Functionality of Inorganic Nanostructured Materials onto Wool Fabric

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Abstract

Silver nanoparticles (AgNPs) were prepared through chemical reduction method and characterized by UV-Vis absorption spectra to examine its formation with different $AgNO_3$ and sodium borohydride concentrations and by transmission electron microscope (TEM) to evaluate its particle size and size distribution. The wool fabric was first treated separately with AgNPs and titanium dioxide nanoparticles (TiO_2NPs) and then dyed with C.I. Acid Orange 74 (AO74). The dye uptake of pre-treated wool fabric with nanoparticles was compared to conventional dyeing of wool. The existence of AgNPs and TiO_2NPs on wool fabric during acid dyeing increases the dye uptake up to 27 and 39%, respectively. The dyeing kinetic of wool fabric was positively affected by treating with AgNPs and TiO_2NPs. Also, the activation energy of AO74 diffusion was calculated before and after NPs-treatment that confirms the physicsorption dyeing process. The NPs-treatment leads to produce a wool fabric with excellent antibacterial and photocatalytic properties for TiO_2NPs-treated wool fabric and very good antibacterial and good photocatalytic properties for AgNPs-treated wool fabric. In addition, NPs-treatment has no adverse effects on fastness properties of the functionalized dyed wool fabric.

Keywords: Silver nanoparticles, Titanium dioxide nanoparticles, Wool, Acid dyeing.

1 Introduction

Using nanotechnology in enhanced functionalization of textile to produce smart fabric with antibacterial, stain resistant, and UV protection properties has been increased dramatically (Patra and Gouda 2013; Radetić 2013; Montazer and Pakdel 2011; Joshi and Bhattacharyya 2011; Dastjerdi and Montazer 2010; Dastjerdi *et al.* 2009). The application of nanoparticles, especially metal oxides and nano-metals, to impart wool fabric with multifunctional performances was the object of this study improving its hydrophilicity, antibacterial properties, and UV-resistance.

Among various metal oxides, TiO_2NPs impart useful properties on wool fabric such as antimicrobial, flame retardant, self-cleaning, anti-wrinkling, and UV protection (Montazer *et al.* 2011). TiO_2NPs are superior to other photocatalysts due to its low cost, reasonable safety, high photocatalytic efficiency, and ability in complete degradation of a broad range of pollutants under certain conditions. Several researches reported the potential of TiO_2NPs photocatalyst for imparting multifunctional properties to different textile materials (Nazari *et al.* 2013; Montazer and Seifollahzadeh 2011; Zhang *et al.* 2009). Along the same lines, Montazer *et al.* (2011) obtained anti-UV and self-cleaning wool fabric through applying the TiO_2NPs. Moreover, Perelshtein *et al.* (2012) reported one-step process for enhancing the antibacterial activity of different fabrics using TiO_2NPs.

Wool fibers contain polar and ionisable groups on the side chain of acidic amino acids that able bind to different charged species of organic or inorganic materials. The presence of this unique characteristic makes them ideal for the selective binding of metal ions. Therefore, the wool fabric with poly-functional ligands can be a suitable template to grow metal nanoparticles (Arshakuni and Gubin 2010; Naik *et al.* 2010; King and Pierlot 2009). Among various nano-metals, AgNPs have attracted significance attention because of their unique optical, electronic, antibacterial, and catalytic properties. The surface plasmon resonance (SPR) property of AgNPs is important for its various applications. Light interacts with AgNPs causing conduction electrons to locally oscillate around NPs at a certain frequency (Kamat 2002). Antibacterial effect of AgNPs on textiles has already been shown by various researchers (Perumalraj *et al.* 2012; Rad *et al.* 2011; Cho *et al.* 2005;). Tang *et al.* (2011) reported that the wool fabrics were dyed by anisotropic AgNPs and the wool treated with AgNPs showed significant antibacterial activity. Also, Kelly and Johnston (2011) described that wool fibres were colored by AgNPs that were synthesized through the reduction of Ag ions in the presence of wool. AgNPs can be synthesized using various methods, such as chemical reduction, electrochemical, sonochemical, γ-radiation, photochemical, and laser ablation. The most popular preparation of Ag colloids is chemical reduction of sliver

salts by sodium borohydride (Barani *et al.* 2012; Hu *et al.* 2008; Cheng *et al.* 2007; Hadad *et al.* 2007; Bogle *et al.* 2006; Ahmad *et al.* 2003; Abid *et al.* 2002).
The present research article involves four major objectives: (1)the use of chemical reduction method to synthesis AgNPs under different concentrations of Ag ions and reducing agent that influence the particle size; (2)functionalization and modification of wool fabric by surface treatment with the prepared AgNPs and TiO_2NPs; (3)improvement of dyeing properties of NPs-treated wool fabric with AO74 by increasing the dye affinity under several parameters such as pH, time, and temperatures of dyeing process; and (4)evaluation of fastness, antibacterial and self-cleaning properties of the NPs-treated wool fabric.

