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# DYEING BEHAVIOUR OF TREATED WOOL WITH SOME METAL IONS

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## Abstract

Interaction of metal ions with wool is currently studied. The absorption of some metal ions such as copper, iron, cobalt, nickel and aluminum by wool from their aqueous salt solutions is investigated. The treatment conditions such as temperature of treatment and the pH values of metal salt solutions are interpreted. The effect of pretreatment of wool with some di- carboxylic acids on the metal uptake by wool is given. The influence of these absorbed metal ions on the dyeing properties of wool is investigated. The mechanical properties, alkali solubility, fastness properties as well as kinetic investigation on the dyeing process are also investigated.

**Keywords:** wool, metal ions, treatment, modification, interaction, absorption, copper, iron, aluminum, nickel, cobalt, salt solutions, dyeing, kinetic, diffusion, acid dye, fastness.

## Introduction

Wool fibres were treated with variety of metal salt solutions useful in different applications. These applications and the gained properties of the treated wool depend on the type of metal ion, its concentration, temperature of treatment and pH value of the treatment solution. Free carboxyl groups of wool are considered the most likely bonding sites over a wide pH range [1]. The possibility of inducing useful changes in the fibre properties by metal ions treatment was previously studied [2]. McLaren and Milligan [3] showed a comprehensive description of metal-wool interactions and their effects on improving the dyeability, wrinkle recovery, shrinkage, abrasion and flame resistance of wool. Fukatsu [4-6] studied the reaction of wool with copper ions. More recently, the tendency of wool fibres to remove the heavy metal pollutants from industrial effluents was studied [7].

The treated silk with metal ions was found to have some improvements in its properties such as yellowing resistance to Ultra Violet irradiation, dyeability and antimicrobial activity [1, 8]. Wool and silk were pretreated with ethylene di-amine tetra acetic di-anhydride (EDTA) to increase the absorption of metal ions such as silver, copper and cobalt. The treated wool fibres with metal ions were found to have higher antimicrobial and deodorization activities [9-13]. Also, silk was treated with tannic acid or EDTA subsequently treated with copper and cobalt solutions at alkaline pH value[14]. The interactions of chromium salts with wool have been studied for their industrial importance in chrome dyeing. Sodium or potassium dichromate was used. The dichromate could be applied before dyeing (chrome mordant method), after dyeing (after-chrome method) or at the same time with dyeing (meta-chrome method)[15-18].

It is aimed in this work to study the absorption of some metal ions such as copper, iron, aluminum, cobalt and nickel by wool. Studying of the treatment conditions such as temperature of treatment and the pH values of the metal salt solutions was included. The effect of pretreatment of wool with some di-carboxylic acids on the amount of metal uptake was compared. A systematic comparative study on the influence of these metal ions on the dyeing properties of wool with both acid and reactive dyes as well as the fastness properties is tried. Tensile properties and alkali solubility of both untreated and treated wool fabric as well as kinetic investigation of the dyeing process are given.

## Experimental

Materials

Wool fabric: white Merino wool light fabric from Misr Company for Spinning and Weaving, Mehalla, Egypt was used. The wool fabric was preliminarily scoured in a solution containing 2g/l nonionic detergent (Egyptol PLM, based on nonyl phenol ethoxylate) at 40°C for 15 minutes.

The used metal salts were aluminum sulphate, copper sulphate, ferric chloride, cobalt sulphate and nickel sulphate. Acetic, nitric, sulphuric, adipic, succinic, oxalic and maleic acids of commercial grades were used. Commercial dyes such as C.I. Acid Blue 221, C.I. Acid Red 41, C.I. Acid Orange 19 and C.I. Reactive Red 21 were used.

*Wool Treatments*

Metal salt solutions of concentrations 1.5 % (o.w.f.) were prepared by dissolving metal salts in distilled water. The initial pH values of the different solutions were adjusted by sulphuric acid to pH 1.5- 6. Wool samples were immersed in the metal salt solutions and then heated at various temperatures (40° and 60°C) for 30 min. The wool samples were then removed, rinsed, and dried at ambient conditions.

Other wool treatments were carried out by treating firstly the wool samples with 0.03 M of some organic acid solutions using a liq. ratio 1:50 at 75 °C for 90 min. Wool samples were then removed from the treatment solutions, thoroughly rinsed and allowed to dry at ambient conditions, then dried in an oven at 105ºC to attain constant weights. The dry weights of wool samples were determined before and after treatment. The acid-treated wool samples were then treated with 3 % (o.w.f.) metal salt solutions at 60°C for 30 min. All treated samples were washed in a soap solution at 60ºC for 30 min several times before subjecting to atomic absorption analysis.

