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Alcohol-Assisted Dyeing Processes: Dyeing and Antimicrobial Finishing of Treated Wool Fabrics with Nano-Powders C.I. Reactive Red 84

G. E. A. Mahmoud
Al-Azhar University - Faculty of Science, Chemistry Department, Nasr City, Cairo, Egypt

Abstract*— *The present study concerns the production of RR 84 in nano-powders during high energy milling. Crystallite size nano-powders characterized using TEM and UV-visible absorption property. The antimicrobial reactive dye was employed in dyeing wool fabrics treated with hydrogen peroxide which exhibited significantly higher exhaustion and fixation than untreated wool fabrics. Dyeing processes of wool were studied with the aim to substitute some auxiliary agents with ethanol at low concentration. The results observed in isothermal dyeing showed a favorable effect of alcohol addition, at about 0.0–3.0 % v/v, on the dye-uptake. The colour performance was compared for nano-RR 84 dye with that of RR 84 dye. The effects of pH, dyeing time, dye concentration and temperature were investigated. The time/dye-uptake isotherms are revealing the enhanced dye-uptake in the second phase of dyeing. The values of dyeing rate constant, half-time of dyeing and standard affinity were calculated and discussed. All the treated fabrics exhibited antimicrobial efficacy against different microbes. Fastness testing for the dyed samples was tested.

Index Terms—**Nano-reactive dye, wool fabrics, Dyeing, Ethanol, antimicrobial finishing.**

I. INTRODUCTION

Nano-particles have attracted the attention of researchers in academia and industry because of their peculiar physicochemical properties. They have large specific surface area, high chemical reactivity and physical affinity as well as interesting optical, electrical and magnetic properties. There is ongoing search for large-scale production of nanoparticles. Gas-phase synthesis and wet-phase synthesis **[1,2]** have found widespread use in practice. High energy-intensive ball milling (vibratory milling, stirred media milling, or attritors) has recently become another route for the production of submicron particles **[3,4]** as well as nanoparticles **[5-8]**. Nano-pigments are organic or inorganic substances; insoluble, chemically and physically inert into the substrate or binders, with a particle size less than 100 nm **[9]**. Although particle sizes in the 100–200 nm range are required in the current manufacturing practice, nano-pigments have recently gained a wide range of industrial applications **[10]**. For example, mica-based pigments (particle size w20 nm) with pearlescent effect are used in cosmetics, automobile coatings, plastics, etc. **[11]**. At any rate, the coloring performance of ceramic pigments depends on both optical properties, which are expected to improve in nanoparticles, and chemical stability, since the adsorption rate is expected to increase with surface area of pigment. The best compromise in conventional ceramic pigments is usually found with particle size distribution in the 1–10 mm range **[12]**. Chemical substitution is to replace process chemicals having high polluting strength or toxic properties with others that have less impact on water quality or that are more amenable to wastewater treatment **[13]**. Among the textile wet processes, the dyeing step generates wastewaters of great chemical complexity due to huge variety of fibers, dyes, process aids and finishing products **[14]**. New and tighter restrictions on discharged effluents as well as the emergence of ecolabels have led to develop ecologically advanced processes to replace the use of synthetic dyeing auxiliaries, such as wetting and swelling agents, dispersants, retardants and softeners, with products derived from natural sources **[15]**. They are environment-friendly, biodegradable and sometimes less costly. Among these, low molecular weight alcohol such as ethanol can be taken into account. In fact, it was proved that the dyeing rate is increased by alcohol absorption on wool and this effect is as higher as the alcohol solubility is lower. Recently it was suggested that the addition of benzyl alcohol increases the effective volume available for the diffusion of dyes and consequently the dye diffusion rate in the wool fiber bulk is enhanced **[16]**. However the effect of addition of water-soluble alcohols at low concentration to dyeing baths was not examined in depth. In conclusion, the introduction of alcohols in synthetic fiber dyeing has been considered until now as a particular case of solvent-assisted dyeing, while the effect of low concentrations of ethanol in water baths has not been taken into account. Recently, the use of ethanol as an additive for dyeing various textile materials was patented **[17]**. The objectives of this invention were the reduction of the dyeing times, with economic advantages in terms of increased productivity, and the decrease of environmental pollution deriving from conventional dyeing processes, allowing a more efficient utilization of the water resources. This patent has suggested the present study, which was carried out with the aim of enlightening on the functions of ethanol as dyeing auxiliary without affecting color quality and dye fastness **[18]**. Simultaneous dyeing and functional finishing of textiles offer economical and environmental advantages in textile manufacturing. Recently, many researchers have explored in this field, such as the simultaneous dyeing and durable press finishing of cotton **[19,20]**, the combination of dyeing and durable press finishing of silk **[21,22]**, as well as the simultaneous dyeing and finishing of wool **[23]**. In this paper assess both colouring performance and potential of nano-RR 84 dye which obtained from high energy-intensive ball milling in wool dyeing. It was carried out with the aim of enlightening on the functions of ethanol as dyeing auxiliary without affecting color quality and dye fastness. In standard dyeing recipes can replacing wetting, retardant and leveling agents with ethanol. Good color imitations were generally shown with respect to standard processes. Finally the environmental benefits arising from chemical substitution of auxiliary agents with ethanol were highlighted and the cost of alcohol introduction was compared with the cost saving of auxiliary substitution. A positive economic balance was obtained. The dyeing, fastness and finishing properties of treated wool fabrics using nano-RR 84 dye and RR 84 dye were thoroughly investigated. Comparative results of the dyeing kinetics of treated wool fabrics using both RR 84 and nano-RR 84 dyeing methods are also presented **[24–26]**, these functional dye will be incorporated into fabrics to provide color and antimicrobial functions simultaneously.

