Wash fastness improvement of malachite green-dyed cotton fabrics coated with nanosol composites of silica–titania

I KARTINI[1],*, I ILMI[1], E S KUNARTI[2] and KAMARIAH[3]

[1]Functional Coating Materials Research Group, Department of Chemistry, FMIPA, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia
[2]Department of Chemistry, FMIPA, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia
[3]Faculty of Industrial Engineering, Universitas Islam Indonesia, Yogyakarta, Indonesia

Abstract. Washing fastness of dyed cotton fabrics by malachite green (MG) blended with nanosols composite of SiO_2–TiO_2 has been significantly enhanced. The nanoparticulate inorganic sols were prepared by acid-catalyzed hydrolysis of titanium (IV) tetraisopropoxide (TTIP) and tetraethylortosilicate (TEOS) in ethanol at room temperature. The effect of silica on the characteristics of nanosols composite of TiO_2–SiO_2 was studied. Nanosols morphology was examined by transmission electron microscope (TEM). The nanosols silica–titania composite showed homogeneous morphology of interconnected spheres of about 20–25 nm. Enhanced dye absorption was observed at nanosols with silica content. The reflection spectra of the samples before and after leaching test using sodium dodecyl sulphate were recorded. The results showed that embedding TiO_2–SiO_2 and SiO_2 sols into the MG dye can improve the wash fastness by 40–95%. The highest improvement was obtained by SiO_2–MG-coated cotton fabrics as well as composites of SiO_2–TiO_2–MG-dyed cotton fabrics at highest silica content. The MG-nanosols composite silica–titania dyed cotton fabric has also shown remarkable antibacterial activity over *Staphylococcus aureus* and *Escherichia coli*.

Keywords. Triphenylmethane dye; functional coating; leaching fastness; antibacterial; nanosols silica–titania.

1. Introduction

Dyeing is an important process in textile industries; therefore, efforts to improve wash and light fastness of the dyed textile are highly studied. One of the typical dyes for textiles is triphenylmethane dyes such as malachite green (MG) and guinea green (GG). They both have been commonly known as textile dyes which have low light and washing (leaching) fastness properties (Mahltig *et al* 2005a; Mahltig and Textor 2006). Today, they are mainly applied to dye polyacrylic fabrics. The structure of the polymer enables the electrovalence interaction resulting in strong dye adherence to the fabrics. Contrary, cellulose based fabrics, such as cotton, does not have sufficient affinity to those dyes (Mahltig *et al* 2004a, b).

Recent studies have shown the improvement of light and wash fastness properties of dyed cotton fabrics by incorporating the dyes into the sol–gel matrices of silica (Min *et al* 2003; Mahltig *et al* 2005a; Mahltig and Textor 2006). They have shown that improved wash fastness can be obtained by modifying the dye sols composition. Mahltig *et al* (2005b) has studied that incorporating UV-absorber such as TiO_2 combined with organic UV absorber such as Tinuvin 213 improved the UV-protecting

properties of the resulting layers on glass. Optimized UV-protecting coatings by the presence of titania and organic UV absorbers were achieved at a certain composition. Yadav *et al* (2006) has shown the incorporation of zinc oxide nanoparticles on bleached cotton fabrics providing UV-blocking properties. Thus, it is interesting to apply such nanosols composite of silica–titania to the dyed cotton fabrics. It is necessary to study the effect of the nanosols composite on the wash fastness of the dyed fabrics. Instead, the fabrics will have UV protection as well as antimicrobial properties.

The present study concerns the preparation and optimization of the silica–titania nanosols composite coating to improve the wash fastness of MG-dyed cotton fabrics. The nanosols are mixed directly with the dyes and used as dye precursors. Details on nanosols characterization are reported. Nano-size features of both silica and titania nanosols are predicted to enhance the wash fastness of the MG-dyed cotton fabrics. It will be shown that the presence of titania may result in lowering the wash fastness of the dyed cotton fabrics. However, a combination of inorganic nanosols composite of silica and titania is needed to get other functional coating, such as UV protection and antimicrobial activity. Thus, optimized composition of silica–titania nanosols will be recommended. Our investigation also revealed the presence of

---

*Author for correspondence (indriana@ugm.ac.id)

Table 1. Mixing chemical compositions of the nanosols.

Mole ratio of SiO_2–TiO_2	TEOS (mL)	TTIP (mL)	Ethanol (mL)	HCl 1 M (mL)
1 : 1	20	20	280	7
2 : 1	40	20	260	7
3 : 1	60	20	240	7
1 : 0	20	0	300	7
0 : 1	0	20	300	7

nanoscale spherical particulates in the nanosols composite with interconnected linkages.