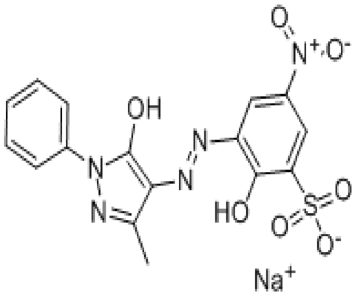
2 Materials and Methods

2.1 Fabric

Medium–sick wool fabric with a mean fiber radius 9.25 µm, 160 g/m^2, supplied by GOLDENTEX, was scoured with sodium dodecyl sulphates, SDS, (ADWIC), rinsed, then dried at room temperature.

2.2 Dye and Chemicals

Acid Orange 74, AO74, was purchased from CLARIANT, its chemical structure is shown in Scheme 1. Silver nitrate (Sisco, India), titanium dioxide, 21 nm, (Aldrich, Germany), tri-sodium citrate dehydrate, TSC, (ADWIC), poly vinyl pyrrolidon, PVP, M.Wt. 40000 (SRL), sodium borohydride, SBH, (BDH, England), and deionized water were used in this research.



Scheme 1. Chemical structure of AO74

2.3 Preparation of Silver Nanoparticles (AgNPs)

AgNPs were prepared by chemical reduction method at different concentrations of silver nitrate (1.25, 2.5, 5.0, 10.0, 15.0 and 20.0 mg) with TSC (3mM) and PVP (0.15 g). The solution was stirred vigorously then SBH as a reducing agent was added at different concentrations (0.1, 0.2, 0.4, 0.8, 1.6, 2.1, 3.0 mM) turning the solution to light yellow.

2.4 Treatment of Wool Fabric with AgNPs and TiO_2NPs

0.5 g of wool was dipped in the prepared AgNPs and TiO_2NPs dispersion (0.150 w/v) separately at LR 1:100, pH 4, 80 °C, for 90 min. The treated wool was washed under tap water then dried in oven at 40 °C.

2.5 Dyeing of Treated and Untreated Wool Fabric with AO74

Wool fabric was dyed with AO74 in absence and presence of nanoparticles (Ag and TiO_2) using the following recipe:

Table 1. Dyeing conditions of wool fabric

Recipe:		
Dye conc.	:	2 % owf
Liquor ratio (LR)	:	1:50
Time	:	120 min
Temperatures	:	70, 80, 90 and 100 ℃
pH	:	2.6

The dyed samples were taken out from dye-bath and allowed to dry in the open air. After dyeing, reduction clearing was performed at 50 ℃ for 30 min, SDS (2 g/L) at LR 1:50 to remove the loosely fixed dye on the surface of dyed fabric. The samples were then rinsed with cold running tap water then dried at oven in 40 ℃.

2.6 Characterization of The Dyeing Properties of Dyestuff onto Wool Fabric

These studies have been directed toward determination of the kinetic and thermodynamic adsorption parameters.

2.6.1 Dyeing Kinetics

In order to characterize the kinetic behavior of a dyeing process (Ferus-Comelo 2011), the pseudo-second order model tested the mechanism of dye adsorption onto wool fabric and its integration equation is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{1}$$

Where k_2 is the rate constant of the pseudo-second order adsorption (g mg^{-1} min^{-1}) and q_e and q_t are the quantity of dye uptake (mg g^{-1}) at equilibrium and at time t, respectively. The rate parameters k_2 and q_e can be directly obtained from the intercept and slope of the plot of t/q_t against t. The quantity of dye uptake was estimated using the following equation:

$$q_t = \frac{(C_0 - C_e)V}{W} \tag{2}$$

Where C_o and C_{o} are the initial and the equilibrium dye concentrations in dye-bath (mg L^{-1}), respectively, V is the volume of dye bath (l) and W is the weight of fabric (g).

