



Comparison of treatments of a cotton fabric modified with a low-temperature TiO₂ coating

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Received 8 May 2017, revised 13 September 2017, accepted 14 September 2017, available online 30 November 2017

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Abstract. We used sol-gel hydrosol to impregnate a commercially available cotton fabric with anatase nanoparticles to produce a self-cleaning cotton material. Three different aftertreatment procedures were used to determine the importance of excess sol removal and how the excess sol is removed. This was done by comparing 3 different aftertreatment procedures: plain drying after impregnation at 100 °C, rinsing and consequent drying at 100 °C, and drying at 60 °C followed by a mild hydrothermal treatment at 97 °C. To further compare these aftertreatments, pretreatments were used. The structure and morphology of the prepared samples was analysed by X-ray powder diffraction and high-resolution field emission scanning electron microscopy. The photocatalytic activity was evaluated by the UV photodegradation of methyl orange. It was determined that an aftertreatment method that involves enough excess sol removal is quite mandatory with the overall best result being produced by applying a mild hydrothermal aftertreatment method.

Keywords: cotton modification, sol-gel, anatase, titanium dioxide.

1. INTRODUCTION

Research related to self-cleaning fabrics and textiles has received considerable attention from the scientific community due to the potential application of its results in day-to-day life [1]. Nowadays, increasingly more time is spent on trying to cut down on the time necessary for household chores such as cleaning and washing clothes. If the clothes were made self-cleaning, it would cut down not only on the time spent on household chores, but also on the energy consumption of households [2]. Self-cleaning textiles are nothing new as some are already commercially available. However, the hunt for better self-cleaning still continues [3].

Self-cleaning can be achieved in two different ways: either by superhydrophobicity or by photocatalysis.

Superhydrophobic textiles have a water contact angle of more than 150°. This allows dirt and other contaminants to be removed by the running of water on the surface of the textile. Photocatalytic coatings, on the other hand, allow the decomposition of organic pollutants on the surface of the textiles [4,5].

Both these mechanisms can be achieved by creating a TiO₂ coating on the fabric as TiO₂ and, more precisely, its phase called anatase are both photocatalysts [6] and possess hydrophobic as well as UV-light induced superhydrophilic properties [7]. Anatase particles with nano-scale sizes have been synthesized using different approaches: hydrothermal [8,9], sol-gel [10], chemical vapour deposition [11,12], and physical vapour deposition [13]. Out of these methods we selected sol-gel synthesis as it does not require expensive apparatus. Although normally anatase is produced when the sol is calcinated at 400 °C, for the past years there have been sol-gel

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routes that use water as the solvent and produce anatase particles at as low temperature as 60 °C [2,10,14,15]. Since textiles decompose at high temperatures, we chose the route known as the hydrosol route, which uses water-based sols to produce the coatings.

When using the hydrosol route and sol-gel technology in general, it is necessary to be very mindful of the types of the precursors and concentrations used, as well as of the pH, temperature, and reaction time. Also, when considering coatings, the cleaning and pretreatment of the substrate are of great importance. In our work, we compared several aftertreatment methods to determine the impact of aftertreatment on the morphology of the sample as well as on its photocatalytic activity.

2. MATERIALS AND EXPERIMENTS

2.1. Materials used

For all experiments, commercially available cotton with a density of 0.31 kg/m² was used. All reagents used are commercially available.

2.2. Sol synthesis

The sol used in the experiments was made as follows: hydrochloric acid (Alfa-Aesar, 36%) and glacial acetic acid (Alfa-Aesar, 99.5%) were added to distilled water heated up to 60 °C. After 5 min of continuous stirring, titanium tetra-isopropoxide (Sigma-Aldrich, 98%) was added dropwise. At first a white precipitate forms as the TTiPr is rapidly hydrolysed. By continuous stirring and maintaining the temperature, the precipitate gradually dissolves. Finally, a clear sol is obtained.

2.3. Analysis of the sols

The size of the particles in the sol was determined by using dynamic light scattering (Brookhaven Instruments 90Plus) at a TiO₂ concentration of 8 g/L. After that the sols were dried at a low temperature (60 °C) and the crystalline phase was determined using X-ray powder diffraction (XRD) (Rigaku Ultima+) with 2 θ values from 5° to 60° using the Cu K α line.