2. Experimental

2.1 *Nanosols preparation*

Silica and titania solutions were made through the hydrolysis of tetraethyl-orthosilicate (TEOS) and titanium (IV) tetra-isopropoxide (TTIP 98%, $\rho = 0 \cdot 955$), respectively. The chemicals were purchased from Aldrich and used as received. The composite sols were prepared by mixing the two solutions into ethanol with mole ratio of SiO_2 to TiO_2 of 1 : 1, 2 : 1 and 3 : 1 as listed in table 1. Hydrochloric acid (1 M) was added drop-wise into the sols of silica–titania. The nanosols were then stirred at room temperature for 24 h and readily used as coating precursors for the cotton fabrics. The nanosols were characterized by UV–Vis spectrophotometer (Genesys 20) and TEM (JEOL JEM 1400 at 120 kV). The dried gels of the corresponding nanosols at room temperature were subjected to characterization using infrared spectrophotometer (Shimadzu 8021) and XRD (Shimadzu XRD 6000 using CuKα radiation). The infrared samples were prepared using KBr pellet method with scanning accumulated at a spectral resolution of 4 cm^{-1}.

2.2 *Nanosols coating on cotton fabrics*

The cotton fabric was obtained from traditional market and was previously tested to contain fully cellulose fibres by fire-burning test. Dip-coating with withdrawn rate of 30 cm/min (Mahltig and Textor 2006) was performed on cotton fabrics (30 × 50 mm^2) for 10 times coating using the nanosols (18 g into 90 mL of ethanol). The as-coated fabrics were then dried at room temperature and at 120 °C for 1 h. The coated cotton samples were characterized using XRD.

2.3 *Dyeing the cotton fabrics with nanosols composite of silica–titania and malachite green dye*

About 18 g of nanosols was mixed with 82 mL of ethanol. Then, the dye, 0·9 g of MG solution (0·004 g in 10 mL ethanol), was mixed with the sols. The fabrics were then dip-coated into the dye–nanosols mixture, using the same procedure as previously used for nanosols coating on cotton fabrics.

2.4 *Leaching test*

The leaching test was performed using 1 wt% of aqueous solution of sodium dodecyl sulphate (SDS) (Mahltig and Textor 2006). The reflectance spectra of the fabrics after and before leaching were examined by reflectance spectrophotometer (Specular Reflectance Shimadzu UV 1700 Pharmaspec). The leaching degree (*D*) was calculated using the equation $D = 100(rA - rB)/(100 - rB)$ (Mahltig and Textor 2006). *rB* and *rA* represent the reflectance before and after the leaching test, respectively. The values of *rB* and *rA* were taken at the most minimum wavelength of the reflection spectra of the dyed fabrics.

2.5 *Antibacterial test*

The antimicrobial effect of the coated cotton fabrics was tested against *Staphylococcus aureus* and *Escherichia coli* using Plate count method. A nutrient agar medium (g/L: peptone 5; beef extract 1·5; yeast extract 1·5; NaCl 5; agar 20 and pH 7·5) was prepared and autoclaved at 121 °C for 15 min. Test organisms were grown overnight at 37 °C, in 10 mL of nutrient broth. The bacteria test Petri plates were incubated at 37 °C for 72 h. At the end of this period, zones of inhibition (ZOI) formed on the medium were measured in millimetres (mm). The results are presented as the ratio of diameter of inhibition to the diameter of the coated cotton samples.

3. Results and discussion

3.1 *Nanosols preparation and characterization*

Silica, titania and the composite sols were prepared by sol–gel technique at pH around 5–6 under acid-catalysed hydrolysis at room temperature. Figure 1 shows the absorption spectra of silica, titania and silica–titania nanosols. All spectra exhibit similar pattern of single broad absorption peak indicating the occurrence of nanoparticulates as the sols building blocks. Similar absorption peak at around 230 nm was also observed for Ti-grafted

MCM-48 (Morey *et al* 2000). The less intense absorption peaks of silica sols were presumably due to the presence of smaller particulates of silica than those of titania sols. Enhanced absorption was obtained as the silica sols were mixed with titania, confirming the additive properties of absorption spectra of the nanosols. The absorption decreases as the silica content increases. Absorption peak of the composite sols was also narrower than titania, indicating the contribution effect of the small silica particulates. Blueshifting absorption peak was observed as the silica content increased, indicating the presence of smaller particulates building blocks as the nanosol constituent.

The nano-sized particulate building blocks of the nanosols were confirmed by the representative TEM images of silica–titania nanosols as depicted in figure 2. The particulates were spherical with diameters of about 20–25 nm (figure 2). Figure 2(a) shows that the spherical nanoparticulates are interconnected. The images also show that the size of particulates was homogeneous, providing better particle attachment to the cotton fibres. Thus, the composite sols can be called as nanosols, as coined by Mahltig *et al* (2005a).