II. EXPERIMENTAL

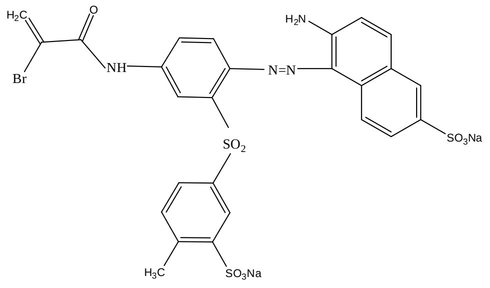
A. Materials

1. Fabrics

Mill scoured 100 % wool fabrics of 500 g/m^2 supplied by Misr Co. for Spinning and Weaving (Mehalla El-Kubra) was used. Before dyeing, the fabrics were treated in aqueous solution containing 2 g/l sodium carbonate and 5 g/l non-ionic detergent (Hostapal CV, from Clariant - Egypt) for 30 min at 50 ^{o}C, then washed thoroughly with water and dried at room temperature.

2. Dyestuffs and chemicals

The dye used in this work was reactive dye namely C.I. Reactive Red 84 (Lanasol Red 6G) kindly supplied by ICI (Imperical Chemical Industries Limited Dyestuffs Division Manchesester, England), the dye was of commercial grade and was used as received (Scheme 1).



Scheme 1. Chemical structure of C.I. Reactive Red 84 (RR 84)

Ethanol (95 % v/v), acetic acid, sodium and ammonium sulphates, sodium carbonate and silicate and hydrogen peroxide (30 %) were reagent grade products supplied by Aldrich.

B. Methods

1. Preparation of nano-powder from RR 84

The nano-powders of the using dye was prepared using RETSCH planetary ball mills Type PM 400. The dye sample was milled using the ball mill at speed 150 rpm for 6-8 h **[27].** The optical absorption spectra of samples were recorded in the UV-Vis absorption spectra Shimadzu UV/Vis, spectrophotometer.

2. Hydrogen peroxide pretreatment procedure

Prior to dyeing, all wool fabrics were pretreated for 1h at 50 ^{o}C in baths containing 0.7 % w/w sodium silicate, 0.2 % w/w sodium carbonate and 40 ml/l hydrogen peroxide (30 %) with a 25:1 liquor-to-goods ratio, then thoroughly rinsed in distilled water and air- dried in a standard atmosphere for testing (20 ± 1^{o}C and 65 ± 2 ^{o}C relative humidity) **[28]**.

3. Dyeing of treated wool fabrics using RR 84

In the alcoholic recipes retarding, leveling and wetting agents, such as Infagal, Albegal Set and Cibaflow FFW, were omitted, while ethanol was added in the range 0.0 –3.0 % v/v **[18]**.Treated wool samples (0.5 g each) were dyed with nan-RR84 and RR 84 at liquor ratio 1:50. Dyeing was carried out in presence of sodium sulphate (10.0 % owf) and ammonium sulphate (2.0 % owf) at different concentrations of dye (37.68 – 484.73 mg/l), pH values (3.51 – 7.02) adjusted by acetic acid, temperatures (40 – 80 ^{o}C), and duration time (30 – 110 min) as detailed in the text. Then the dyed samples were rinsed with cold water and washed for 25 min in a bath containing 2 g/l of non-ionic detergent (Hostapal CV, Clariant), at 45 – 50 ^{o}C. Finally, the fabrics were rinsed with water and air dried.

4. Dyeing rate

Treated wool fabric samples (4.0 g each) were cut into pieces approximately 1 cm^2 and dyed at pH 4.03 in 250 ml closed dyeing bottle with 200 ml aqueous solution composed of 75.35 mg/l from dye with liquor ratio 50:1 at 60 ^{o}C with frequent shaking. Dyeing was conducted using both nano-RR 84 powder dye and RR 84 dye. After selected time intervals, 0.5 ml of the dye bath was pipette into test tubes to measure its absorbance at λ_{max} for each.