***Measurements***

*Metal Uptake*

The amount of metal uptake was determined by atomic absorption technique (ICP plasma 400 of Perkin Elmer). Wool samples of 5-20 mg were digested with 2 ml of 65 % nitric acid solution at 95º C for 60 min. One ml of hydrogen peroxide was added and then subjected to further heating for 60 min. The mixtures were adjusted to 10 ml with distilled water and then subjected to atomic absorption analyzer. Average result of the duplicate tests was evaluated [(19)].

*Increase in Weight*

The increase in weight (weight gain) of wool fibres treated with organic acids (oxalic, maleic, succinic and adipic acids) was calculated as a percentage of the difference between the dry weight of the wool samples before and after treatment.

*Alkali Solubility*

Alkali solubility of untreated and treated wool fibres with metal salts was carried out. The alkali solubility % was estimated as reported elsewhere [(20)].

*Tensile Strength and Elongation at Break*

The tensile strength and elongation at break were determined according to Justify ASTM procedure D- 2296-66T [(19, 21)].

*Dyeing*

The untreated and treated wool fabrics with metal salts were dyed by the exhaustion technique using liq. ratio of 1:50. Dyeing was performed at 75°-95˚C for different time intervals up to 120 min. The pH value of the dyebath was adjusted to

4.5 by adding acetic acid. After dyeing, the samples were washed and rinsed several times with water, squeezed and air dried at room temperature. The original bath and the exhausted one were subjected to spectrophotometeric analysis to estimate the amount of dye taken by wool using Jenna 6405 UV/Vis. Spectrophotometer, U. K.

*Colour Measurements*

The spectral reflectance measurements of the dyed fabric were carried out using a recording filter spectrophotometer (model ICS Texicon Ltd., Kennetside Park Newbarge, Berkshire AG 145TE, U. K.). The colour intensity expressed as K/S values of the dyed samples was determined by applying the Kubelka-Munk equation[(22)].

*Colour Fastness*

The washing colour fastness (alteration and stain) was measured according to the AATCC test method 61-1075 using a laundrometer. Evaluation of the washing fastness was given using the Gray Scale reference for colour change [(23)].

**Results and Discussion**

*Metal Uptake*

Wool fabric was treated with copper sulphate and ferric chloride solutions (1.5% o.w.f.) at 40° and 60° C for 30 min. After treatment the samples were rinsed carefully to remove solid metals deposited on wool due to formation of metal hydroxide [(12)], and then the metal uptake was estimated. The effect of starting pH value of the salt solution on the acquired uptake of copper and iron by wool is illustrated in Fig. 1. It can be noticed that the metal uptake increases linearly and strongly for both copper and iron in the range of pH value 3-6 and 1.5-3.5 respectively. Increasing the temperature from 40° to 60°C led to an increase in the amount of metal uptake but the rate was considered to be almost the same or slightly changed.

The metal uptake by protein fibres could be enhanced by chemically modifying the fibre with chelating agents able to coordinate metal ions. It was found that treatment of wool and silk with tannic acid and EDTA increases the metal uptake by wool and consequently increase the weight gain [(9, 10)]. Wool was pretreated with oxalic, maleic, succinic and adipic acids at 75°C for 90 min. There was a weight gain in wool accompanied to these di-carboxylic acids treatments. The % increase in weights of wool was 3.6, 3.2, 2.6 and 2.5 for wool pretreated with the aforementioned organic acids respectively. In a previous work [(13)], this increases in weights was found to correspond the increase in the carboxyl content of wool from 421.7 meq/100 g fibres for untreated one to 622.1, 530.5, 457.3 and 425 meq/100 g fibres for pretreated wool with the aforementioned acids respectively. Although these increase in the carboxyl content which are positive sites for accessibility of metal ions [(1)] the metal uptake by wool increases only for wool pretreated with oxalic acid as shown in Table 1. Other acids pretreatment did not enhance the metal uptake property. This may be due to the large molar volume of these acids which may restrict the penetration of metal ions into wool [(13)].