The infrared spectra of the dried gels (figure 3) have confirmed the observed silica–titania interaction in the nanosol composites as indicated by their UV–Vis spectra. Vibrations at ~1100 and 1200 cm^{-1} (displayed as a shoulder) observed at SiO_2 and Si–Ti dried gels can be assigned to the asymmetric stretching of Si–O–Si, while peaks at ~820 and small peak at ~470 cm^{-1} can be attributed to the symmetric stretching and deformation modes of Si–O–Si, respectively (Dutoit *et al* 1995; Hutter *et al* 1995). The Si–Ti composite gels present vibrations at 950 cm^{-1}, suggesting to the distorted Si–O tetrahedron due to the formation of Ti–O–Si bonds (Boccuti *et al* 1989;

Dutoit *et al* 1995; Hutter *et al* 1995; Galan-Fereres 1995; Navarrete *et al* 1996; Seco *et al* 2000). Similar phenomenon has been observed for the formation of titania–silica hydrophobic xerogels (Mariscal *et al* 2000). The silica–titania material has a hydrophilic surface. It is generally accepted that water adsorbed on the silica or titania surface due to the formation of hydrogen bonding with silanol (≡Si–OH) or titanol (≡Ti–OH) groups (Mariscal *et al* 2000; Nizar *et al* 2013). Thus, water adsorption should be related to the number of –OH group at the silica or titania surface. The more the number of –OH groups, the more hydrophilic the surface. Infrared spectra identify the –OH groups as broad stretching vibrations of O–H
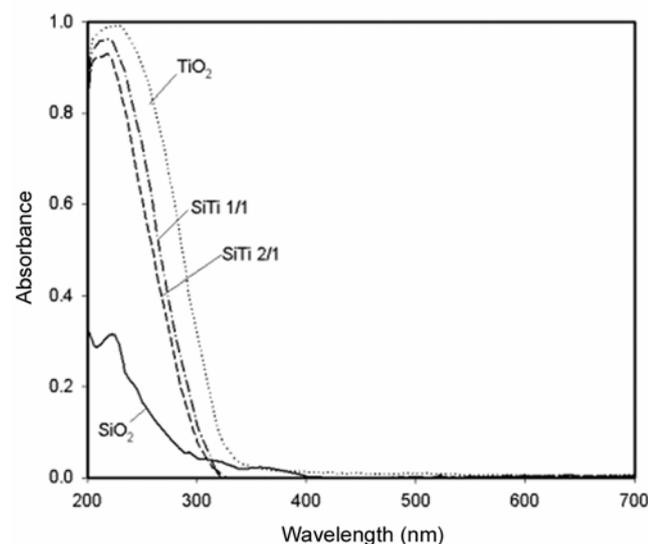

Figure 2. TEM images of silica–titania nanosols at lower (**a**) and higher magnifications (**b**).

Figure 1. Absorption spectra of silica (SiO_2), titania (TiO_2), and silica–titania (SiTi) nanosols.

(hydrogen-bonded surface silanols) at ~ 3500 cm^{-1} and bending at ~ 1630 cm^{-1}. The first vibration actually includes the contribution of all hydroxyl-containing species, whereas O–H stretching of free water is observed as a small peak at ~ 3700 cm^{-1} (Mariscal *et al* 2000). It is also observed that broadband around ~ 3500 cm^{-1} of Si–Ti dried gel are less pronounced compared to that of TiO$_2$ indicating reduced hydrophilicity of titania surfaces as the silica interacted with titania. This is in agreement with findings of several other researches for silica–titania prepared from TEOS and TTIP (Zhou *et al* 1996; Mariscal *et al* 2000; De Paz *et al* 2012; Nizar *et al* 2013). The decreased intensity of the O–H vibrations might be due to the formation $\equiv$Si–O–Ti$\equiv$ bond (Nizar *et al* 2013). Even the hydrophilicity of TiO$_2$ dried gels was slightly removed as interacted with SiO$_2$, the nanoparticles aggregation on the corresponding nanosol was still observed (figure 2a), resulting in more interconnected nanoparticulates. This feature will provide a strong attachment of dye molecules that can be entrapped in interstitial voids between particulates, leading to the low degree of leaching of the attached dye on cotton fabrics.