C. Measurements

1. Dye exhaustion and fixation

Shimadzu UV/Vis spectrophotometer was used to measure the UV-Vis, absorbance of the dye solutions before and after exhaustion. The concentration of dyes was calculated based on a previously established absorbance concentration relationship at the λ_{max} of nano-RR 84 dye and RR 84 dye. Unfixed dye from the samples was extracted by hot water and also measured by the UV-Vis, spectrophotometer. The exhaustion and fixation of dye on treated wool was calculated by measuring the absorbance of the residual dyebath liquor. The percentages of dyebath exhaustion (*E%*) and fixation (*F%*) were calculated according to Equations (1) and (2), respectively.

$$E\,(\%) = [1 - (A_1/A_o)]\ x100 \qquad (1)$$

$$F(\%) = [(A_o - A_1 - A_2)/\ A_o]\ x100 \qquad (2)$$

where A_o and A_1 are the absorbance of the dye solution at λ_{max} before and after dyeing, respectively, A_2 is the absorbance of the soaped dye solution **[29]**.

2. Dye uptake

The UV/Vis, absorption spectra in water were recorded using Shimadzu UV/Vis spectrophotometer. The quantity of dye-uptake was estimated using the following Equation (3):

$$Q = (C_o - C_f)\, V/W \qquad (3)$$

Where Q is the quantity of dye-uptake (mg/g), C_o and C_f are the initial and final concentration of dye solution (mg l^{-1}), respectively, V is the volume of dye bath and W is the weight of fabrics (g). The concentration of dye solutions was determined after reference to the respective calibration curve of nano-RR 84 dye and RR 84 dye using Lambert-Beer law **[30]**.

3. Transmission electron microscope (TEM)

TEM were examined with a JEM-1010 CX (JEOL Ltd). The TEM is measured in National Center for Radiation Research and Technology and made in Japan. Examination was at 70KV.

4. Fastness testing

The dyed samples were tested to washing, rubbing and light fastness according to ATCC standard methods **[31-33]**.

5. Test organisms

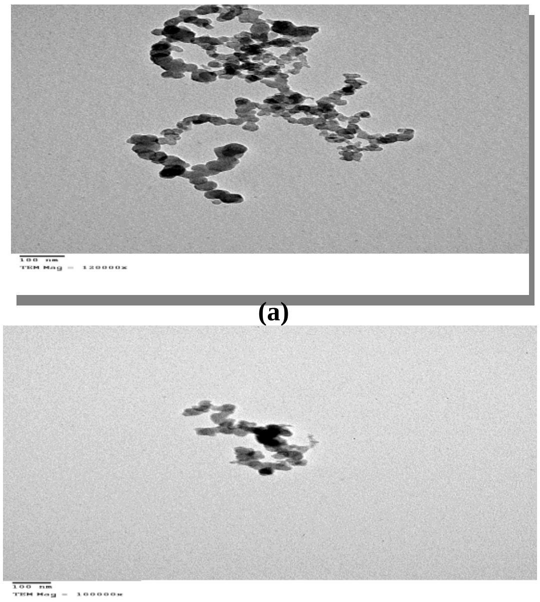
The anti-microbial properties of the nano-RR 84 dye and RR 84 dye were studied using the cup-plate agar diffusion technique **[34,35]**. The effect of the anti-microbial efficacy of the absorbed dye onto wool fabrics were assessed using the AATCC 147 test procedure **[34,36]**. This method is simple, visual and suitable for qualitative analysis of bacterial growth on incubated plates: thus, anti-microbial behavior of dyed fabrics against microorganisms used in the study: Geotricum candidum and Candida albicans (fungi); Streptococcus pneumonia and Bacillus subtilis (Gram Positive Bacteria); Pseudomonas aeruginosa and Escherichia coli (Gram negative Bacteria). Test bacteria and fungi were provided from The Regional Center for Mycology and Biotechnology, AL-Azher University, Nasr city, Cairo.

III RESULTS & DISCUSSION

A. Characterization

1. Transmission electron microscope (TEM)

TEM analysis revealed the morphology of the samples and allowed straight forward deduction of mean particle size by direct sample observation. Figure 1 (a and b) with different view shows a TEM photograph of the prepared nano-RR 84 dye nano-particles, in which it can be seen that they are all spherical, with an average size of 70 nm. The spherical dye nano-particles are aggregates and agglomerates to some extent. These aggregated nano-particles exist in cluster format. The nano-RR 84 dye with particle size in nano-scale have a massive potential market, because of their high surface area, which assures higher surface coverage, higher number of reflectance points and hence improved scattering **[2, 38]**.