2.6.2 Diffusion Coefficient and its Activation Energy

The diffusion coefficient was calculated from the following equation (Ferus-Comelo 2011):

$$\frac{C_t}{C_e} = 4\sqrt{\frac{Dt}{\pi r^2}} \tag{3}$$

Where C_t and C_e represent the dye concentrations in dye-bath at time t and at equilibrium (mg l^{-1}), D is a diffusion coefficient (cm^2 min^{-1}), and r is a radius of the fibre (cm). The activation energy of the diffusion was calculated from the following Arrhenius equation:

$$\ln D = \ln D_0 - \frac{E}{\mathrm{R}T} \tag{4}$$

Where D_0 is a constant, E is an activation energy (kJ mol^{-1}), R is a gas constant (8.314 J mol^{-1} K^{-1}) and T is an absolute temperature (K).

2.7 Determination of Wool Fabric Properties

2.7.1 Color Fastness Testing

The treated dyed samples were tested according to ISO standard methods. The specific tests were: ISO 105-X12 (1987), color fastness to rubbing; ISO 105-C02 (1989), color fastness to washing; ISO 105-E04 (1989), color fastness to perspiration; and ISO 105-B02 (1988), color fastness to light (carbon arc).

2.7.2 Antibacterial Activity

Biological activity of untreated and NPs-treated wool was tested by Kirby-Bauer modified method (Matsen *et al.* 1969; Bauer *et al.* 1966). Plates were incubated with filamentous gram-positive bacteria as staphylococcus aureus (S. aureus) and gram-negative bacteria as Escherichia coli (E. coli) at 35-37 ℃ for 24-48 hours. For the disc diffusion, the zone diameters were measured with slipping calipers of the national committee for clinical laboratory standards.

2.7.3 Photo-induced Discoloration onto Wool Fabric

60 µl coffee (2.5 g/10 ml) was spotted on untreated and NPs-treated wool fabric. The samples were irradiated by UV lamp for 24 hours.

3 Results and Discussion

3.1 Effect of Concentrations of $AgNO_3$ by Chemical Reduction Method

A great deal of information can be obtained due to the unique optical properties of AgNPs by analyzing the spectral properties of AgNPs in solution. It is known that metallic AgNPs exhibit an intense absorption band due to surface plasmon resonance (SPR) effects because SPR occurs in particles having a particle size smaller than a 100 nm. According to Mie theory (Richard and Anna 2008), the SPR arises from interactions of small metallic particles with an external electromagnetic field resulting in a coherent oscillation of the conduction (free) electrons at the surface.

The visible absorption spectra of AgNPs were studied at different concentrations of $AgNO_3$ (1.25, 2.5, 5.0, 10.0, 15.0 and 20.0 mg) and in presence of TSC (0.3 mM) and SBH (0.4mM) as a reducing agent, Figure 1. As the silver concentration increases, the peak plasmon resonance shifts to shorter wavelengths which corresponding to smaller particle size. At concentration higher than 5.0 mg, the peak plasmon resonance shifts to longer wavelengths. This may be due to a multi-nanoparticle aggregate; hence, the plasmon resonance will be red-shifted to a longer wavelength than the resonance of an individual nanoparticle.

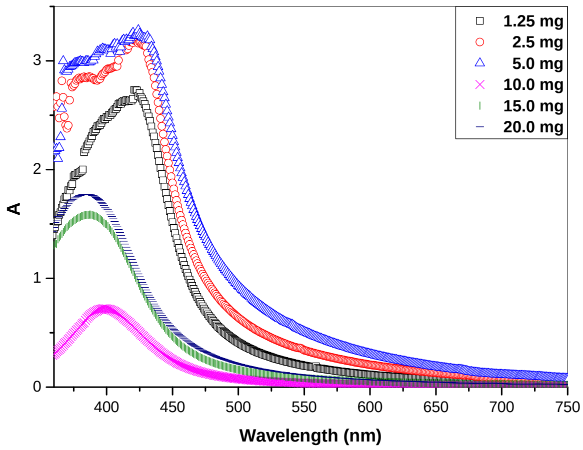


Figure 1. UV-Vis absorption spectra of different concentrations of AgNPs

3.2 Effect of Concentrations of Reducing Agent

The effect of different concentrations of SBH (0.1, 0.2, 0.4, 0.8, 1.6, 2.1 and 3.0 mM) as a reducing agent for $AgNO_3$ (5.0 mg) in presence of TSC (0.3mM) was studied as shown in Figure 2. As the concentration increases, the peak plasmon resonance shifts to shorter wavelength. At concentration higher than 0.4 mM of SBH, the peak plasmon resonance shifts to longer wavelengths, due to a multi-nanoparticle aggregation. It is observable as an intensity increase in the red/infrared region of the spectrum. Hence, the optimum concentration of SBH (0.4 mM) that gives maximum wavelength at 400 nm. The color of the solution turned to yellow could be expressed as the reaction mechanism shown below:

$$4Ag^{+} + NaBH_4 + 2H_2O \rightarrow 4Ag + BH_4^{-} + Na^{+} + 4H^{+} + O_2$$

Transmission electron microscopy (TEM) image of AgNPs reduced by SBH shows fine and homogeneous nanoparticles that have diameter less than 15 nm, Figure 3.

