

Cotton fabric finished with β -cyclodextrin: Inclusion ability toward antimicrobial agent



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ABSTRACT

β -Cyclodextrin was grafted onto cotton fabric through crosslinking with butane tetracarboxylic acid in presence of sodium hypophosphite monohydrate as a catalyst. This finished cotton fabric was loaded with the antimicrobial agent octenidine dihydrochloride. β -Cyclodextrin-grafted cotton fabrics, both after loading with octenidine dihydrochloride or before loading (control) were characterized for their antimicrobial activity against two types of bacteria (Gram positive and Gram negative) and two types of fungi, using the Diffusion Disk Method. The antimicrobial cotton fabric was subjected to several washing cycles and the antimicrobial activity was measured after each washing cycle to examine the durability of this antimicrobial finishing against repeated washing. The measurements showed that the finished cotton fabrics retain reasonable deal of their antimicrobial activity, even after 20 washing cycles. This long-lasting antimicrobial activity is attributed to the hosting ability of the cavities present in cyclodextrin moieties, which host the antimicrobial agent molecules and release them gradually.

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1. Introduction

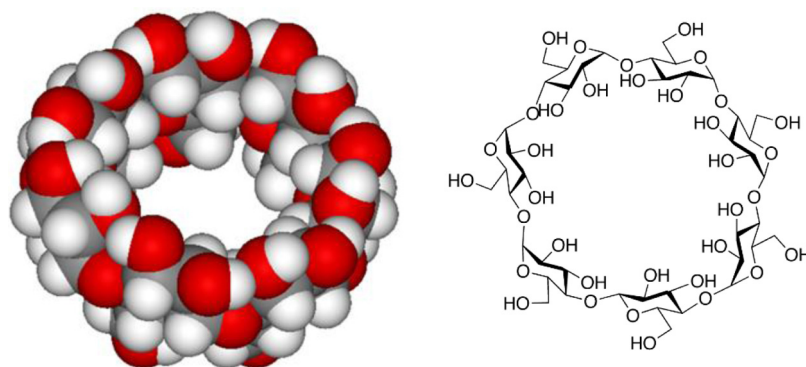
The family of chemical compounds known, as cyclodextrins are group of oligosaccharides in a cyclic form. These cyclic oligosaccharides are arranged in cone shape arrangement composed of at least five glucopyranose units which are bonded together covalently through carbon number one and carbon number four (Baudin, Camara, & Navaza, 2007; Puliti, Mattia, & Paduano, 1998). Each glucopyranose unit in the cyclodextrin molecule have three hydroxyl groups, which are free for interaction and each of them has its own reactivity. The lower and upper faces of the torus-shaped cavity contain secondary and primary hydroxyl groups (Szejtli, 1988). These hydroxyl groups are oriented outside the cavity and the oxygen atoms of the glycosidic bonds are inside the cavity, which makes the environment in the cavity interior very rich in electrons (Ouziel & Kulke, 2007). The distribution of the hydroxyl groups below and upper the cavity, makes the exterior of the cavity hydrophilic in nature, while the concentration of the oxygen electrons inside the cavity makes the interiors of cyclodextrins hydrophobic in nature (Dodziuk, 2006), that is why cyclodextrins have high ability to host a large variety of hydrophobic compounds inside their cavities and this inclusion ability is aided by means of complexation mechanism between the host cavity and the guest molecules (Abdel-Halim, Fouda, Hamdy, Abdel-Mohdy, &

El-Sawy, 2010; Abdel-Halim et al., 2011; Shao, Martel, Morcellet, Weltrowski, & Crini, 1996).

The cyclodextrin having seven glucopyranose units and known as β -cyclodextrin is the most common and commercially available type of cyclodextrins (Scheme 1). This is because of ease of synthesis and reasonable prices. In the structure of β -cyclodextrin, the cavity is surrounded by the hydroxyl groups from the upper and down sides, while the lone pairs of electrons of the oxygen atoms in the glycosidic bonds are directed to the interior of the cavity, giving rise to rich electron density inside the cavity, thus making the cavity interior is relatively hydrophobic, while the exterior of the cavity is hydrophilic due to the high availability of the hydroxyl groups (Del Valle, 2004). Due to this high hosting and inclusion ability resulting from the difference in the hydrophilicity of the exterior and the interior, cyclodextrins can form inclusion complexes and host a wide variety of compounds. These types of inclusion complexes lead to change in the physical properties of the substances to be hosted by cyclodextrin cavities, and these phenomena found wide variety of applications like the encapsulation characterized by controlled release of the hosted substances, like drugs, flavoring agents, fragrances and pesticides (Ishiwata & Kamiya, 1999; Nguyen, Liu, Zhao, Thomas, & Hook, 2013; Pedersen, Bjerregaard, Jacobsen, & Sørensen, 1998; Veiga & Ahsan, 2000). Inclusion ability of cyclodextrin gives high benefits and presents easy solutions for some problems facing people in some applications like for example, the high solubility of some molecule in aqueous media, which can be controlled through hosting as a guest molecule in cyclodextrin cavity in order to release them gradually. Another example is

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Scheme 1. Structure of β -cyclodextrin (β -CD).

the controlled release of the highly volatile guest molecules, upon hosting in cyclodextrin cavity. This is in addition to protecting some molecules against some factors like oxidation and thermal or chemical degradation, when hosted inside cyclodextrin cavity (Ghosh, Biswas, & Ghosh, 2011; Li & Xu, 2010; Wang, Cao, Sun, & Wang, 2011; Yamamoto, Kurihara, Mutoh, Xing, & Unno, 2005).