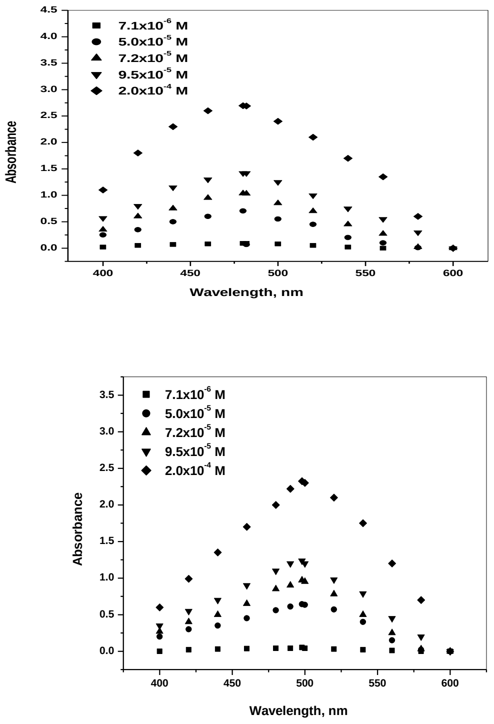
(a)

(b)

Fig 1. TEM images of nano-RR 84 dye

2. UV-visible absorption property of nano-RR 84

The UV-visible spectrum for the nano-RR 84 dye prepared using the high energy ball milling shows a narrow peak at approximately λ_{max}= 498 nm (Figure 2, curve b). Compared with the normal size RR 84 at λ_{max}= 480 nm (Figure 2, curve a), the UV-Visible absorption of uniquely nano-RR 84 dye usually shows the shift of the absorption to longer wavelengths indicating that the nano-RR 84 dye is in nano-scale **[37]**.



(a)

(b)

Fig 2. UV-visible absorption spectra: (a) RR 84 dye and (b) Nano-RR 84 dye.

B. Exhaustion and fixation of nano-RR 84 and RR 84 on untreated and treated wool fabrics

Hydrogen peroxide treatment was applied to improve the moisture transport properties, water absorbing properties and other related properties of wool fabrics **[38]**. The wicking properties of wool fabrics were dramatically increased after hydrogen peroxide treatment. Shrink proof properties were observed after the treatment as the shrinkage of treated fabrics were lower than that of untreated fabrics; this were due to the modification on the scale of wool fabrics. Whiteness of the fabrics were increased dramatically owing to the bleaching effect of hydrogen peroxide. Less than 4% weight loss was also noticed after the treatment and the fabrics became a little weaker and flexible **[39]**. Dyeing properties of the untreated and treated wool fabrics with nano-RR 84 dye and RR 84 dye were investigated. The exhaustion and fixation of nano-RR 84 dye and RR 84 dye on untreated and treated wood fabrics are summarized in Table 1. It indicates that the exhaustions and fixations of nano-RR 84 dye and RR 84 dye on the treated wool fabrics were significantly higher than those of them on the untreated fabrics. Generally, the hydrogen peroxide treated wool fabrics exhibited significantly higher exhaustion and fixation than untreated wool fabrics and nano-RR 84 dye exhibited higher exhaustion and fixation than RR 84 dye. Hydrogen peroxide pretreatment partly destroys the scale-like structure of wool and improves the uptake of reactive dyes.

Table 1. Dyeing properties of the dyed treated and untreated wool fabrics using nano-RR 84 dye and RR 84 dye. Dyeing conditions: treated wool fabrics 0.5 g, L.R. 1:50, 1.0 % v/v ethyl alcohol, pH 4.03, 60 ^{o}C, salts and dye concentration 75.35 mg/l at 60 min.

Dye samples	Untreated fabric		Treated fabric with H_2O_2	
	E (%)	F (%)	E (%)	F (%)
RR 84	69.11	60.51	89.32	82.91
Nano-RR 84	75.61	70.54	98.20	96.67

C. Dyeing of treated wool fabrics with nano-RR 84 and RR 84

1. Factors affecting dyeing process

1.1. Effect of ethyl alcohol

In standard dyeing recipes wetting, retardant and leveling agents can be replaced with ethanol. Good color imitations were generally shown with respect to standard processes. The environmental benefits arising from chemical substitution of auxiliary agents with ethanol were highlighted and the cost of alcohol introduction was compared with the cost saving of auxiliary substitution. A positive economic balance was obtained. Wool dyeing with reactive dyes is critical since the high affinity of these dyes makes their migration into the fabrics difficult; hence retarding and leveling agents such as Albegal Set are required **[18]**. In alcoholic recipe Albegal Set was substituted with ethanol (0.0 – 3.0 % v/v) in presence of salts and acetic acid for dyeing treated wool with nano-RR84 dye and RR 84 dye yielded satisfactory results in the presence of 1.0 % v/v of ethanol (Figure 3). Therefore ethanol can be introduced in dyeing recipes to replace less biodegradable surfactants without affecting the dyed product quality. Such chemical substitution is supported by environmental benefits as well as by cost savings, confirming the validity of the invention patented by **[40]**.