2.4. Pretreatment of the cotton samples

Several previously described pretreatment methods were used to enhance the resulting self-cleaning properties of the samples. These methods include exposure to UV light in ambient air and in a hermetically sealed container, washing the cotton with a commercially available

detergent, boiling the cotton in water, as well as treatment with an alkali solution and an acidic solution. An untreated control sample was also prepared.

For 30 min prior to the treatment with the sol UV light exposure was carried out using a mercury UV lamp at ambient pressure and temperature. The cotton was washed with a commercially available detergent (*Radomat Oxi Activ*) for 30 min at 60 °C, followed by rinsing in distilled water for another 30 min, and finally drying at 60 °C until no mass change could be detected. Boiling of the cotton was carried out in distilled water for 30 min, followed by the same drying procedure as after washing. Alkali and acid treatments were carried out using a 15% NaOH solution and a 15% H₂SO₄ solution, respectively. The cotton was immersed in the solution for 3 h at room temperature. To remove excess alkali and acid solution, the samples were thoroughly rinsed with distilled water until the fabric had a pH of ~7.

2.5. Sol treatment of the samples

The cotton samples were immersed in the sol for 10 min at room temperature and ambient pressure under constant stirring. Excess sol was removed by pressing the samples between two sheets of a moisture absorbent material. For the 1st aftertreatment method, the samples were stirred in distilled water for 10 min, followed by drying at 100 °C for 5 min. For the 2nd aftertreatment method, the samples were just dried at 100 °C for 5 min. Finally, for the 3rd aftertreatment method, the samples were first dried at 60 °C for 30 min followed by hydrothermal treatment for 3 h at 97 °C and drying once more at 60 °C for 1 h.

2.6. HR-FESEM analysis of the coated fabrics

High-resolution field emission scanning electron microscopy (HR-FESEM) analysis was carried out using a FEI Nova NanoSEM 650 field-emission SEM with an acceleration voltage of 5 kV in a low vacuum of 60 Pa. The size of the particles was determined using ImageJ software.

2.7. Photocatalytic activity studies

The study of the photocatalytic activity of the samples was carried out by measuring the degradation of methyl orange (M-O) in the presence of UV light, using a mercury UV lamp. A 1 cm × 1 cm sample was cut out and immersed in 2 mL of 0.05 g/L M-O solution inside a low density polyethylene (LDPE) container that was sealed airtight.

3. RESULTS AND DISCUSSIONS

3.1. XRD studies

The XRD results showed that the particles were comprised of anatase with good crystallinity (see Fig. 1) and no rutile. The crystallite size was calculated using the Debye–Scherrer equation with the full width at half maximum (FWHM) of the main peak at $2\theta = 25.5^\circ$, which corresponds to the (101) lattice plane. The crystallite size was calculated to be 8.0 nm. Since the dynamic light scattering (DLS) results showed a particle size of 37.1 ± 0.1 nm with a polydispersity index of 0.266, we can assume that the samples contain nanoparticles that are polycrystalline in nature.

3.2. HR-FESEM studies

The FE-SEM micrographs show that the fibres were successfully coated with anatase nanoparticles. Also, it could be observed that for the samples produced with the 2nd aftertreatment method (drying after coating without rinsing) the coating had started to peel off from the fibres (see Fig. 2). This could happen if the coating was too thick and the adherence was not strong enough. For samples produced with the 1st method the nanoparticle coating, although well adherent, was uneven as it displayed mounds of nanoparticles on the surface of the coating. Samples produced with the 3rd aftertreatment method had the most even coating of the fibres with no mounds, which was also well adherent as no flaking could be seen.

Although the 3rd method showed a uniform coating of the fibres, it should be noted that in all cases the fibres had some excess sol stuck between them, effectively binding them together. This can have an effect of stiffening

the fabric. Furthermore, such cross-linking means that this excess sol can dislodge and fall off when the fabric would be in use, thus polluting the environment. A potential solution to this would be shortening the impregnation time as that way less sol could bind to the surface. This should solve the cross-linking of fibres.

The nanoparticle distribution for all samples was 30–60 nm with larger agglomerates also being present on the sample surface. This is not a surprise as no surfactants were used in order not to hamper the adherence of the particles to the fibre surface. The particles size determined with SEM is in agreement with the particle size obtained from the sol via DLS measurements.