3.2 *Nanosols-coated cotton fabrics characterization*

Figure 4 displays the XRD pattern of the nanosols-coated cotton fabrics. It is observed that all patterns show the reflection peaks of cellulose (Vainio 2007). The diffraction pattern of pristine cotton exhibited typical reflection peaks of native cellulose at 14° (d_{101}), 16° ($d_{10\bar{1}}$), 22·5° (d_{002}) and 34° (d_{040}), indicating predominantly cellulose-Iβ (Wada *et al* 2001; Lee *et al* 2012). The intensity of cellulose reflections is getting stronger as the fabrics coated by sols containing silica, but they are weaker for TiO$_2$ nanosols-coated fabrics. It is supposed that titania
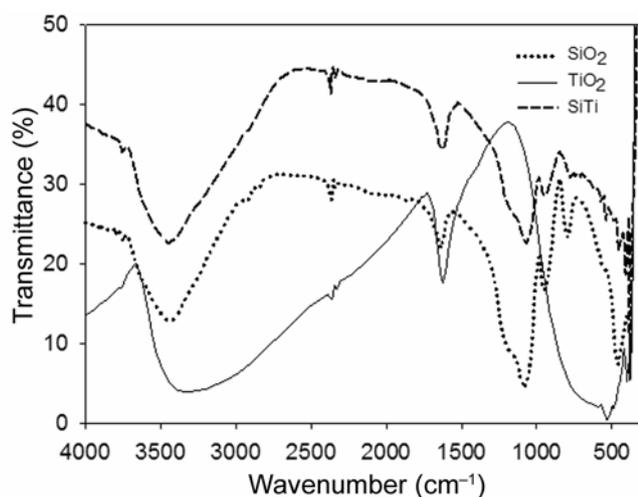
nanosols coat the fibres strongly than silica, resulting in more uniform and possibly thicker coating leading to enhanced intensity of cellulose reflections. This behaviour may also lead to stronger dye attachment of the composition of silica nanosols–MG onto the cotton surfaces than titania nanosols–MG. Moreover, the coating of silica–titania nanosols composite will have moderate adherence to the cotton fibres. The XRD patterns of the hydrogel of the corresponding nanosols (Kunarti *et al* 2012) showed that silica and titania retain the amorphous nature of their structure, while titania has slightly increased its crystallinity in the presence of silica. However, the titania is still amorphous. No crystalline polymorph of titania was detected on the corresponding hydrogels. Hence, probable photocatalytic degradation of the coated dye by the presence of photoactive titania polymorph such as anatase or rutile can be hindered. Whereas the amorphous nature of silica and titania is expected to provide more –OH surfaces beneficial for linking via hydrogen bonding with cellulose surface. In turn, it will increase the sols adherence to the surface of cotton fabrics. The proposed interaction between the cotton fabric and the silica–titania nanosols is illustrated in figure 5.

3.3 *Characterization of MG–nanosols and the corresponding coated cotton fabrics*

Figure 5 shows the absorption spectra of MG dye solution and the dye precursors of MG with nanosols of silica, titania and silica–titania composite. The dye characteristic is shown by the appearance of a sharp peak at 620 nm (Mahltig and Textor 2006) with three weaker absorptions
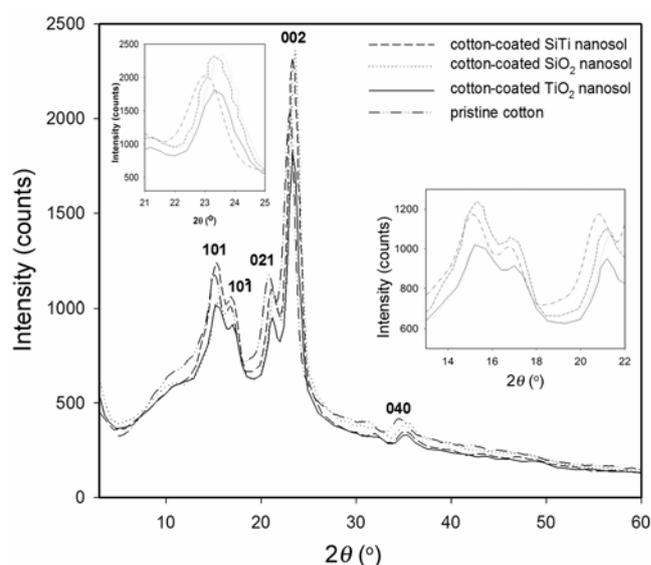
Figure 3. Infrared spectra of silica (SiO$_2$), titania (TiO$_2$) and silica–titania (SiTi) dried gels.

Figure 4. XRD patterns of the pristine cotton fabrics and cotton fabrics coated with silica nanosol, titania nanosol and silica–titania nanosols composite.

at 320, 430 and 550 nm. The absorptions are due to electron transitions from n to $\sigma*$ of the chromophores and from π to $\pi*$ of the benzene ring of the dye structure. Proposed interaction between the MG and the composite silica–titania nanosols has also been illustrated in figure 5. The surface of silica sol particulates has been known to be negatively charged in a broad pH range (pH > 2) (Park *et al* 2006). The negative sites will interact readily with the cationic nature of MG dyes. Cationic MG is supposed to interact with the nanosols via direct electrostatic attraction to the silica matrix (Mahltig *et al* 2004b).