*Mechanical Properties and Alkali Solubility*

The elongation %, tensile strength at break and alkali solubility of untreated and treated wool with metal salts solution at 60 ºC are illustrated in Table 2. The results indicate that nearly no changes in the mechanical properties of treated wool were noticed. Treated Wool with metal salts has approximately the same tensile strength and alkali solubility values as the untreated one. It is well known that the tensile properties of wool could be affected negatively during dyeing process especially at high temperature [(24)] that may require using of protective agents. This treatment makes it possible to dye wool at lower temperature as will be discussed later and reflects on more protection of wool from damage during dyeing process, besides this treatment does not damage wool (Table 2).

*Dyeability*

Four steps could be envisaged in the process of dye uptake: a) diffusion to the fibre surface, b) transfer across the surface, c) diffusion within the fibre to appropriate sites and d) bonding at those sites [(25)]. Various algebraic expressions have been derived from Fik's laws of diffusion in an attempt to describe experimental dyeing rates. Almost it comes to parabolic rates [(25)]. The equilibrium for the dye-wool interaction can be separated into the following

$$W\text{-}NH_3^+.OCC\text{-}W + Dye \rightleftharpoons W\text{-}NH_3^+.\,^-Dye + {}^-OCC\text{-}W$$

$$H^+ + {}^-OCC\text{-}W \rightleftharpoons H.OCC\text{-}W$$

Probably the rate of the second step would be fast and thus the first step would be the rate determining. Combining the metal ions with carboxyl group led to increasing the reaction in the forward direction and consequently increasing the rate of dyeing.

The effect of treatment of wool with copper sulphate on a reactive dye uptake in relation to the time of dyeing is illustrated in Fig. 2. The dyeing process is performed at different dyeing temperatures (75º-95ºC). It can be seen that the dyeing behaviour of the treated wool with copper ions was enhanced and directly proportional to the time and the temperature of dyeing as well as the treatment temperature.

The dyeing behaviour of pretreated wool with copper sulphate towards the acid dye was examined and illustrated in Figs. 3 and 4. The dyeing was proceeded at 85ºC for different time intervals up to 120 min. using C.I. Acid Red 41 (Fig. 3). It can be shown that the dyeability of wool with acid dye was found to be improved by this treatment especially at the early stage of dyeing. It was also found that the dyeing behaviour is temperature of treatment dependent and consequently is metal uptake dependent at the aforementioned applied treatment conditions. Fig. 4 represents the dependence of dye uptake of pretreated wool with copper sulphate on the time of dyeing with C.I. Acid Blue 221 at different temperatures. The dyeability of pretreated wool was markedly enhanced at all applied dyeing temperatures (75º, 85º and 95 ºC). Approximately complete dye exhaustion was noticed for fabric pretreated with copper ions after about 40 min. of dyeing at 95ºC compared to about 90 % exhaustion after 120 min. of dyeing for untreated one. That may reflect on saving energy consumption and reducing the pollution effects in the dyeing process.

The effect of treatment of wool with iron and aluminum ions in the form of ferric chloride and aluminum sulphate on the wool dyeability with acid dye was carried out. The results were represented in Figs. 5 and 6. Both aluminum and iron salts were found to improve wool dyeability with acid dyes at different dyeing temperatures (75º, 85º and 95 ºC).

The effect of treatment of wool with copper sulphate on the colour intensity of dyed wool with C. I. Acid Blue 221 in relation to time of dyeing was shown in Fig. 7. It was noticed that there is an enhancement in the colour intensity of dyed pretreated wool with copper ions. Matching Fig. 7 with Fig. 4 to compare the dye taken by wool and the acquired colour intensity shows that the same colour intensity of untreated wool after dyeing with C. I. Acid Blue 221 for 120 min at 95 ºC ( K/S = 7.6) could be attained after shorter dyeing time for pretreated wool as well as lower temperature. These times were observed to be 30 and 20 min for pretreated fabric at 40º and 60ºC respectively. The same colour intensity of untreated fabric could be attained by pretreated one at lower dye consumption (1.8 g dye/ 100 g fibre for untreated compared to 1.77 g dye / 100g fibre for treated one). This may be due to the slight blue shade acquired by wool after treatment with copper sulphate which consequently reflects on the colour intensity. It would be useful to use different metals that contribute different colours reflecting on decreasing dye consumption.