3.3. Photocatalytic studies

Comparison of the photocatalytic activity reveals distinct differences between the three aftertreatment methods across all the different pretreatment methods. After the calculation of the reaction rate constant k , we can see that across all the aftertreatment methods, boiling of the cotton samples seems to have resulted in the greatest improvement on the photocatalytic activity. The k values for the 1st, 2nd, 3rd methods (comparing the boiled samples) were 0.0042, 0.0083, and 0.0048 min⁻¹, respectively (see Fig. 3). However, each of the methods had a different sample with the best k value: for the 1st method boiling gave the best result, for the 2nd method detergent washing and for the 3rd method UV-irradiation in an open environment were the best.

Calculation of the average k value for each aftertreatment method shows clearly by which method samples with the highest photocatalytic activity could be produced. It is obvious that the 2nd method gives us

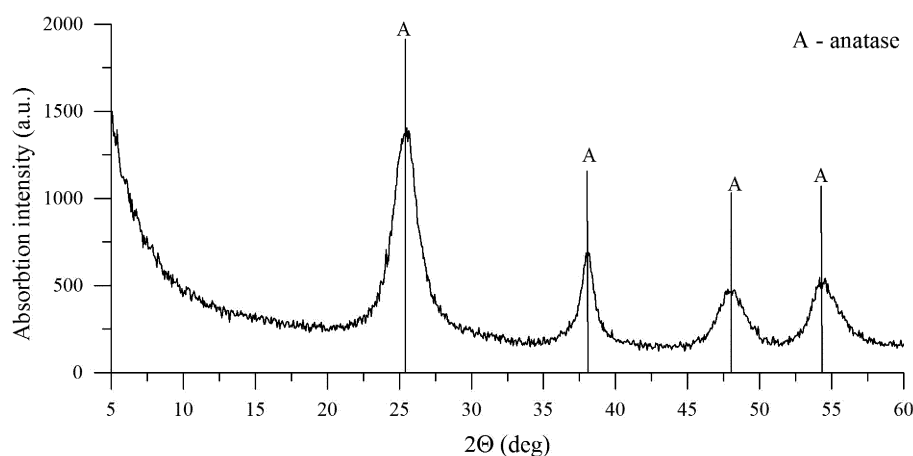


Fig. 1. XRD results for the synthesized particles.