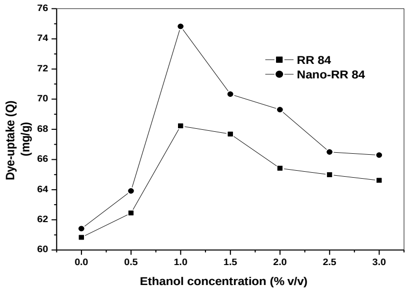
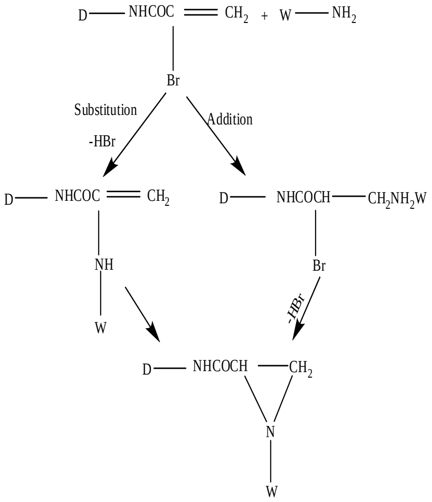


Fig 3. Effect of ethyl alcohol (0.0 – 3.0 % v/v) on the dye-uptake of the dyed treated wool fabrics using nano-RR 84 dye and RR 84 dye. Dyeing conditions: treated wool fabrics 0.5 g, L.R. 1:50, pH 4.03, 60 ^{o}C, salts and dye concentration 75.35 mg/l at 60 min.

1.2. Influence of pH

pH is an important factor that controls the sorption of dye from aqueous solutions on to fabrics. Therefore, the pH effect on the sorption of nano-RR 84 dye and RR 84 dye on treated wool was studied in the pH range of 3.51 – 7.02. The pH of dye solution was adjusted by acetic acid solution. The variation of dye-uptake with pH of the solution is shown in Figure 4. It is obvious from this figure that maximum sorption of dye on treated wool occurred at pH values of 4.03. Scheme 2 show the wool fabrics react by nucleophilic substitution and nucleophilic addition mechanism via the Br and C=C reactive groups **[41]**. This helps to explain why the dye-uptake value was shown to be pH dependent and more favorable in the range of pH 4.03. Figure 4 shows the dye-uptake for dyed samples using nano-RR 84 dye and RR 84 dye. It can be seen that the dye-uptake exhibit gradual increasing with increasing the pH of the dyeing bath up to pH 4.03 and then decreases as the pH increases, with improvement in the dyeability in case of the nano-RR 84 dye.



Scheme 2. Reaction mechanism between Lanasol reactive dye and wool.

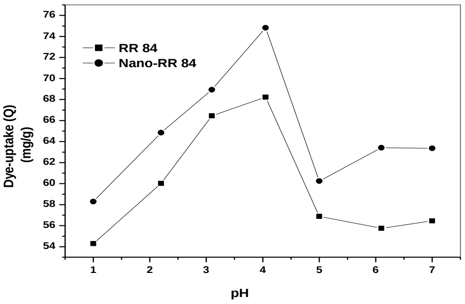


Fig 4. Effect of pH (3.51 – 7.02) on the dye-uptake of the dyed treated wool fabrics using nano-RR 84 dye and RR 84 dye. Dyeing conditions: treated wool fabrics 0.5 g, L.R. 1:50, 1.0 % v/v ethyl alcohol, 60 ^{o}C, salts and dye concentration 75.35 mg/l at 60 min.

1.3. Effects of shaking time

Investigations were conducted to ascertain the time required for maximum sorption of nano-RR 84 dye and RR 84 dye on treated wool. This study was carried out at different shaking time (30 – 110 min) and fixed concentration of dye (75.35 mg/l). As shown in Figure 5, the dye-uptake obtained was increased as the time of shaking increased for both dye forms on treated wool, with a much higher uptake value at any dyeing time in the nano-RR 84 dye case.

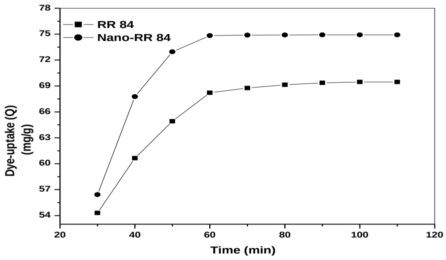


Fig 5. Effect of shaking time (30 – 110 min) on the dye-uptake of the dyed treated wool fabrics using nano-RR 84 dye and RR 84 dye. Dyeing conditions: treated wool fabrics 0.5 g, L.R. 1:50, 1.0 % v/v ethyl alcohol, pH 4.03, 60 ^{o}C, salts and dye concentration 75.35 mg/l.