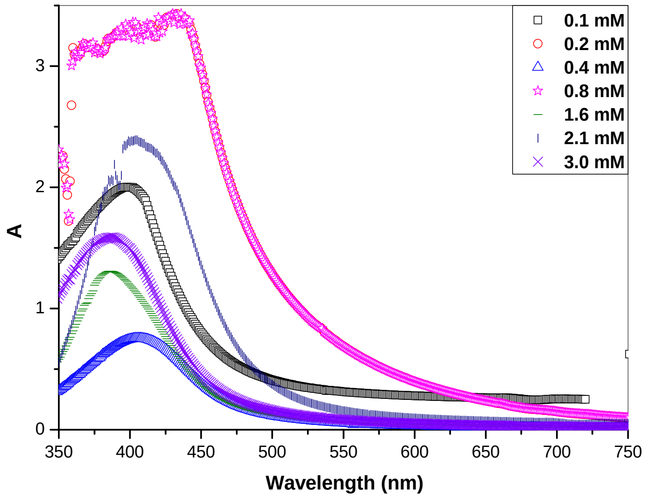


Figure 2. UV-Vis absorption spectra at different concentrations of SBH

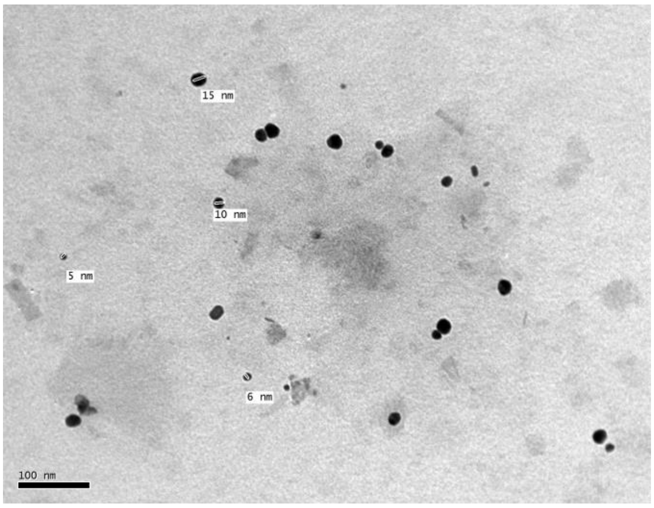


Figure 3. TEM image of AgNPs reduced by SBH

3.3 *Effect of NPs-treatment on Wool Dyeing Process*

Pre-treatment method with AgNPs and TiO_2NPs was used for wool dyeing process. It is noticed that, the color of the light cream of the wool fabric changed to yellow for AgNPs, and white for TiO_2NPs. Figure 4 shows the dye uptakes of AgNPs (0.228 mg g^{-1}) and TiO_2NPs (0.250 mg g^{-1}) -treated wool fabrics are higher than that of the corresponding untreated wool (0.180 mg g^{-1}) at 100 ℃ for 90 min [2% (owf); LR 1:50; pH=2.6]. This result indicates that the presence of nanoparticles increases the dye affinity towards the wool fabric improving its dye uptake. The nanoparticle in the fabric thus acts as mordent forming a chelation with OH^{-} and azo groups of AO74; one site with the wool fabric and the other site with the dye which enhancing the interaction between the wool fabric and the dye.

The treatment of wool fabric with AgNPs and TiO_2NPs increases the AO74 uptake by about 27 and 39%, respectively. This may be due to the small particle size of prepared AgNPs (7- 40 nm) that enables the entrance of AgNPs in between the wool molecules as a crosslinking agent which contributes increase the AO74 loading onto wool fabric. Also, TiO_2NPs have a positive impact as co-catalyst on enhancing the bonding of AO74 to wool fabric during the dyeing process. Actually, the homogeneous small particle size of TiO_2 (21 nm) facilities the formation of bonding in between the wool fibres and AO74. On the other hand, the superhydrophilic property of TiO_2NPs causes its high ability in creating hydrogen bonds with water molecules resulting in good wettability and hence higher dye ability.