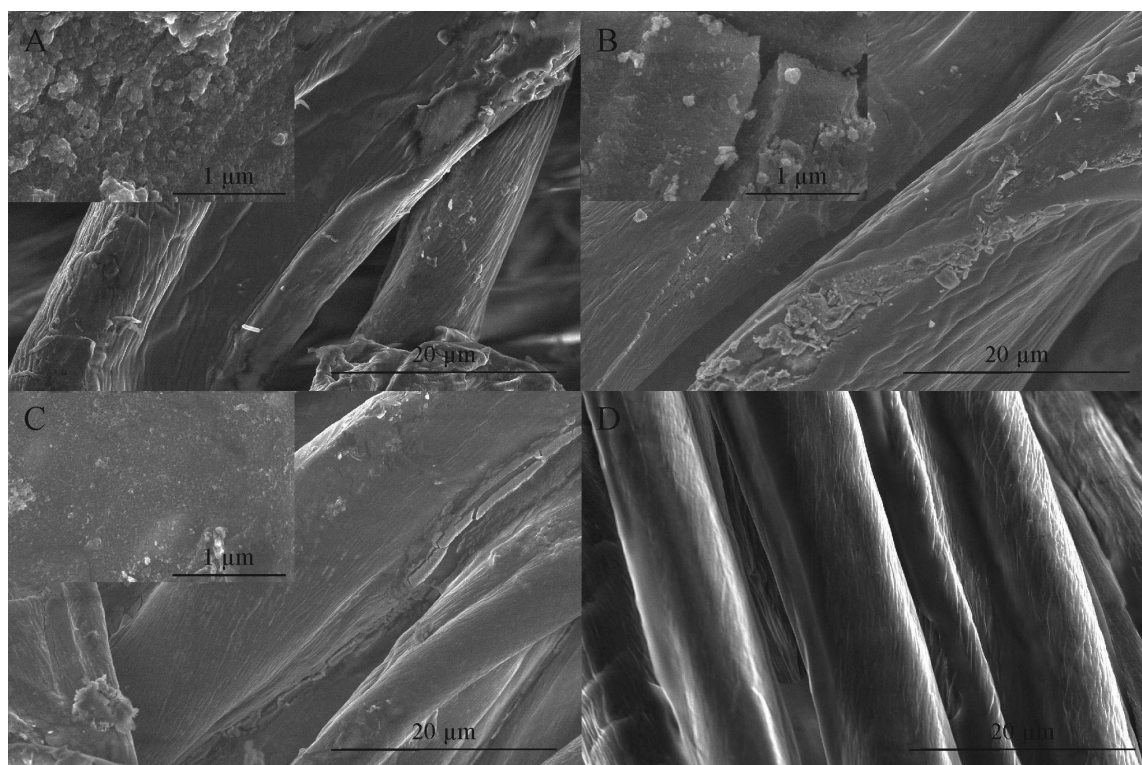


Fig. 2. FE-SEM micrographs of cotton coated using three different aftertreatment methods. (A) Sample created using the 1st method; (B) sample created using the 2nd method; (C) sample created using the 3rd method; (D) sample of an untreated cotton fibre. The overlaid micrographs of A, B, and C show the cotton fibres surface with a greater magnification, displaying the anatase nanoparticles on the surface.

the best results with a k value of 0.0069 min^{-1} . The next best result was produced by the 3rd method with a k value of little over half of that of the 2nd method – 0.0037 min^{-1} .

In most cases the control samples performed poorly compared to all the other samples that were made with different pretreatment methods. This means that such pretreatment as UV-irradiation can double the photocatalytic activity when compared to the control sample as seen for the 3rd aftertreatment method (see Fig. 3E).

Fluctuations in the concentration graphs of M-O indicate that the prepared samples were not uniformly coated: some spots had more nanoparticles and some had less as well as excess sol, which explains the uneven photocatalytic activity.

4. CONCLUSIONS

Self-cleaning cotton material was successfully created by coating a cotton fabric with anatase nanoparticles obtained with a low-temperature sol-gel process. From the three compared aftertreatment methods, the 2nd

method (drying at $100 \text{ }^\circ\text{C}$ for 5 min) showed the overall highest photocatalytic activity. However, the coating on those samples was too thick and started to peel off. Therefore, it can be concluded that the samples produced with the 3rd aftertreatment method (drying at $60 \text{ }^\circ\text{C}$ for 30 min followed by 3 h hydrothermal treatment at $97 \text{ }^\circ\text{C}$ and drying at $60 \text{ }^\circ\text{C}$ for 1 h) showed the best results.

For all the aftertreatments both UV irradiation and boiling showed the best increase in photocatalytic activity compared to the control samples. Thus, combinations of these methods (boiling under UV-irradiation) could increase the activity even further. Further studies are required to enhance the quality and performance of the coatings.

ACKNOWLEDGEMENTS

The publication costs of this article were covered by the Estonian Academy of Sciences and the University of Tartu.

