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Antibacterial functionalization of reactive-cellulosic prints via inclusion of bioactive Neem oil/βCD complex

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ABSTRACT

In the present research enhancing the antibacterial activity of cellulosic fabrics printed with reactive dyes was achieved through combined reactive printing and βCD loading in one step followed by subsequent treatment with Neem oil, as an eco-friendly antimicrobial agent. Retention of Neem oil with its main compound azadirachtin within the hydrophobic cavities of βCD moieties-attached the reactive cellulosic prints, via formation of host–guest inclusion complexes, to impart antibacterial functionality against G+ve (*Staphylococcus aureus*) and G−ve (*Escherichia coli*) bacteria was carried out. The experimental results reveal that post-treatment with Neem oil results in a remarkable improvement in the antibacterial activity of the treated reactive prints along with darker depth of shade and without adversely affecting the UV-blocking properties of the final products. Mode of interactions, surface morphology as well as washing durability of antibacterial and anti-UV functions were also investigated.

1. Introduction

In recent years, development and manufacturing of high added value textile products with multifunctional properties like antimicrobial, UV-protecting, insect repellent, self cleaning and anti-radiation, taking in consideration fashion, comfort, ecological and economic demands, have been become extremely important (Growri et al., 2010; Ibrahim, Refaie, & Ahmed, 2010; Schindler & Hauser, 2004; Simonic & Tomsic, 2010). As a consequence, a wide range of finishing additives suitable for textile applications has been used to bring new functional properties to the final textile products. The extent of improvement in the demanded functional properties depends on the type of substrate, chemical structure and functionality of the nominated finishing agent, method of application and durability to wash (Bajaj, 2002; Holme, 2007; Ibrahim, Refaie et al., 2010).

Antimicrobial finishing of textile materials protects both the users from pathogenic or odor-generation microorganism and the textiles from damage and/or undesirable aesthetic changes (Gao & Cranston, 2008; Purwar & Joshi, 2004; Simonic & Tomsic, 2010). Antimicrobial agents can be classified according to their effectiveness, mode of action and washing resistance (Simonic & Tomsic, 2010). Antimicrobial finishes can be divided into biocides that kill bacteria and fungi, and biostats that inhibit the growth of microorganism (Gao & Cranston, 2008; Ibrahim, El-Gamal, Gouda, & Mahrous, 2010; Simonic & Tomsic, 2010). The major classes of antimicrobial agents for textile include quaternary ammonium compounds (Gao & Cranston, 2008; Marini, Bondi, Iseppi, Toselli, & Pilati, 2007; Zhao, Sun, & Song, 2003), N-halamines (Ibrahim, Aly & Gouda, 2008; Ibrahim, Fahmy, Rehim, Sharaf, & Abo-Shosha, 2010; Ibrahim, 2008; Ren, Kocer, Worley, Broughton, & Huang, 2009; Simonic & Tomsic, 2010), chitosan (Lim & Hudson, 2009; Öktem, 2003; Shanmugasundaram, 2006). Polybiguanides (Kawabata & Taylor, 2007; Simonic & Tomsic, 2010), triclosan (Orhan, Kut, & Gunesoglu, 2009), nanosized inorganic particles (Growri et al., 2010; Gorensek & Pecelj, 2007; Ibrahim, Eid, Hashem, Refie, & El-Hossamy, 2010; Ibrahim, Refaie et al., 2010), and bioactive plant based products (Gupta, Khare, & Laha, 2004; Holm, 2005; Ibrahim, El-Gamal, et al., 2010; Simonic & Tomsic, 2010). On the other hand, the application of herbal oil, e.g. Neem oil, onto textile materials to impart antimicrobial activities as well as to get medicinal fabrics has very recently received growing interest (Joshi, Ali, & Rajendran, 2007; Sayed & Jawale, 2006; Vaideki, Jayakumar, Thilagavathi, & Rajendran, 2007).

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In the current study, our attention was focused both on upgrading the antibacterial efficiency of cellulosic reactive prints via incorporation of MCT-βCD in the printing formulations followed by subsequent treatment of the obtained prints with Neem oil, and on evaluating the impact of this after-treatment on the UV-protecting properties.

2. Experimental

2.1. Materials

Mill-scoured and bleached plain weave cotton (130 g/m^2) and viscose (110 g/m^2) fabrics were used throughout this work.