It can be seen from the spectra (figure 6) that increased intensity is apparent for the absorption spectrum of dye precursor containing silica nanosols only due to the preferred interaction between the dye and negatively charged silica nanosols. The presence of titania nanoparticle is also obvious from the existence of broad absorption around
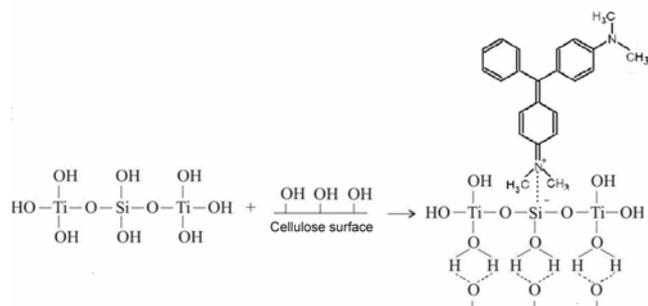
200–300 nm. The broad absorption bands have been confirmed previously in figure 1 as the characteristic of titania electronic absorption. Lower absorptions of the dye in precursors containing titania (TiO_2–MG and SiTi–MG) are presumably caused by the weaker interaction between the dye and TiO_2, which has more positive surface potential compared to SiO_2 particle (Park *et al* 2006).

Figure 7 shows the reflectance spectra of MG-nanosols dyed cotton fabrics. The dye characteristic is shown by the appearance of the minimum of the reflectance spectra at 620 nm (Mahltig and Textor 2006). It is clear that the peak positions of the dye do not change as the dye interact with the silica–titania nanosols and adsorbed on the cotton fabrics. But the peaks are broader than the corresponding peaks in the solution (figure 6). It is assumed that there is a strong interaction between the surfaces and the adsorbed molecules that often lead to the aggregation effect (Kamat 1993).

3.4 *Wash fastness*

The results of the leaching test are depicted in figure 8. The graph shows that MG-dyed cotton fabrics without nanosols coating have the highest degree of leaching at around 45%. High wash fastness improvement of ∼95% was achieved for cotton fabrics dyed with MG–silica and MG–SiTi (3 : 1). It is also observed that MG–titania nanosols-dyed cotton fabrics have only a small improvement of the wash fastness of the dye (∼40%). The increased dye leaching is supposed to be the effect of the photocatalytic activity of titania nanoparticles (Jiang *et al* 2008). Even in the less crystalline anatase form, titania may still exhibit photoactivity to degrade the dye (Bozzi *et al* 2005). Hence, the nanosols composite generated

Figure 5. Illustration of the proposed interaction among the cotton fabric, the malachite green dye and the silica–titania nanosols.

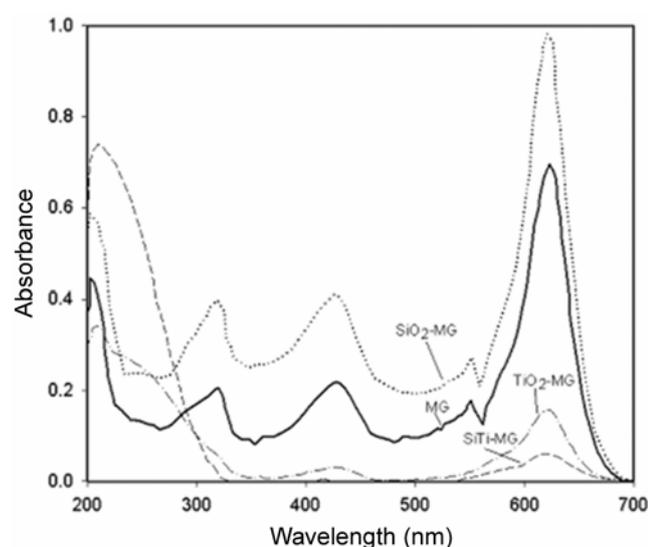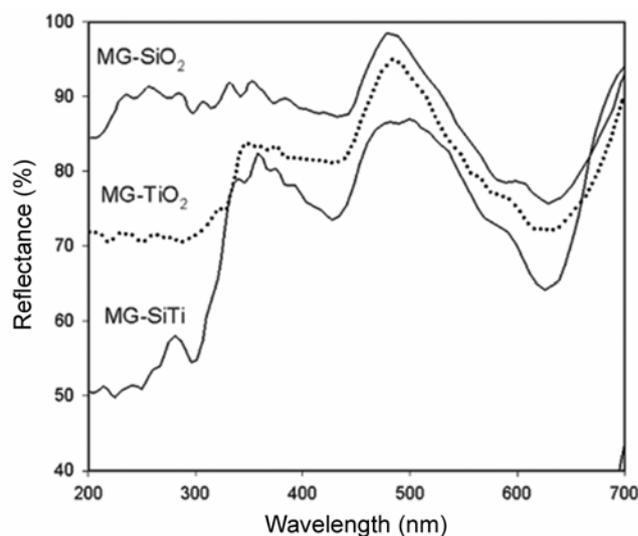**Figure 6.** Absorption spectra of malachite green dye solution (MG) and MG-dye combined with silica nanosol (SiO_2–MG), titania nanosol (TiO_2–MG), and silica–titania nanosols composite (SiTi–MG).

