive and Gram-negative bacterial strains. The application of high molecular weighted polyethyleneimine resulted in acquirement of excellent antimicrobial activity; while the application of low molecular-weighted polymer displayed negligible activities (Lin et al. 2003).

Metal organic frameworks

The metal organic frameworks (MOFs) are the coordination polymers, composed of the inorganic center presented in metal ion and organic coordinating linker presented in poly-functional organic acid (Abdelhameed et al. 2017c, 2018b). Porosity, crystalline feature, different dimensional structures (1D, 2D, 3D) and high surface area are characteristic properties which permit MOFs to be widely applicable in diverse fields (Horcajada et al. 2010; Sumida et al. 2011; Hu et al. 2014; Liu et al. 2014; Abdelhameed et al. 2017a, b). The insertion of MOFs within cellulosic textiles was recently studied to impart various functions (Abdelhameed et al. 2016, 2017d, e, 2018a; Emam and Abdelhameed 2017a, b; Emam et al. 2018a). Concerning antimicrobial applications, cobalt imidazolate metal-organic frameworks were used as biocidal materials (Quirós et al. 2015; Aguado et al. 2014). The biocidal activity of MOFs, mainly corresponds to the release of metal from the bulk MOFs and subsequently it is linearly proportional with the ease of metal release (Wyszogrodzka et al. 2016). Furthermore, the biological active ligands and incorporation of active substances both exhibited biocide effect (Wyszogrodzka et al. 2016). The action of MOFs ingredients to kill bacterial cell could occur by destruction of bacterial cell wall, penetration inside bacteria and interaction with protein, or disruption of bacterial cell wall permeability (Wyszogrodzka et al. 2016; Quirós et al. 2015; Lu et al. 2014; Zhuang et al. 2012). In case of biocidal textiles by MOFs material, few studies were published. MOF based on copper-benzene tri-carboxylic acid (Cu-BTC) was introduced inside synthetic and proteinic textiles to acquire antimicrobial activity (Emam et al. 2018b; Abbasi et al. 2012). As shown in Table 2, antibacterial cellulosic materials were produced by the direct generation of Cu-BTC MOF within the fibers' structure (Rodríguez et al. 2014; Wang et al. 2015). The work in biological active cellulosic textiles based on MOFs materials is still limited and just few studies were found in literature, and hence it could be prophesied that MOFs will be largely used in near future to produce antimicrobial cellulosic textiles.

Conclusion

The current review provides an overview about the recent advancements in antimicrobial finishing of cellulosic textile. The represented antimicrobial reagents offer prolonged

biocidal actions without environmental toxicity. The emergence of microbial resistant species is one of the vital defects with small molecular antibiotics as a result of their specific targets of action; however, in case of the currently reviewed antimicrobial reagents; physically destroying microbial cell membranes is reported to be the main route for preventing the microbial growth. In this review, the application of organic antimicrobial finishing agents (natural and synthetic in origin), as one of the main classes for antimicrobial textile finishing agents, has been widely illustrated. The natural origin-based textile antimicrobial agents were revealed to be environment-safe, such as chitosan, cyclodextrins, and natural dyes. The application of synthetic resourced antimicrobial agents, such as, polybiguanides, *N*-halamines, quaternary ammonium salts, polyethyleneimine, and metal organic frameworks were also well discussed. From all the previously mentioned antimicrobial agents, quaternary ammonium salts and metal organic frameworks, could be predicted to be the most commonly applicable organic compounds in future perspectives, and still not widely studied for biologically active cellulosic textiles.

Compliance with ethical standards

Conflict of interest Author wants to declare that no scientific or financial conflicts of interest exist.

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