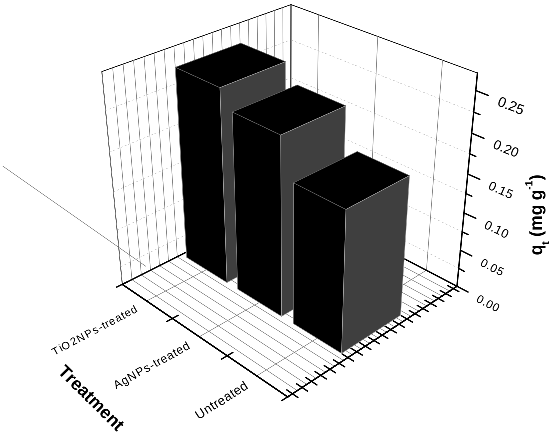


Figure 4. Dye uptake of AO74 onto untreated and AgNPs- and TiO_2NPs-treated wool fabric [Dyeing conditions: 2% owf, pH 2.6, LR 1:50, time 90 min and temperature 100 ℃]

3.4 Rate Constant of The Dyeing Process

Several models can be used to express the mechanism of solute adsorption onto an adsorbent. In order to characterize the kinetic behavior of the dyeing process, it is desirable to determine how the rate of dyeing varies as the reaction progresses. Pseudo-second order rate kinetic model has been most widely used to describe the dye adsorption onto wool fabric where adsorption capacity was assumed to be proportional to the number of active sites occupied on the adsorbent.

The effect of temperatures on the pseudo-second order adsorption kinetics of AO74 onto untreated and AgNPs and TiO_2NPs-treated wool fabric has been represented in Figure 5. The values of rate constants k_2, the calculated and the experimental quantity of dye uptake at equilibrium, q_e and $q_{e,exp}$, respectively, initial adsorption rates h and correlation coefficients, r_2^2, of the pseudo-second order adsorption kinetics of AO74 onto untreated, AgNPs and TiO_2NPs-treated wool fabric at various temperatures are represented in Table 2.

By increasing the dyeing temperature from 70 to 100 ℃, the rate constants of pseudo-second order model directly increased for untreated wool from 0.110 to 0.252, AgNPs-treated wool from 0.188 to 0.352 and TiO_2NPs-treated wool from 0.182 to 0.297 g mg^{-1} min^{-1}. This indicates the endothermic nature of the dyeing process.

It is appeared that a good agreement between the experimental and the calculated equilibrium dye uptake for the pseudo-second order kinetic model for AO74 onto wool. Also, the correlation coefficients, r_2^2, for the pseudo-second order kinetic model are between 0.965 and 1.0. It is probable, therefore, that this dyeing process fits the pseudo-second-order kinetic model.