Pretreatment of wool prior the metal treatment with some organic acids such as oxalic, maleic, succenic and adipic was examined in relation to the wool dyeability with acid dye. The results are illustrated in Table 3. It was found that pretreatment with the aforementioned acids enhances the wool dyeability. Pretreated wool with oxalic acid followed by treatment with copper or nickel sulphate led to nearly complete exhaustion of dye from the dyebath after 30 min at 95ºC compared to 90 % exhaustion for untreated one dyed for 60 min. at the same temperature.

*Fastness Properties*

Both alteration (alt.) and staining (st.) washing fastness properties of dyed wool with acid dye at 95ºC were found to be good. The washing fastness was found to be 4 (alt.) and 4-5 (st.) for untreated wool dyed with C. I. Acid Blue 221 compared to 4-5 and 5 for treated wool with both aluminum and copper sulphate. The colour fastness of treated wool with cobalt and nickel sulphate dyed with C. I. Acid Red 41 was found to be the same for untreated and treated fabric (4-5 for alt. and st.). These values were evaluated by 4 (alt. and st.) for treated fabric with ferric chloride dyed with C. I. Acid Orange 19 compared to 3-4 (alt. and st.) for untreated one.

*Kinetic investigation*

Kinetic investigation on the wool dyeing process was estimated [22]. The half dyeing time ($t_{1/2}$), dyeing rate constant (k') and diffusion coefficient (D) were determined and given in Table 4. It was found that the dyeing rate constant and the diffusion coefficient increased by the aforementioned treatment while the half dyeing time decreased.

Table 1: Effect of pretreatment of wool with some organic acids on its tendency for metal uptake

| Wool Samples | Metal uptake (mg/100 g wool) | | |
|---|---|---|---|
| | Copper | Cobalt | Nickel |
| -Treated with metal salts | 262.0 | 154.6 | 180.5 |
| -Pretreated wool with: | | | |
| Oxalic acid | 366.0 | 172.1 | 196.71 |
| Maleic acid | 157.1 | 21.9 | 44.3 |
| Succenic acid | 150.4 | 11.0 | 19.2 |
| Adipic acid | 129.2 | 8.2 | 19.9 |

Treatment: 0.03 M organic acid/100 g fibre, 75 °C, 90 min., liq. ratio 1:50, 3 % (o.w.f.) metal salt, 60 °C, 30 min., liq ratio 1:30

Table 2: Tensile strength, elongation % at break and alkali solubility of treated wool fibre with metal salts

| Type of Sample | Elongation % | Tensile Strength (Kg) | Alkali Solubility |
|---|---|---|---|
| 1-Untreated wool | 26 | 41.5 | 8.82 |
| 2-Treated wool with: | | | |
| -Aluminum sulphate | 25 | 45.5 | 8.67 |
| -Copper sulphate | 20 | 37.5 | 8.23 |
| -Ferric chloride | 22 | 43.5 | 8.42 |
| - Cobalt sulphate | 21 | 41.6 | 8.81 |
| - Nickel sulphate | 21 | 42.0 | 8.80 |

Treatment: 1.5 % (o.w.f.) metal salt solution; 30 min., pH 3.5; liq. ratio 1:30.

**Table 3: Dyeability of pretreated wool fabric with some organic acids followed by metal treatment**

| Type of Samples | Dye uptake (g dye / 100 g fibre) | | |
|---|---|---|---|
| | Cobalt sulphate | Nickel sulphate | *Ferric Chloride |
| Treated wool | 1.89 | 1.9 | 1.92 |
| Pretreated wool with: | | | |
| - oxalic acid | 2.0 | 2.0 | 1.96 |
| -Maleic acid | 1.99 | 2.0 | 1.96 |
| -Succenic acid | 1.94 | - | - |
| - Adipic acid | 1.96 | - | - |

Treatment: 0.03 M organic acid/100 g fibre, 75 °C, 90 min., liq. ratio 1:50, 3 % (o.w.f.) metal salt, 60 °C, 30 min., liq ratio 1:30. Dyeing: 2% (o.w.f.) C.I. Acid Red 41, * C. I. Acid Orange 19, 95ºC, 30 min, pH 4.5, liq. ratio 1: 50.