1.4. Effects of temperature

The effect of temperature on the dye ability of the treated wool fabrics dyed with 75.35 mg/l concentration of nano-RR 84 dye and RR 84 dye at different temperatures (40 – 80 ^{o}C) was investigated. As shown in Figure 6, it is clear that the dye-uptake values increase with increasing in the dyeing temperature with a more pronounced increase in case of the nano-RR 84 dye than the RR 84 dye. The increased sorption of dye with rise in temperature can be related to the structure of the wool; diffusion of the dye and dye–wool interactions. As the temperature increases, the pores of the wool fabrics enlarge results in the increased surface for the sorption, the diffusion and penetration of dye molecules within the pores of the wool becomes easier and increased sorption. It can also be explained in term of the involvement of endothermic hydrophobic interactions. Wool fabrics are swollen by polar solvent such as water; there are additional hydrophobic interactions between the non-polar chains of the macromolecules. Such interactions also occur between the non-polar chains of dyes and the macromolecules. The macromolecular structure in case of wool opens up as a result of lyses of salt bridges, hydrogen bonds and hydrophobic interaction thus markedly increased the number of sorption sites; thus resulting high values of sorption for dyes with increasing temperature **[42]**.

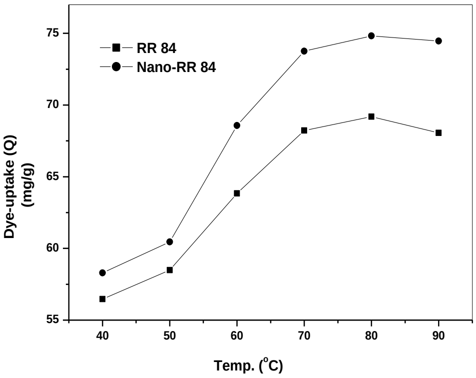


Fig 6. Effect of temperature (50 – 80 ^{o}C) on the dye-uptake of the dyed treated wool fabrics using nano-RR 84 dye and RR 84 dye. Dyeing conditions: treated wool fabrics 0.5 g, L.R. 1:50, 1.0 % v/v ethyl alcohol, pH 4.03, 60 ^{o}C, salts and dye concentration 75.35 mg/l at 60 min.

1.5. Effect of dye concentration (dye shade)

The dye-uptake of nano-RR 84 dye and RR 84 dye on treated wool was studies as a function of dye concentration. This study was performed in the concentration range from 75.35 to 484.73 mg/l for dye. From Figure 7, it was found that the dye-uptake for the dyed fabrics using nano-RR 84 dye structures is higher than the dye-uptake using RR 84 dye. First the uptake values of dyed fabrics using the nano-RR 84 dye structure are higher than their corresponding mates produced by the RR 84 dye. The size of RR 84 dye with wool fabrics play significant role in deciding the extent of the sorption process. The dye concentration affected the diffusion of dye molecules through the solution to the surface of the adsorbent. Higher concentration resulted in higher driving force of the concentration gradient. This driving force accelerated the diffusion of dyes from the solution into the adsorbent **[43]**.

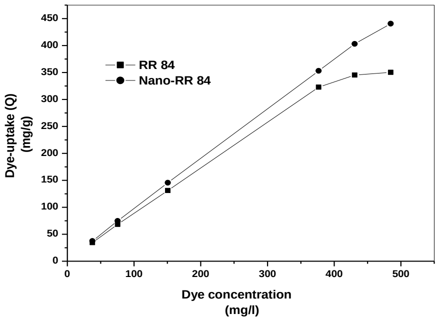


Fig 7. Effect of dye concentration (37.68 – 484.73 mg/l) on the dye-uptake of the dyed treated wool fabrics using nano-RR 84

dye and RR 84 dye. Dyeing conditions: treated wool fabrics 0.5 g, L.R. 1:50, 1.0 % v/v ethyl alcohol, pH 4.03, 60 °C, and salts at 60 min.

D. Kinetics of dyeing [44,45]

It is known that the rate of any process means a change in one of the starting materials that takes place in the process or the product that obtained per unit time. Applying this definition in the dyeing process can be regarded as the change in the dye-uptake per unit time. Time dye-uptake isotherms of treated wool fabrics dyed with nano-RR 84 dye and RR 84 dye are shown in Figure 8. The figure shows that the dye-uptake values of nano-RR 84 dyed samples are generally higher than those obtained from RR 84 dye. The isotherms of both methods started to be differentiated from each other to show better dye-uptake for nano-RR 84 dye in comparison with RR 84 dye. The data in Figure 8 can be analyzed by using the derivable general form of the first order rate Equation (4)

$$(A_t - A_f) / (A_o - A_f) = e^{-kt} \quad (4)$$

where At is the absorbance at time t, Ao is the initial absorbance, Af is the final absorbance, t is the reaction time and k is the reaction rate. Since the absorbance of solution is directly related to the concentration by Lambert-Beer law, therefore, Equation (4) can be rewritten in terms of dye-uptake to give Equation (5)