The natural polymer cellulose, which comes from renewable resource, is considered one of the most important natural polymers on earth due to its abundance. As a natural polymer, cellulose is an environmentally friendly polymer, biocompatible and in addition to that, cellulose is easily modified to a wide variety of cellulose derivatives useful in unlimited number of applications. All these features make cellulose a promising source of raw material for industry in the future as a substituent to other exhaustible resources. Cotton fabric has excellent performance properties like high hydrophilicity and high capability to discharge static electricity, which make cotton fabric very comfortable for wear compared to other synthetic fabrics like polyester and acrylic fabrics. In its native state, cotton fabric is composed of more than 95% cellulose and the rest is noncellulosic materials like pectin, hemicelluloses, natural waxes and oils, in addition to coloring matters. In order to make cotton fabric ready for different finishing processes and dyeing with different shades, gray cotton fabrics must undergo some chemical pretreatments to increase its water absorbency and remove coloring matter and make the fabric ready for light shade dyeing. These pretreatments involve scouring (Abdel-Halim, Fahmy, & Fouada, 2008; Abdel-Halim, Konczewicz, Zimniewska, Al-Deyab, & El-Newehy, 2010; Agrawal, Nierstrasz, & Warmoeskerken, 2008; Peng, Gao, Sun, Yao, & Qiu, 2009; Tanapongpipat, Khamman, Pruksathorn, & Hunsom, 2008), bleaching (Abdel-Halim, 2012a, 2012b, 2013; Abdel-Halim & Al-Deyab, 2011, 2013; Basto, Tzanov, & Cavaco-Paulo, 2007; Mistik & Yükselöglu, 2005; Tian, Branford-White, Wang, Nie, & Zhu, 2012) and finishing (Abdel-Halim, Abdel-Mohdy, Al-Deyab, & El-Newehy, 2010; Fahmy & Abdel-Halim, 2010; Mohsin, Rasheed, Farooq, Ashraf, & Shah, 2013; Teli, Sheikh, & Bhavsar, 2013; Xiao, Zhang, Yang, & Huang, 2007; Yang & Yang, 2005).

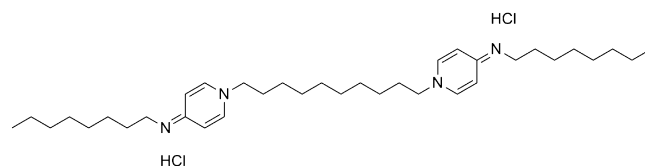
Recently, many routes and procedures have been developed to increase the functionality of cotton fabrics and to produce fabrics known as smart fabrics. A very famous procedure to produce cotton smart fabric is to modify cotton fabric with cyclodextrin through grafting/crosslinking and apply the so obtained functionalized cotton in different areas (Desmet, Takács, Wojnárovits, & Borsá, 2011; Scalia et al., 2006; Vismara, Melone, Gastaldi, Cosentino, & Torri, 2009; Wang & Cai, 2008). Cyclodextrin can be applied to the fabric either physically by immersing the fabric in cyclodextrin solution to give temporary finishing effect or chemically by fixing the cyclodextrin on the fabric surface through formation of chemical bonds to give permanent finishing effect (Buschman,

Denter, Knittel, & Schollmeyer, 1998; Murthy & Shown, 2009). The use of cyclodextrins derivatives in different textile applications has attracted the attention of many researchers and new approaches for hosting varying molecules inside cyclodextrin cavities have been reported (Denter, Buschmann, Knittel, & Schollmeyer, 1997; Szejtli, 2003). Some of the researches reported the improvement in finishing ability and dye ability of cyclodextrin-finished fabrics (Savarino, Viscardi, Quagliotto, Montoneri, & Barni, 1999; Voncina & Le Marechal, 2005; Wang & Chen, 2006). Others reported the ability of resin-finished cotton in the presence of cyclodextrins to capture the bad perspiration smell (Buschmann, Knittel, & Schollmeyer, 1991) or to control the release of antibacterial agents (Voncina & Majcen, 2004).

Topical disinfectants are broad spectrum antimicrobial agents, which are used for disinfecting skin contaminated wounds and mucous membranes. Octenidine dihydrochloride (octenidine) (Scheme 2) is considered a unique antimicrobial agent that can penetrate the cell wall and form chemical complexes with the cell components resulting in killing the bacterial cells, that is why octenidine dihydrochloride has high antimicrobial activity.

The chemical structure of octenidine dihydrochloride is bis-(dihydropyridinyl)-decane derivative. It is a kind of cationic surfactants which is used for disinfection as an aqueous solution of concentrations 0.1–2.0%. Its antimicrobial action is quite similar to the action of quaternary ammonium compounds, abbreviated quats but octenidine dihydrochloride has broader spectrum of activity toward both Gram positive and Gram negative bacteria (Dogan et al., 2008; Kramer & Assadian, 2013; Krishna & Gibb, 2010). Many countries in Europe use octenidine dihydrochloride to replace quaternary ammonium compounds or chlorhexidine derivatives. Octenidine dihydrochloride is generally used for disinfection purposes in aqueous solutions, where 2-phenoxyethanol is added to increase its disinfection potential (Stahl, Braun, Siebert, & Kietzmann, 2010).

The aim of the present work is to impart antimicrobial activity to cotton fabric. This is achieved by grafting β -cyclodextrin onto cotton fabric by use of butane tetracarboxylic acid as cross linking agent, through formation of ester linkage between the carboxyl groups of the polycarboxylic acid and the hydroxyl groups of both cellulose and cyclodextrin. The cavities of β -cyclodextrin fixed on the cotton



Scheme 2. Structure of octenidine dihydrochloride (OCT).

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