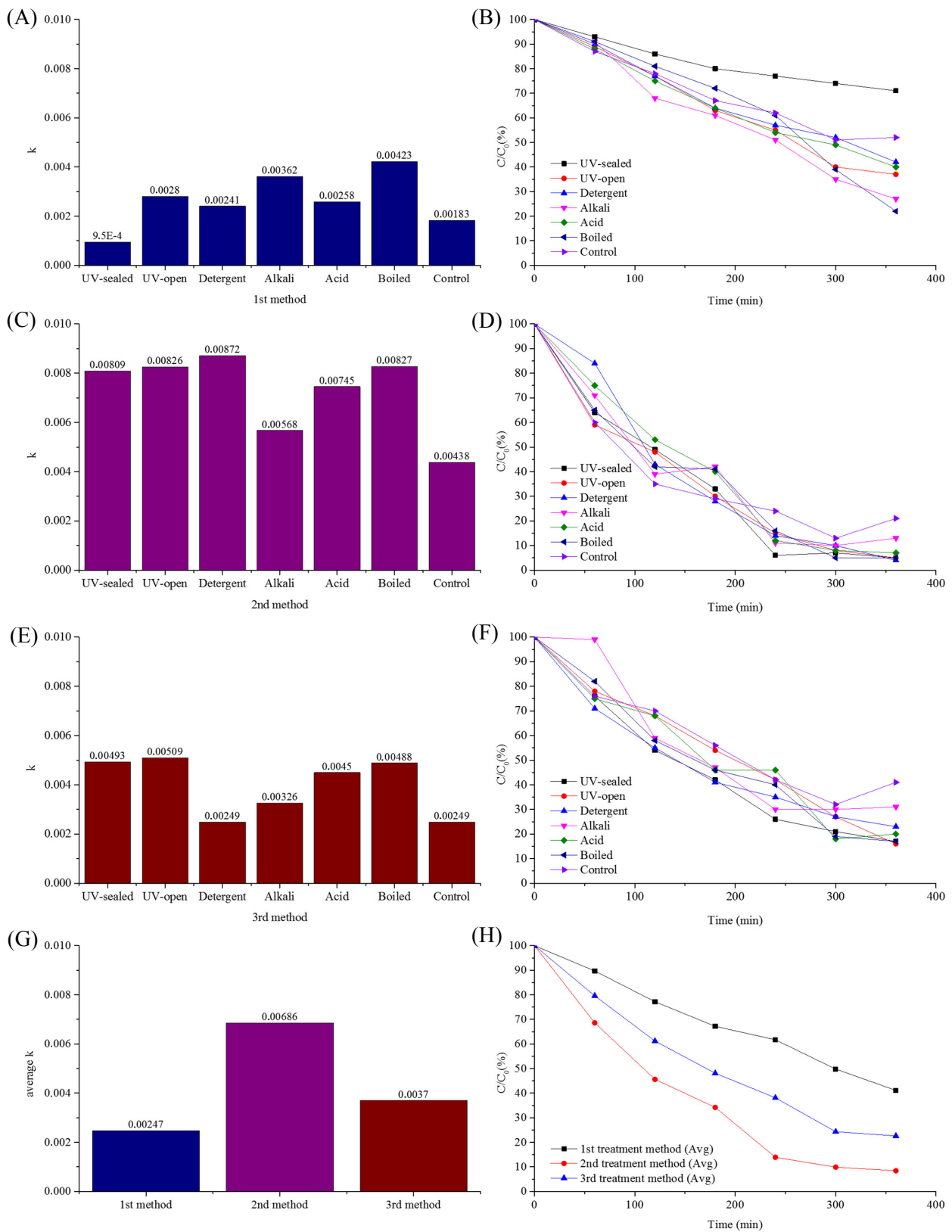


Fig. 3. Reaction rate constant k (min⁻¹) for all samples and the change in M-O concentration C/C_0 (%) for each sample during irradiation. (A, C, E) reaction rate constants for the samples of the 1st, 2nd, and 3rd treatment methods; (B, D, F) their respective C/C_0 graphs; (G) average reaction rate constant for the samples of the 1st, 2nd, 3rd treatment methods; (H) average C/C_0 graph for the 3rd method.

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Madalatemperatuurilise TiO₂-kattega modifitseeritud puuvillakanga töötlemismeetodite võrdlus

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Uuriti kaubanduslikult kättesaadava puuvilla immutamist anataasi nanoosakestega sool-geelhüdrosooli abil eesmärgiga saada isepuhastuv puuvillane kangas. Üleliigse sooli eemaldamiseks ja selle tähtsuse kindlakstegemiseks võrreldi kolme erinevat järeltöötlusprotseduuri. Nendeks olid tavaline kuivatamine pärast immutamist temperatuuril 100 °C, loputamine ja järgnev kuivatamine temperatuuril 100 °C ning kuivatamine temperatuuril 60 °C, millele järgnes kerge hüdrotermiline töötlemine temperatuuril 97 °C. Valmistatud proovide struktuuri ja morfoloogiat analüüsiti röntgendifraktsiooni ning suure eraldusvõimega välikatoodiga skaneeriva elektronmikroskoopia abil. Fotokatalüütilist aktiivsust hinnati metüüloranži lagunemise järgi UV-kiirguse mõjul. Näidati, et järeltöötlusmeetod, mis sisaldab piisavat liigse sooli eemaldamist, on hädavajalik, kusjuures prima tulemuse annab see koos kerge hüdrotermilise järeltöötusega.