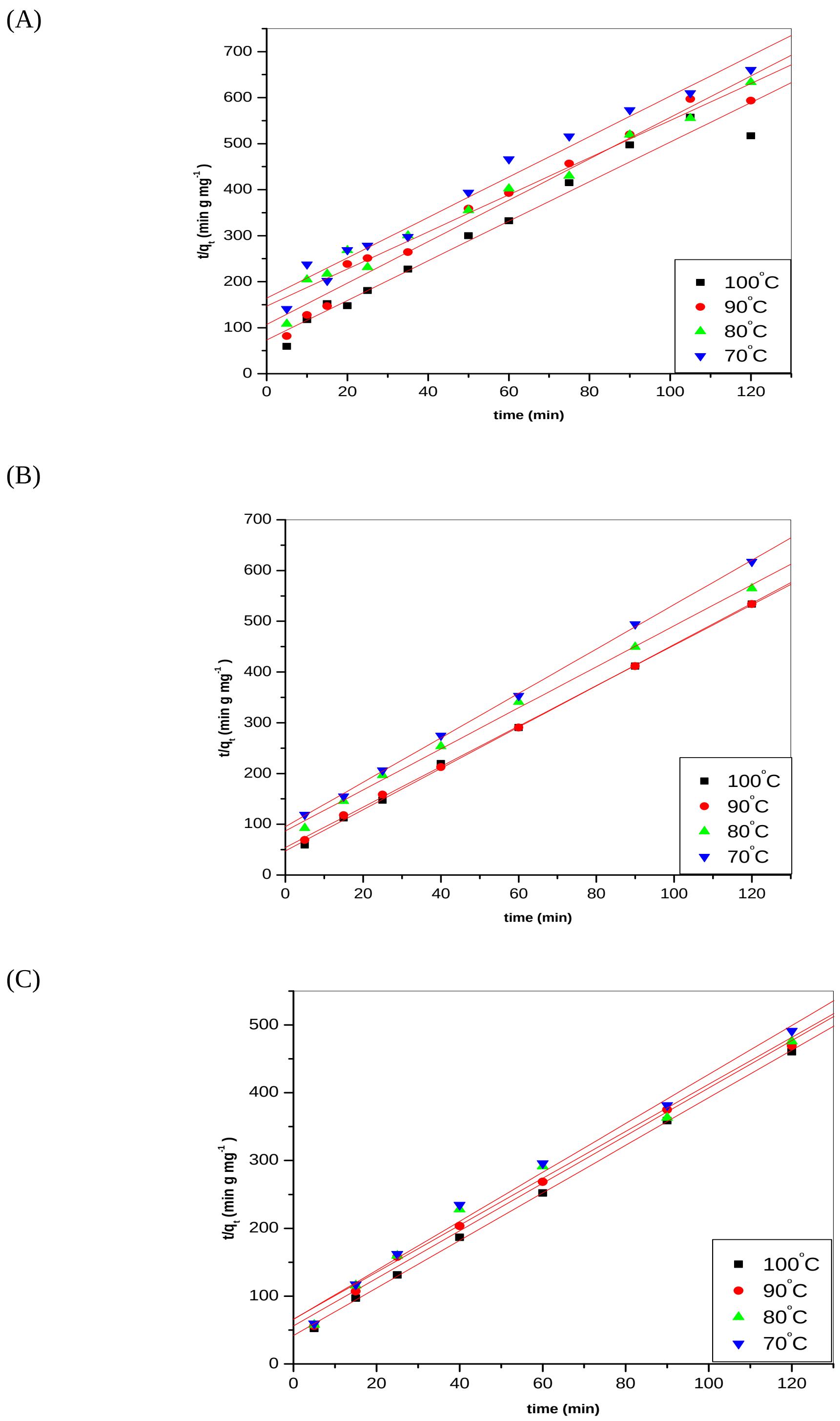


Figure 5. Pseudo-second order adsorption kinetic of AO74 onto wool fabric at various temperatures. (A)Untreated, (B) AgNPs, and (C) TiO_2NPs-treated [Dyeing conditions: 2% (owf), LR 1:50 and pH 2.6]

Table 2. Pseudo-second order adsorption kinetic parameters of AO74 onto untreated and pre-treated wool fabric at various temperatures

Wool fabric	Temp. (℃)	k_2(g mg^{-1} min^{-1})	q_e(mg g^{-1})	q_e(exp.) (mg g^{-1})	r_2^2
Untreated	100	0.252	0.232	0.212	1.000
	90	0.189	0.222	0.202	0.991
	80	0.117	0.201	0.189	0.965
	70	0.110	0.180	0.181	0.986
AgNPs-treated	100	0.352	0.245	0.234	0.999
	90	0.293	0.250	0.224	0.999
	80	0.201	0.247	0.212	0.999
	70	0.188	0.228	0.194	0.999
TiO_2NPs-treated	100	0.297	0.284	0.260	0.999
	90	0.220	0.288	0.255	0.997
	80	0.199	0.285	0.252	0.992
	70	0.182	0.276	0.244	0.994

3.5 *Diffusion Coefficient and Activation Energy of The Dyeing Process*

The physical adsorption (physisorption) or chemical (chemisorption) mechanisms are often an important indicator to describe the type of interactions between dye molecules and wool fabric. Figure 6 shows the linear relationship between ln*D* and 1/T. The increased diffusion coefficient of dye with temperature rise can be related to the wool swelling which increases the adsorption surface; the higher diffusion and consequently easier penetration of AO74 and AO74–wool interactions. It can also be explained in term of the involvement of endothermic hydrophobic interactions.

The obtained data represent that the mobility of the NPs-treated wool chains greatly increased with increasing temperature. The presence of NPs onto wool surface results in marked increase of the sorption sites number by forming salt bridges, and complex bonds that additionally increase the hydrophobic interactions between the non-polar chains of wool fabric and AO74.

The activation energy describes the dependence of the diffusion coefficient on the dyeing temperature and also represents the energy barrier that a dye molecule should have to overcome to diffuse into wool fabric. The low activation energies are characteristic for a physical adsorption (5-40 kJ mol^{-1}), while higher activation energies (40-800 kJ mol^{-1}) suggest chemical adsorption (Taher 2012). The activation energy of AO74 dyeing onto untreated wool fabric is 19.3 KJ mol^{-1} that indicates the physisorption process. The corresponding activation energies onto AgNPs-treated and TiO_2NPs-treated wool fabric were decreased by 4.1 and 47.15%, respectively. It can be explained in term of decreasing the resistance of wool fabric to the dye diffusion and the more relaxation of the NPs-treated wool fabric.