Figure 7. The reflectance spectra of MG-nanosols dyed cotton fabrics.

higher wash fastness improvement than those of MG-dyed without nanosols and MG–titania nanosols-dyed cotton fabrics due to the presence of silica. Hydrolyzed metal alkoxide solutions have been proven as an excellent tool to convey new properties to the cellulosic materials (Schramm *et al* 2005).

Another important feature of dyeing is the drying temperature. From figure 8, it can be seen that dyed cotton fabrics dried at 120 °C exhibit better wash fastness than those dried at room temperature. A strong adherence of the coating materials is likely to occur at high drying temperature in a similar manner of annealing leading to the lower degree of leaching.
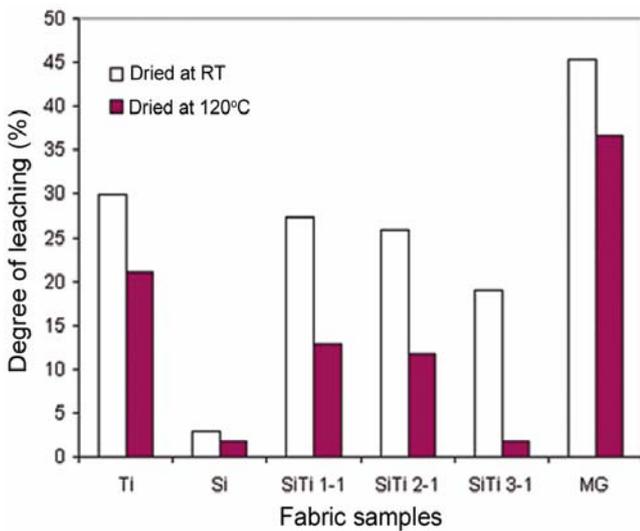
The reflectance spectra of the MG–silica, MG–titania and MG–silica titania composite nanosols dyed after and before leaching test as depicted in figures 9–11, respectively, show a clear evidence of the wash fastness improvement of dyeing the cotton fabrics using dye precursors containing nanosols of silica and the composite with titania. The absorption of the dye, which is the minimum of the reflectance spectra, at around 620 nm, is reduced strongly for the dyed MG–titania nanosols. Significant improvement is achieved when introducing silica nanosols into the composites. However, titania can still be used in the nanosol composite in certain limited

Figure 8. Wash fastness of the dyed cotton fabrics (MG) and functionalized dyed cotton fabrics at various Si : Ti nanosols composition.
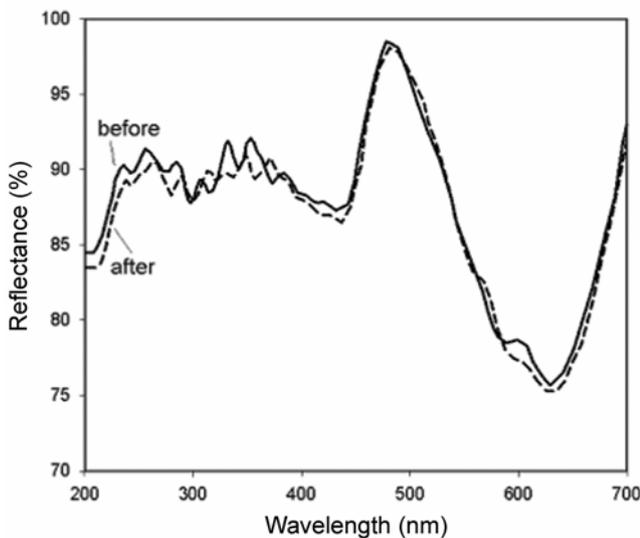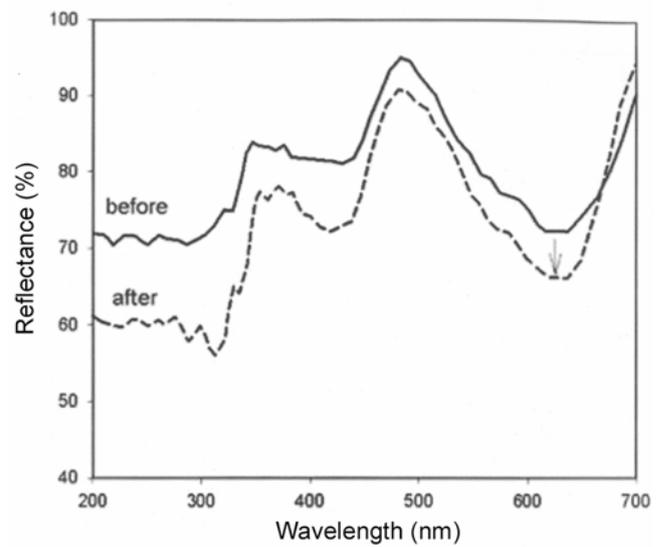