$$(Q_t - Q_f) / (Q_o - Q_f) = e^{-kt} \quad (5)$$

where Qt is the dye-uptake at time t, Qo is the dye-uptake at zero time, and Qf is the final dye-uptake, t is the dyeing time and k is the dyeing rate. Taking the logarithm of Equation (5) would lead to Equation (6) and since Qf is known, Qt _ Qf can be calculated

$$\ln |Q_t - Q_f| = \ln |Q_o - Q_f| - kt \quad (6)$$

A plot of ln |Qt _ Qf| vs. time is expected to be linear with a slope of _k and an intercept of ln |Qo _ Qf| if the reaction is first order. The time of half dyeing t1/2, which is the time required for the fabrics to take up half of the amount of dye taken at equilibrium, is estimated either from each isotherm directly and/or from the following equation:

$$t_{1/2} = \ln 2 / k \quad (7)$$

A plot of ln |Qt _ Qf| versus t (min) results is a linear graphical relation indicating the applicability of the above model for nano-RR84 and RR84 as shown in Figure 8 The values of k calculated from the slope and t1/2 are listed in Table 2. The observed linear relationship is statistically significant as evidenced by the r values (which are close to unity).

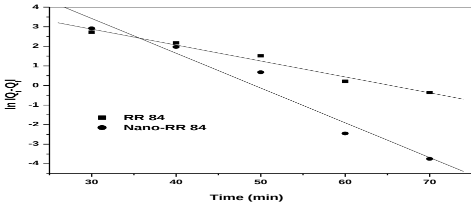


Fig 8. Plots of ln $|Q_t - Q_f|$ versus time of dyeing of treated wool fabrics by using nano-RR 84 dye and RR 84 dye. Dyeing conditions: treated wool fabrics 0.5 g, L.R. 1:50, 1.0 % v/v ethyl alcohol, pH 4.03, 60 °C, salts and dye concentration 37.68 mg/l at 70 min.

E. Standard affinity [46]

It is well established that dyeing of most fabrics is a thermodynamically reversible process. Therefore, it is permissible to apply thermodynamic functions to the dye fabrics system. In a dye fabrics system, dye distributed in both the fabrics and the dyebath. The data for dyeing equilibrium are generally reported as the standard affinity of dyeing, _Δμ. Therefore, the standard affinity can be calculated using Equation (8)

$$-\Delta\mu = RT \ln [C]_f/[C]_s \quad (8)$$

where R is the gas constant, T is the absolute temperature (K), Cf and Cs are dye concentrations in the fabrics and the dyebath, respectively. On dyeing, _Δμ is termed as the standard affinity and is a measure of the tendency of the dye to move from its standard state in the dyebath onto the fabrics [47]. The data (Table 2) also indicate that the _Δμ values for RR 84 in nano-scale is higher than RR 84 dye, and thus higher fixation is observed than those of RR 84 dye in normal size.

Table 2. Dyeing rate constant K, time of half dyeing $t^{1/2}$, standard affinity $-\Delta\mu$ and amount of final dye up-take for treated wool fabrics using nano-RR 84 dye and RR 84 dye. Dyeing conditions: treated wool fabrics 0.5 g, L.R. 1:50, 1.0 % v/v ethyl alcohol, pH 4.03, 60 °C, salts and dye concentration 75.35 mg/l at 70 min.

Dye samples	k (min^{-1})	-Δμ (KJ/mol)	$t^{1/2}$ (min)	Q_f (mg/g)
RR 84	4.13×10^{-2}	16.77	16.78	68.76
Nano-RR 84	8.75×10^{-2}	21.92	7.92	74.88

F. Color fastness

The Table 3 shows the fastness tests of washing, light and rubbing of samples that had been dyed with nano-RR 84 dye and RR 84 dye. Dyeing at L.R. 1: 50, pH = 4.03, 1.0 % v/v ethyl alcohol, salts, dye concentration 430.12 mg/L, temperature 60 °C, and time 1h. As shown in Table 3, the fastnesses are excellent to very good indicating the existence of strong bonds between the dye molecules and the fabrics (ionic ionic bonds for reactive dye) and the best results obtained were from those nano-RR 84 dye **[31-33]**.

Table 3. Fastness properties of nano-RR 84 and RR 84 dye on treated wool.