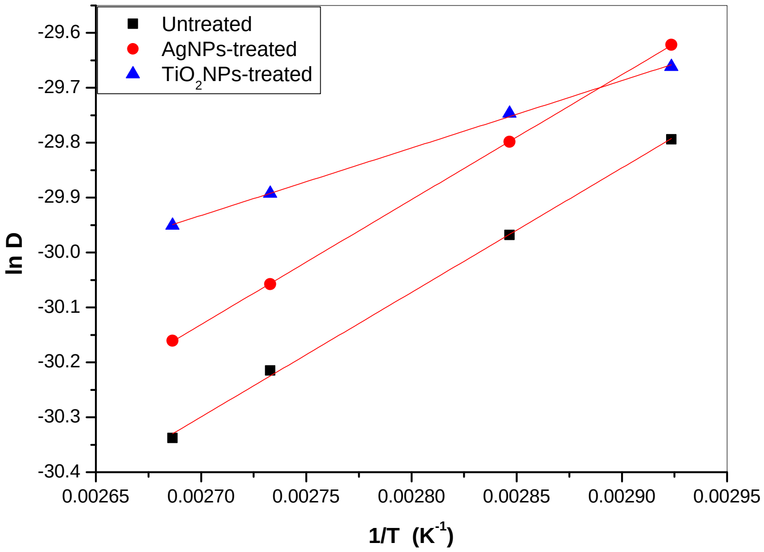


Figure 6. Relation between ln D and 1/T for AO74 adsorption onto wool fabric

3.6 Fastness Properties of NPs-treated Wool Fabric

Fastness properties of the untreated, AgNPs, and TiO_2NPs-treated dyed fabric were measured as seen in Table 3. The NPs-treated dyed wool has slightly decreased in washing and rubbing fastness of the good fastness properties of the untreated dyed wool. This might be due to the unwell-washed adhered dye particles onto wool fabric. There is no difference in perspiration and light fastness for the dyed wool fabric either untreated or NPs-treated that is in general gives very good indication.

Table 3. Fastness properties of untreated and NPs-treated dyed wool fabric

Wool fabric	Rubbing		Washing			Perspiration						Light
						Acid			Alkaline			
	Dry	Wet	St.*	St.**	Alt.	St.*	St.**	Alt	St.*	St.**	Alt	35 h
Untreated	4-5	4	4-5	4	3– 4	4	4	4	3- 4	4	4	6
AgNPs-treated	3-4	3	4	4	3– 4	4	4	4	4	4	4	6
TiO_2NPs-treated	4	2-3	3-4	4	3– 4	4	4	4	4	4	4	6

Where: St.*= staining on cotton St. **= staining on wool Alt. = Alterations on color

3.7 Antibacterial Activity of NPs-treated Wool Fabric

E. coli bacterium which causes urinary tract and wound infections is a popular test organism. *S. aureus* bacterium is a pathogenic microorganism causing many diseases such as toxic shock, fibrin coagulation, and endocarditic. Bacterial activities of untreated and the NPs-treated wool against both E. coli and *S. aureus* bacteria were calculated, Figure 7. The results demonstrate that incorporation of NPs onto wool fabric remarkably improves its antibacterial activity according to the ascending order: untreated < AgNPs < TiO_2NPs. This variance can be attributed to their differences in chemical structure, size distribution of NPs and interaction mechanism onto wool fabric during treatment process.

AgNPs antibacterial mechanism might be attributed to (1) the interaction between silver ions and phosphorous groups of DNA of bacterial cell structure; (2) the interaction between silver ions and sulfur containing amino acids of DNA; (3) DNA strand structure condensation and replication; and (4) the oxygen radical production by the silver catalyst effect of water-oxygen interaction. Consequently, the AgNPs negatively affect the electron transport chain, cell division and segregation processes, resulting in cell membrane metabolisms inhibition, cell membrane destruction and cell death.

On the other hand, the photocatalytic effect of TiO_2NPs, i.e. nano-metal oxides, is the main reason for its antibacterial activity by the production of extremely active oxygen species, e.g. super oxide anions, hydrogen peroxide, singlet oxygen, hydroxyl radicals that causes death of bacterial cell.