**Table 4: Half dyeing time ($t_{1/2}$)**, dyeing rate constant (k') and diffusion coefficient (D) of untreated and treated wool with metal salts.

| Type of Sample | $t_{1/2}$ min | k' x $10^{-4}$ $(cm/sec)^{1/2}$ | D x $10^{-7}$ $cm^2\ sec^{-1}$ |
|---|---|---|---|
| - Untreated wool and dyed at: | | | |
| 75˚C | 14.5 | 4.976 | 2.7611 |
| 85˚C | 13.3 | 6.01 | 2.8151 |
| 95˚C | 9.0 | 8.12 | 3.5684 |
| - Treated wool with aluminum sulphate at 40˚C and dyed at: | | | |
| 75˚C | 12.2 | 7.417 | 2.7914 |
| 85˚C | 11.1 | 8.08 | 2.9277 |
| 95˚C | 7.8 | 9.901 | 4.2467 |
| - Treated wool with aluminum sulphate at 60˚C and dyed at: | | | |
| 75˚C | 10.0 | 8.487 | 3.0113 |
| 85˚C | 8.9 | 9.343 | 3.2365 |
| 95˚C | 6.7 | 10.954 | 4.5914 |
| - Treated wool with *copper sulphate at 40˚C and dyed at: | | | |
| 75˚C | 9.3 | 17.3 | 3.5014 |
| 85˚C | 8.4 | 18.762 | 3.638 |
| 95˚C | 7.4 | 20.692 | 4.1716 |
| - Treated wool with *copper sulphate at 60˚C and dyed at: | | | |
| 75˚C | 8.8 | 18.1288 | 3.6961 |
| 85˚C | 8.2 | 19.6198 | 3.6427 |
| 95˚C | 6.5 | 22.3721 | 4.6041 |
| - Treated wool with **ferric chloride at 40˚C and dyed at: | | | |
| 75˚C | 12.3 | 6.668 | 3.0978 |
| 85˚C | 11.7 | 7.754 | 3.2777 |
| 95˚C | 8.6 | 9.3165 | 4.3088 |
| Treated wool with **ferric chloride at 60˚C and dyed at: | | | |
| 75˚C | 11.7 | 7.1703 | 3.1014 |
| 85˚C | 10.5 | 8.2731 | 3.3779 |
| 95˚C | 8.0 | 9.7906 | 4.5258 |

Treatment: 1.5 % (o.w.f.) metal salt solutions, 30 min, pH 4.5, **pH 3.5, liq. ratio 1: 30.
Dyeing: 1% (o.w.f.), * 2% (o.w.f) C.I. Acid Blue 221, pH 4.5, liq. ratio 1: 50.

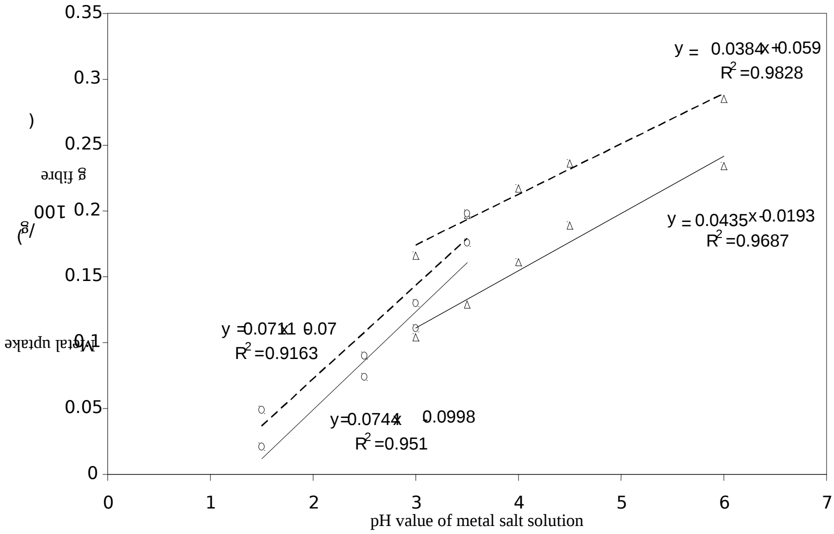


**Fig. 1: Dependence of metal uptake by wool on the pH value of its solution at different temperatures.**

Treatment: 1.5 % (o.w.f), Δ-Δ copper sulphate, o-o ferric chloride, _____40º C, _ _60 ºC, 30 min, liq. ratio 1:30.

