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Effect of copper and copper alginate treatment on wool fabric. Study of textile and antibacterial properties

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ABSTRACT

Alginate and copper ions were used for the preparation of modified wool fabrics with antimicrobial properties. The modified fabrics were characterized using FTIR spectroscopy, SEM and thermogravimetric analysis. The antimicrobial activity of wool fabrics was assessed before and after repeated washings (up to 50 cycles), against the test organism *Escherichia coli*. The resulting materials showed excellent antibacterial effect up to 100% reduction of bacteria after 24 h contact time, even after 50 wash cycles. Also, they have very good washing and rubbing fastness properties. Alginate treatment improves textile abrasion resistance and slightly enhances the fabrics mechanical strength, prevents copper loss during washing, but mainly helps increase sorption, doubling the amount of copper in the final product, resulting in increased antibacterial protection even at zero contact time (97.7% reduction of bacteria compared to 91.3% for the non-alginate containing sample).

1. Introduction

Wool, one of the oldest more complex and versatile of all textile manufacturing fibers has survived the test of time because of its unique natural properties. Wool resists dirt, retains its appearance and stays cleaner longer while its ability to absorb moisture prevents a build-up of static electricity and therefore wool does not attract lint and dust from the air.

Natural wool belongs to a group of proteins known as keratins that can act as nutrients and energy sources for microorganisms and bacteria under certain conditions. Soil, dust, sweat and some textile finishes can also be nutrient sources onto wool fabrics [1]. The increasing interest for the personal health and hygiene, has created the necessity to improve the antibacterial properties of wool fabrics. Several different types of antimicrobial agents such as metals and metal compounds, quaternary ammonium salts, poly(hexamethylene biguanide), triclosan, chitosan, dyes, regenerable N-halamine compounds and peroxyacids have been employed so far in the textile industry to give wool fabrics antimicrobial properties [2].

Copper ions, either alone or in copper complexes, have been used as a biocide for centuries [3]. While human tissue does not exhibit high sensitivity to copper [4], microorganisms are extremely sensitive [5,6]. Toxicity occurs through several mechanisms, such as displacement of essential metals from their native binding sites or through ligand interactions, changes in the conformational structure of nucleic acids and proteins and interference with oxidative phosphorylation and osmotic balance [4].

Alginic acid is a constituent of brown seaweed and has a characteristic structure that consists of two uronic acids, β-D-mannuronic acid and α-L-guluronic acid. In the presence of divalent cations, alginic acid forms stable gels through ionic interactions [7]. In addition to its traditional application as a thickening agent in textile printing, alginate has special properties such as low cost and easy availability, biocompatibility, ability to enhance wounds healing, high moisture adsorption and strong ion-exchange capacity [8,9].

The ability of wool keratin to absorb metal ions [10–12] is attributed to its mercapto groups and its carboxylic or sulphonic groups that are able to form salts with metal ions [13]. On the other hand, the abundance of carboxylic groups existing in alginates makes this biopolymer a potential modifier of textile fiber surfaces [14,15], which combined with its exceptional metal sorbing capacity may provide additional sites for metal binding.

In this study, alginate has been used as a wool textile modifier, in order to increase its metal sorbing capacity and copper was used as a biocide to give wool fabrics antibacterial properties. The resulting materials were studied as to their mechanical and textile quality properties as well as their effect on the growth of *Escherichia coli*.

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2. Experimental

2.1. Materials and methods

Commercial undyed 100% wool fabric (weight, 155 g/m^2) with plain weave was used for antimicrobial finishing. Medium viscosity (200 cP) sodium-alginate, average molecular weight 6000, Mannuronic/Guluronic acid ratio 1.75 ± 0.12, and $Cu(NO_3)_2 \cdot 5H_2O$ were purchased from Sigma-Aldrich. Levantin LNB was purchased from BASF. Acetic acid 100% was purchased from Merck and Tetrachloroethylene from Panreac.

The *E. coli* strain used was Dh5α purchased from Invitrogen. The medium used for growing and maintaining the bacterial liquid cultures was Luria-Bertani (LB) growth medium [1.0% Tryptone (Panreac), 0.5% Yeast Extract (Merck), 1.0% Sodium Chloride (Panreac), pH adjusted to 7.0 with 5.0 N NaOH (Merck)]. For the solid bacterial cultures, LB was supplemented with 7.5–15.0 g/L Agar (Panreac). For the AATCC 100-2004 test, a neutralizing solution (3% Tween 80 (Sigma) and 0.3% lecithin (USP) in sterile tap water) was also used.

All chemicals were analytic grade reagents, and used without further purification.

2.2. Preparation of wool fabrics

Wool fabric was cleaned in a bath containing 1.0% non-ionic washing agent Levantin LNB at a liquor-to-fabric ratio of 30:1 for 15 min at 40 °C. The pH was adjusted at 4.5 by addition of acetic acid solution (10 g/L). The fabric was subsequently rinsed with warm bi-distilled water (40 °C) for 3 min and then with cold bi-distilled water (25 °C) for 9 min. The samples were then dried at room temperature.