Moreover, the NPs-treated wool fabric showed a better antibacterial activity against G+ve bacteria in companion with G−ve due to the presence of the outer cell wall membrane in the G−ve bacteria thereby acting as a barrier to the antibacterial effect.

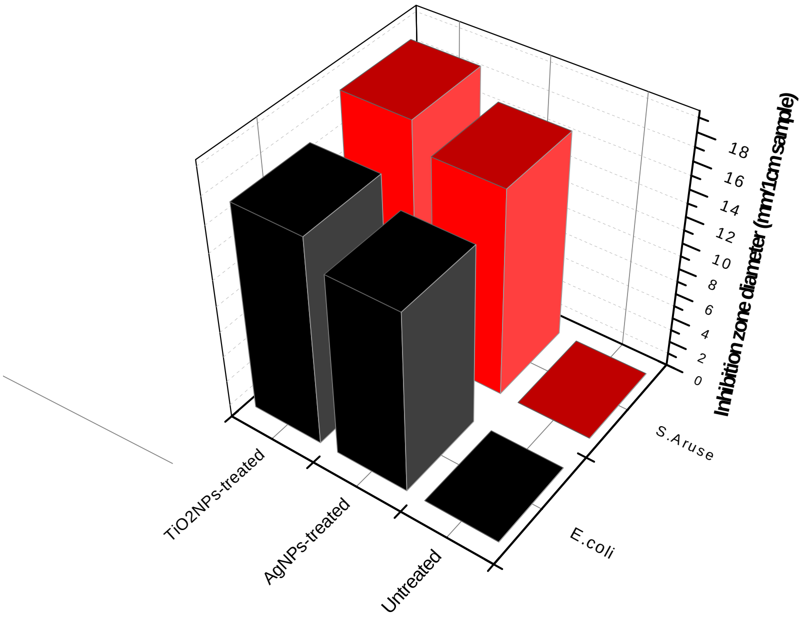


Figure 7. Inhibition zone for untreated and NPs-treated wool fabric

3.8 *Self-cleaning of NPs-treated Wool Fabric*

One of the capabilities of NPs-treated fibers is transforming the absorbed light into the self-cleaning materials to decompose its stain. Table 4 shows the effect of coffee stain on untreated and AgNPs and TiO_2NPs-treated wool fabric after 24 hours UV-irradiation.

A partial discoloration of coffee stain induced by UV-light was observed for AgNPs-treated wool fabric. The treatment of wool with AgNPs is led to the formation of thin layer AgNPs that increases its hydrophilic properties. The high degradation effect of TiO_2NPs has been appeared on the treated wool fabric. The two types of surfaces that result from treating of wool with TiO_2NPs may explain its self-cleaning ability. Both hydrophilic and hydrophobic surfaces can remove the dirt as coffee from the wool based on different mechanisms. The idea of producing hydrophobic surfaces has been developed based on Lotus effect (Stamate and Lazar 2007). A hydrophobic surface prevents the adsorption of dirt, maintaining the surface of wool clean in all the time. Conversely, on hydrophilic surfaces water droplets are spread and therefore the pollutants are removed by a stream of water existing on the surface of wool.

Table 4. Effect of stain (coffee) on untreated and AgNPs, and TiO_2NPs-treated wool fabric

Wool fabric	Self-cleaning of coffee spot
Untreated	No Removal
AgNPs-treated	(10-15)%
TiO_2NPS-treated	(70-80)%

4 Conclusion

This research was conducted to examine the effect of treating of wool fabric with AgNPs and TiO_2NPs before dyeing process on producing a functionalized wool fabric. Different concentrations of $AgNO_3$ and SBH were adopted to evaluate silver particle size and size distribution of the prepared AgNPs. Dyeing properties of AO74 and its wool fabric properties were tested to characterize the incorporation effect of NPs-treatment. Their antibacterial, photocatalytic and fastness properties were evaluated. The results showed that the TiO_2NPs-treated wool fabric dyed with AO74 exhibited excellent antibacterial and photocatalytic effect while the fastness remained unchanged. However, AgNPs-treated dyed wool fabric has very good and good antibacterial and photocatalytic effect, respectively. Also, the NPs-treatment has no significant change in fastness properties of the dyed samples.

Finally, it can be concluded that the AgNPs and TiO_2NPs pre-dyeing is a very promising, simple and practical method for obtaining dyeings with great protection properties against the harmful UV-radiation and bacteria infection without affecting the fastness properties. Further work is going to be assessed by functionalization with Ag/TiO_2 nanocomposite.

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