Commercial grade reactive dyes used in this study are Reactive Red 120, Reactive Red 141, Reactive Blue 160, Reactive Red 195 and Reactive Red 198. They are kindly supplied by Oh Yon Ind. Co, Ltd., China.

Cavasol® W7MC, monochlorotriazine-β-cyclodextrin MCT-βCD [average molecular weight ≈ 1560, degree of substitution 0.3–0.6 anhydroglucose unit, Wacker, Germany], Neem seed oil [Ozone Biotech Division, Shivanshu Sintered Product Pvt. Ltd., India], as well as Cecalginate® HV/KL-600 [medium viscosity sodium alginate-Ceca Kolloid-Chemie, Paris] were of commercial grade. Other chemicals such as polyethylene glycol, sodium bicarbonate ($NaHCO_3$), urea and methyl alcohol were of laboratory reagent grade.

2.2. Methods

2.2.1. Reactive printing

Fabric samples were printed with the following printing formulation:

Constituent	g/kg paste
Reactive dye	20
Stock thickening (10%)	700
MCT-βCD	20
Na-bicarbonate	20
Urea	50
PEG-600	20
Water	170
Total	1000

using the flat screen technique

After printing, the fabric samples were then dried at 100 °C for 3 min and steam fixed at 110 °C for (5–15 min) using Ariolt® CSL-Steamer-Italy, rinsed thoroughly in water and washed according to the dyestuff manufacturer recommendations to remove unreacted and any soluble byproducts followed by drying at 80 °C/5 min.

2.2.2. Post-treatment with Neem oil

The printed fabric samples were immersed in the methanolic solution (20 g/L) of the Neem oil with LR of 1/20 for 30 min at room temperature followed by roll squeezing to a 80% wet pick up and drying at 80 °C/15 min.

2.3. Testing

Percentage added-on (wt. add-on%) was calculated from the following equation:

$$\text{Add-on} \quad (\%) = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 are the weight of the printed and printed → post-treated fabric samples, respectively.

The depth of the obtained prints, expressed as K/S, was measured at the wavelength of maximum absorbance using an automatic filter spectrophotometer and calculated by the Kubelka–Munk equation (Ibrahim, Mahrous, El-Gamal, Gouda, & Husseiny, 2010):

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$

where K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance of the printed samples. The higher the K/S value is, the darker the depth of the reactive prints.

Color fastness to washing, perspiration and rubbing were evaluated according to AATCC Test Methods: (61-1972), (15-1973) and (8-1972), respectively.

UV-protection factor (UPF) was determined according to the Australian/New Zealand Standard (AS/NZS 4399-1996).

Anti-bacterial activity assessment against Gram-positive bacteria (G+ve, *Staphylococcus aureus*) and Gram-negative bacteria (G−ve, *Escherichia coli*) was evaluated according to AATCC Test Method (147-1988) and expressed as zone of growth inhibition (mm).

SEM analysis was made to compare surface morphology of the untreated and printed fabric samples without reactive dye using Scanning Electron Microscope JEOL-JZA-840A, after the samples were plated with gold.

Durability to washing was evaluated according to AATCC test method 124.

3. Results and discussion

Since the main task of the present work was to render reactive cellulosic prints antibacterial and anti-UV blocking properties without adversely affecting their printing properties, attempts have been made to include MCT-βCD in reactive printing formulations to get reactive prints having the ability to host a guest bioactive agent, Neem oil, in their internal cavities thereby imparting antibacterial properties to the post-treated reactive prints. Variables studied include: type of cellulosic substrate, type and concentration of additive, steaming time, type of reactive dye as well as Neem oil concentration. The results obtained along with the appropriate discussion follow.

3.1. $NaHCO_3$ concentration

Fig. 1 shows that, the K/S values of the obtained reactive prints reaches a maximum at 20 g/kg and then decrease for both the cellulosic substrates. The data so obtained reflect the positive impact of the using $NaHCO_3$ at proper concentration on enhancing the swellability of the cellulose structure, accessibility of its reactive sites, OH groups, and inducing ionization of the cellulose-hydroxyl groups thereby increasing the extent of dye fixation via formation of covalent bond as follows:

$$\text{Cell-OH} + {}^{-}\text{OH} \rightarrow \text{Cell-O}^{-} + H_2O \quad (1)$$

$$\text{Cell-O}^{-} + \text{RD-X} \rightarrow \text{Cell-O-RD} + X^{-} \quad (2)$$

where Cell-OH: cellulose substrate, RD-X: reactive dye