For the preparation of wool/copper fabrics (WCF), the washed wool specimens were immersed under agitation in an orbital shaker at 180 rpm in aqueous solutions of 5000 mg/L $Cu(NO_3)_2 \cdot 5H_2O$ at 25 °C for 24 h, at a liquor-to-fabric ratio 30:1. Finally, the samples were rinsed with cold bi-distilled water and dried at room temperature. The wool/alginate/copper fabrics (WACF), were prepared as follows. Alginate solution was prepared by dissolving sodium alginate powder in bi-distilled water at a concentration of 2.0% (w/v) in which pre-weighed wool fabric samples, cut in sizes of around 20 × 12 cm, were immersed for 15 min at room temperature, squeezed to 100% wet pick-up on a laboratory padding mangle and dried at room temperature. Finally, the wool-alginate samples were immersed under agitation in an orbital shaker at 180 rpm in aqueous solutions of 5000 mg/L $Cu(NO_3)_2 \cdot 5H_2O$ at 25 °C for 24 h, at a liquor-to-fabric ratio 30:1, for the preparation of a Cu alginate coating. Finally, the samples were rinsed with cold bi-distilled water and dried at room temperature.

The total content of Cu in the wool and wool-alginate fabrics was quantitatively determined by measuring the remaining copper concentration on the liquid using a GBC GF 300 Avanta atomic absorption spectrometer (AAS) using the following equation:

$$q_m = \frac{\left(C_{in} - C_f\right) \times V}{m_s}.$$

Where q_m (mg g^{-1}) is the sorbed copper, C_{in} (mg L^{-1}) the copper concentration in the initial solution, C_f (mg L^{-1}) the copper concentration after sorption, V (L) the volume of the solution and m_s (g) the mass of the wool or wool/alginate fabric (WAF) sample used.

2.3. SEM analysis

Fiber morphology was characterized by scanning electron microscopy (SEM, JEOL JSM 6460 LV).

2.4. FTIR spectral analysis

IR spectra were collected on a Thermo Scientific Nicolet 6700 FTIR with N_2 purging system. The instrument was also equipped with a LN2 cooled wide range Mercuric Cadmium Telluride detector (MCT-B), which exhibits 4–10 times higher sensitivity and better linearity than classic DTGS detectors. Spectra were acquired using a single reflection ATR (Attenuated Total Reflection) SmartOrbit accessory equipped with a single-bounce diamond crystal (Spectral range: 10,000–55 cm^{-1}, Angle of incidence: 45°). A total of 32 scans were averaged for each sample and the resolution was 4 cm^{-1}. The spectra were ratioed against a single-beam spectrum of the clean ATR crystal and converted into absorbance units. Data were collected in the range 4000–400 cm^{-1}.

2.5. Thermal properties

Thermogravimetric analysis for all the prepared samples was performed on a SETARAM SETSYS Evolution 18 TGA/DSC Analyser, by heating under air flow of 16 mL/min from room temperature up to 700 °C with a heating rate of 5 °C/min.

2.6. Determination of color strength and related parameters

Reflectance values of the treated samples were measured using UV–Vis spectrophotometer (Datacolor SF600 Plus-CT) at λ_{max} and K/S value of the fabrics were determined using the Kubelka–Munk equation given below [16]:

$$\frac{K}{S} = \frac{\left(1 - R_{\lambda_{max}}\right)^2}{2R_{\lambda_{max}}} \quad (1)$$

where K is the absorption coefficient, S is the scattering coefficient and $R_{\lambda_{max}}$ is the decimal fraction of the reflectance value of the fabric at peak wavelength.

The relative color strength and the color difference between copper and alginate-copper coated wool samples and raw wool sample were also obtained using following relationships:

$$\text{Relative colour strength } (\%) = \frac{K/S \text{ of treated sample}}{K/S \text{ of untreated sample}} \times 100 \quad (2)$$

$$\Delta E^* = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2} \quad (3)$$

where: $\Delta L^* = L^*_{coated} - L^*_{uncoated}$, $\Delta a^* = a^*_{coated} - a^*_{uncoated}$, $\Delta b^* = b^*_{coated} - b^*_{uncoated}$ and 'L*' describes lightness, 'a*' measures redness or greenness and 'b*' measures yellowness or blueness [17].

2.7. Wash fastness analysis

Two washing procedures were used to evaluate the durability of the antimicrobial activity of the copper and alginate-copper wool fabrics upon repeated laundering.

According to the first procedure [18], samples were washed in a Rotawash M228-SDL International machine with tetrachloroethylene without other solvents. The test was repeated 5 times.

For the second test, fabric samples were washed with liquid carbon dioxide (liqCO_2). As carbon dioxide is non-toxic and non-flammable it provides a good alternative to potentially toxic and environmentally harmful solvents such as tetrachloroethylene or other hydrocarbon solvents used in dry cleaning procedures. Moreover, as carbon dioxide evaporates from the fabrics during depressurization of the cleaning-vessel, it does not need the additional stage of drying while it can be recovered, recycled and reused. Samples were soaked in liquid CO_2 at room temperature and then were kept under constant CO_2 flow of