Sample	Washing			Rubbing		Light fastness 35 h
	Alt. change colour	Staining on cotton	Staining on wool	Dry	Wet	
RR 84 on fabrics	4-5	4-5	4-5	4-5	4-5	7
Nano-RR 84 on fabrics	5	5	5	5	5	7

Light fastness: 1- poor 2- slight 3- moderate 4- fair 5- good 6- very good 7- excellent
Wash & Rubbing: 1- poor 2-fair 3- good 4- very good 5- excellent

G. The antimicrobial results

The antimicrobial efficacy of the dyed treated wool fabrics was studied. Initially, the microbes growth were observed on undyed wool fabrics, whereas the microbes growth were inhibited onto the dyed treated wool fabrics, as shown in Figure 9. The growth of selected microbes, Geotricum candidum and Candida albicans (fungi); Streptococcus pneumonia and Bacillus subtilis (Gram Positive Bacteria); Pseudomonas aeruginosa and Escherichia coli (Gram negative Bacteria), on treated wool fabrics were categorized depending on whether a zone of inhibition of microbes were observed on the agar gel or whether microbes growth were observed only on wool fabrics. A zone of inhibition of bacteria on the agar slope indicated that biocide had eluted from the fabrics, which dyed with these nano-RR 84 dye and RR 84 dye into the agar as shown in Figure 9. Ideally, no microbes growth should be observed on the fabrics. Thus, a no growth category represents ideal anti-bacterial efficacy; that is, no bactericide elutes into the bulk of the agar but no bacteria growth is observed on wool fabrics. The results obtained from the antimicrobial effects indicated that nano-RR 84 dye and RR 84 dye exhibited variable activities against the microbes used (Table 4 and Figure 10). It is believed that these phenomena may be explained by the antimicrobial mechanism of the dye forms. It has been reported that quaternary ammonium salts (QAS), the active antimicrobial component of the dyes, kill microorganisms by disturbing their cytoplasmic membranes **[36]**. Based on the above, it may be concluded that dyeing of treated fabrics with nano-RR 84 dye have excellent antimicrobial effect which could be ascribed to particle size in nano-scale have a massive potential market, because of their high surface area, which assures higher surface coverage, higher number of reflectance points and hence improved scattering. In paint formulations, for example, the small particle size allows uniform dispersion by homogenous mixing with binders, which enhances the mechanical strength of the paint after drying. When properly dispersed, the nano-sized pigments exhibit superior effectiveness also in critical abrasive and polhing application **[38]**.

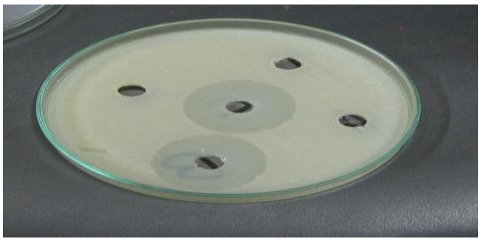


Fig 9. Zone of inhibition of microbes for nano-RR 84 dye and RR 84 dye on treated wool leached from fabrics and observed on agar plate.

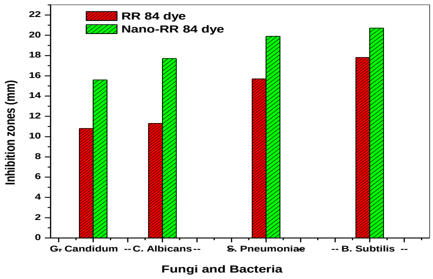


Fig 10. Antimicrobial activity for nano-RR 84 dye and RR 84 dye on treated wool.

Table 4. Zone of inhibition for nano-RR 84 dye and RR 84 dye on treated wool against selected microbes

Acrylic fabrics	Zone of inhibition (diameter in mm)					
	FUNGI		Gram-Positive Bacteria		Gram-negative Bacteria	
	Geotric m candidu m (RCM 05097)	Candid albican (RCM 05031)	Streptoc cus pneumor ae (RCM 010010)	Bacillis subtili (RCM 01006	Pseudom as aeruginos (RCMB 010043)	Escheric a coli (RCMB 010052)
Untreated Treated	NA	NA	NA	NA	NA	NA
RR 84 on fabrics	10.8 ± 0.32	11.3 ± 0.24	15.7 ± 0.24	17.8 ± 0.21	NA	NA
Nano-RR 84 on fabrics	15.6 ± 0.15	17.7 ± 0.18	19.9 ± 0.31	20.7 ± 0.28	NA	NA

IV. CONCLUSION

Wool fabrics treated with hydrogen peroxide and dyed by the antimicrobial RR 84 dye forms in lower ethanol concentration (1.0 % v/v) can used as leveling and retarding agents: good color imitations were obtained with homogeneous dye distribution. Nano-powder dye proved prepared using RETSCH planetary ball mills effectiveness in the dye-uptake of treated wool fabrics than dye in normal size.

The nano-dye with particle size in nano-scale has a massive potential market, because of their high surface area, which assures higher surface coverage, higher number of reflectance points and hence improved scattering. This technique in addition to its advantage of saving the processing time and energy offers better environmental impact as it helps much in improving dye-uptake. As expected, the nano-RR 84 dye on treated wool fabrics give higher antimicrobial activity and fastness properties than RR 84 dye. In addition, dye sizes may also play an important role in the wool dyeing, smaller dye may diffuse faster into the fabrics, while the larger ones may diffuse slower.

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