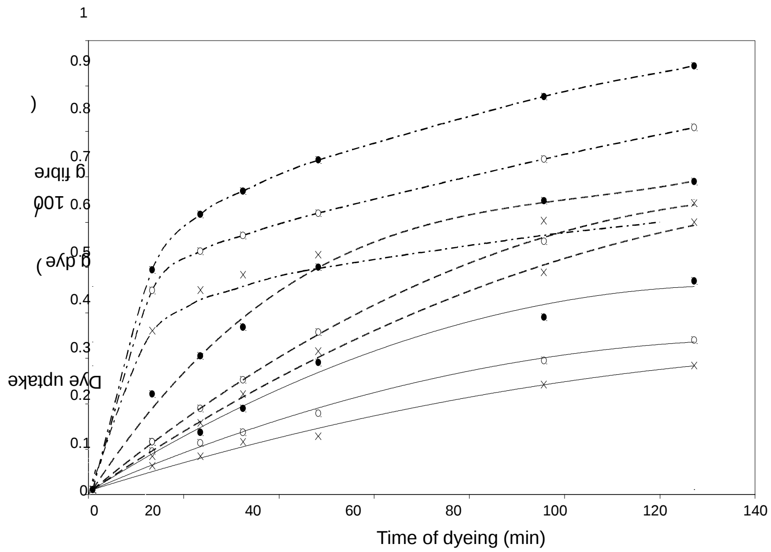


**Fig 2: Effect of time of dyeing with reactive dye on the dye uptake of pretreated wool fibre with copper sulphate.**

Treatment: 1.5 % ( o.w.f.) Copper sulphate, 30 min., pH 4.5, liq. ratio 1:30
x-x untreated wool , o-o treated wool at 40ºC , ●-● treated wool at 60ºC.

Dyeing: 1% (o.w.f.) C.I.Reactive Red 21, pH 4.5, liq. ratio 1:50, ___75°C, _ _85°C, — · —95°C

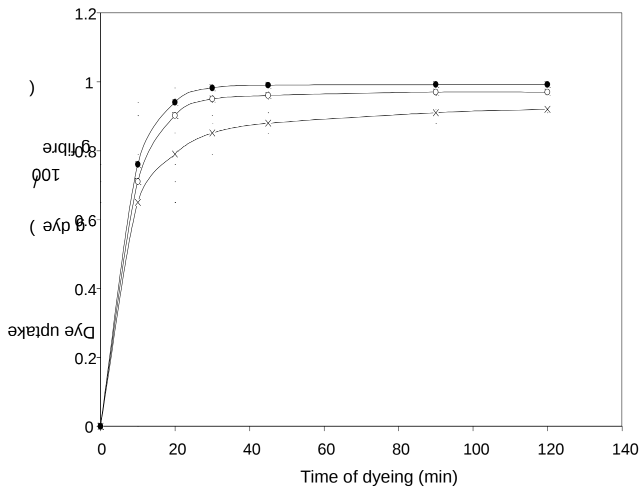


**Fig.3: Effect of time of dyeing with acid dye on the dye uptake of pretreated wool fibre with copper sulphate.**

Treatment: 1.5 %(o.w.f.) Copper sulphate, 30 min., pH4.5, liq. ratio 1:30

x-x untreated wool , o-o treated wool at 40ºC , ●-● treated wool at 60ºC.

Dyeing: 1 %(o.w.f.) C.I. Acid Red 41, 85°C, pH 4.5, liq. ratio 1:50

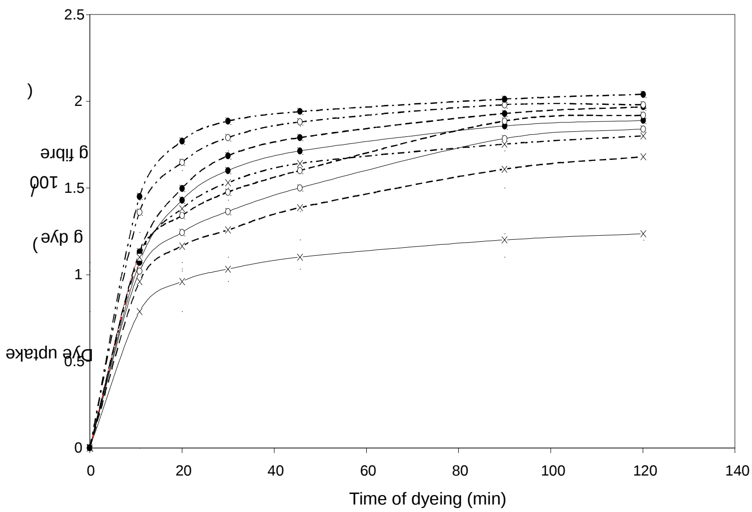


**Fig.4: Effect of time of dyeing with acid dye on the dye uptake of pretreated wool fibre with copper sulphate at different temperatures.**

Treatment: 1.5 % (o.w.f.) Copper sulphate, 30 min., pH4.5, liq. ratio 1:30

x-x untreated wool , o-o treated wool at 40ºC , ●-● treated wool at 60ºC.