Figure 10. Reflectance spectra of the MG-dyed cotton fabrics coated with titania nanosols: before and after leaching test.

Figure 9. Reflectance spectra of the MG-dyed cotton fabrics coated with silica nanosols: before and after leaching test.
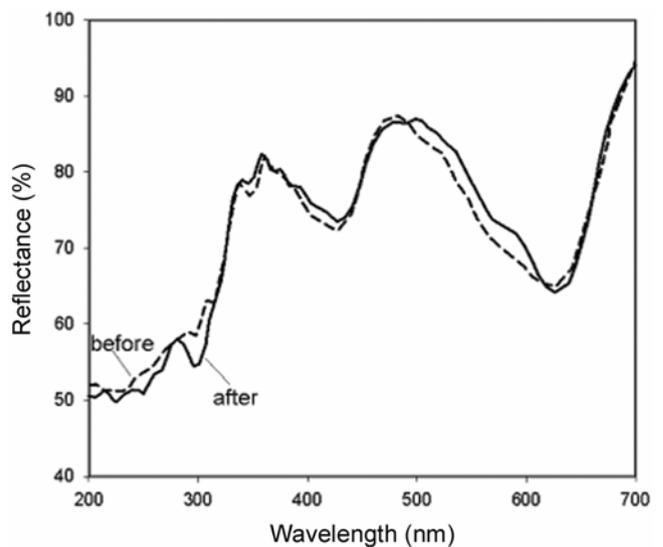

Figure 11. Reflectance spectra of the MG-dyed cotton fabrics coated with composite nanosols of silica–titania (3/1): before and after leaching test.

Table 2. Antibacterial activity.

Samples	Diameter ratio of ZOI to fabric's diameter	
	S. aureus	*E. coli*
Cotton fabric	1·00	1·00
SiTi-coated cotton	1·00	1·00
SiTi–MG-dyed cotton	3·85	3·78

amount. The mole ratio of silica to titania of 3 : 1 is the recommended formulation for nanosols blended with MG-dye as the dye–sols precursor. Considering high mechanical and stability of silica, higher silica content is hindered due to the increased toughness of the cotton fabrics.

3.5 *Antibacterial activity*

Cotton fabrics are the most susceptible substrates for the settling of microorganisms, since they provide large specific surfaces with good adhesion and water absorption. Therefore, it is necessary to have functional cotton fabrics with antimicrobial finishes. In this research, the MG-dyed nanosols-coated cotton fabrics were tested over Gram-positive bacteria (*S. aureus*) and Gram-negative bacteria (*E. coli*) using Plate count method. The results are listed in table 2.

From table 2, it is clear that the MG-dyed cotton fabrics coated with silica–titania nanosols composite showed antibacterial activities towards both bacteria. The SiTi-coated cotton only exhibits antibacterial activity on the surface of the cotton, while the dyed one has inhibitory effect in larger area over the surface of the cotton. The nanoparticle oxides affect the cell physiological activities by interacting with lipopolysaccharide and lipoteichoic acid through hydrogen bonding and ligand exchange. Bacterial toxicity of nanoparticle oxides is more likely due to protein structural changes and phospholipid molecular damage (Jiang *et al* 2010; Jisha *et al* 2012). The changes are possibly causing the loss of the cell membrane integrity and the leakage of the periplasm. Damage to phospholipid structure, henceforth, the cell membrane, may lead to bacterial cell death. The dye itself has already been known to have antibacterial properties due to its cationic nature (Tutak and Gun 2012). Electrostatic interaction between positively charged nitrogen and the predominantly anionic components of the microorganisms surface (such as Gram-negative lipopolysaccharide and cell surface proteins) plays a primary role in antibacterial activity. This property leads to almost 4 times higher antibacterial activity for SiTi–MG dyed cotton. It is noteworthy that blending the nanosols with MG dye resulted in synergistic effect of high wash fastness and antibacterial activity.

4. Conclusions

The role of silica–titania, titania and silica nanosols to improve the wash fastness of the dye on the cotton fabrics has been presented. Wash fastness improvement was obtained using dye precursors containing high silica content. It is clear that silica supports the dye attachment due to its amorphous, nano-sized features and its surface nature. While titania weakens the dye attachment, probably due to its photocatalytic activity. The cotton fabrics dyed with MG solution containing nanosols composite of silica–titania at a mole ratio of 3 : 1 has also shown remarkable antibacterial activity toward Gram-positive bacteria (*S. aureus*) and Gram-negative bacteria (*E. coli*).

Acknowledgement

References

Boccuti M R, Rao K M, Zecchina A, Leofanti G and Petrini G 1989 *Stud. Surf. Sci. Catal.* **48** 133

Bozzi A, Yuranova T, Laub D, Kiwi J and Guasaquillo I 2005 *J. Photochem. Photobiol. A: Chem.* **174** 156

De Paz H, Chemtob A, Croutxe-Barghorn C, Le Nouen D and Rigolet S 2012 *J. Phys. Chem.* **B116** 5260

Dutoit D C M, Schneider M and Baiker A 1995 *J. Catal.* **153** 165

Galan-Fereres M, Alemany L J, Mariscal R, Banares M A, Anderson J A and Fierro J L G 1995 *Chem. Mater.* **7** 1342

Hutter R, Mallat T and Baiker A 1995 *J Catal.* **153** 177

Jiang D, Xu Y, Wu D and Sun Y 2008 *J. Solid State Chem.* **181** 593

Jiang W, Yang K, Vachet R W and Xing B 2010 *Langmuir* **26** 18071

Jisha E R, Balamurugan G, Selvakumar P, Edison N and Rathiga R 2012 *Internat. J. Pharm. Tech. Res.* **4** 1323

Kamat P V 1993 *Chem. Rev.* **93** 267

Kunarti E S, Kartini I, Kamariah and Kholilah 2012 unpublished results

Lee K-Y, Tammelin T, Schulfter K, Kiiskinen H, Samela J and Bismarck A 2012 *ACS Appl. Mater. Interfaces* **4** 4078

Mahltig B and Textor T 2006 *J. Sol–Gel. Sci. Technol.* **39** 114

Mahltig B, Bottcher H, Knittel D and Schollmeyer E 2004a *Text Res. J.* **74** 521

Mahltig B, Knittel D, Schollmeyer E and Bottcher H 2004b *J. Sol–Gel. Sci. Technol.* **31** 293

Mahltig B, Bottcher H, Rauch K, Diekmann U, Nische R and Fritz T 2005a *Thin Solid Films* **485** 108

Mahltig B, Helfried H and Bottcher H 2005b *J. Mater Chem.* **15** 4385

Mariscal R, López-Granados M, Fierro J L G, Sotelo J L, Martos C and van Grieken R 2000 *Langmuir* **16** 9460

Min L, Xiaoli Z and Shuilin C 2003 *Coloration Technol.* **119** 297

Morey M S, O'Brien S, Schwarz S and Stucky G D 2000 *Chem. Mater.* **12** 898

Navarrete J, Lopez T, Gomez R and Figueras F 1996 *Langmuir* **12** 4385

Nizar U K, Efendi J, Yuliati L, Gustiono D and Nur H 2013 *Chem. Eng. J.* **222** 23

Park J H, Yang, J H, Yoon J B, Hwang S J and Choy J H 2006 *J. Phys. Chem.* **B110** 1592

Schramm C, Rinderer B, Binder W H, Tessadri R and Duelli H 2005 *J. Mater. Sci.* **40** 1883

Seco A M, Goncalves M C and Almeida R M 2000 *Mater. Sci. Eng.* **B76** 193

Tutak M and Gun F 2012 TEKSTİL ve KONFEKSİYON **22** 48

Vainio U 2007 *Report Series Phys: HU-P-D145* (Finlandia: Helsinki University Printing House)

Wada M, Okano T and Sugiyama J 2001 *J. Wood Sci.* **47** 124

Yadav A, Prasad V, Kathe A A, Raj S, Yadav D, Sundaramoorthy C and Vigneshwaran N 2006 *Bull. Mater. Sci.* **29** 641

Zhou Q F, Zhang Q Q, Zhang J X, Zhang L Y and Yao X 1996 *Mater. Lett.* **31** 39