Dyeing: 2 % (o.w.f.) C.I. Acid Blue 221, pH 4.5, liq. ratio 1:50 ___75º C, _ _ 85ºC,− · − 95ºC

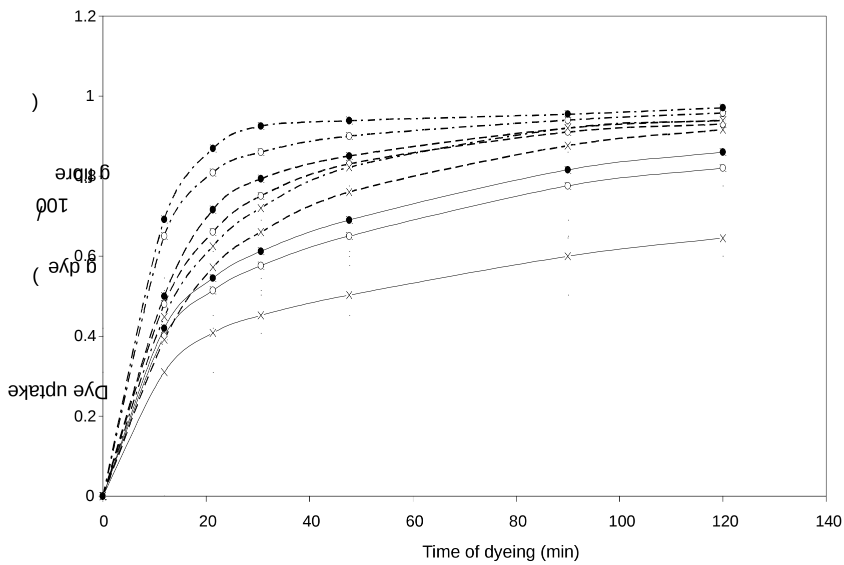


**Fig 5: Effect of time of dyeing on dye uptake of pretreated wool fabric with ferric chloride at different dyeing temperatures.**

Treatment: 1.5 % (o.w.f.) ferric chloride, 30 min, pH 3.5, liq. ratio 1: 30,

x-x untreated wool , o-o treated wool at 40ºC , ●-● treated wool at 60ºC.

Dyeing: 1% (o.w.f.) C.I. Acid Blue 221, pH 4.5, liq. ratio 1: 50, ____75º C,_ _ 85ºC,−·− 95ºC

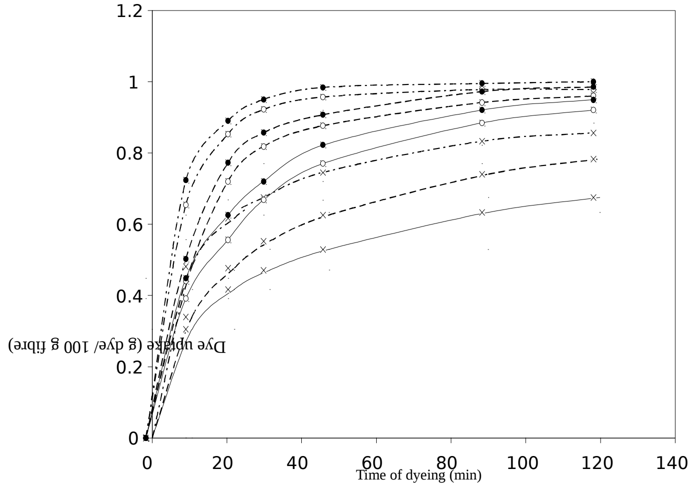


**Fig.6: Effect of time of dyeing on dye uptake of pretreated wool fabric with aluminum sulphate at different dyeing temperatures.**

Treatment: 1.5 % (o.w.f.) aluminum sulphate, 30 min, pH 4.5, liq. ratio 1: 30,

x-x untreated wool , o-o treated wool at 40ºC , ●-● treated wool at 60ºC.

Dyeing: 1% (o.w.f.) C.I. Acid Blue 221, pH 4.5, liq. ratio 1: 50, ___75º C, _ _ 85ºC,−·− 95 ºC

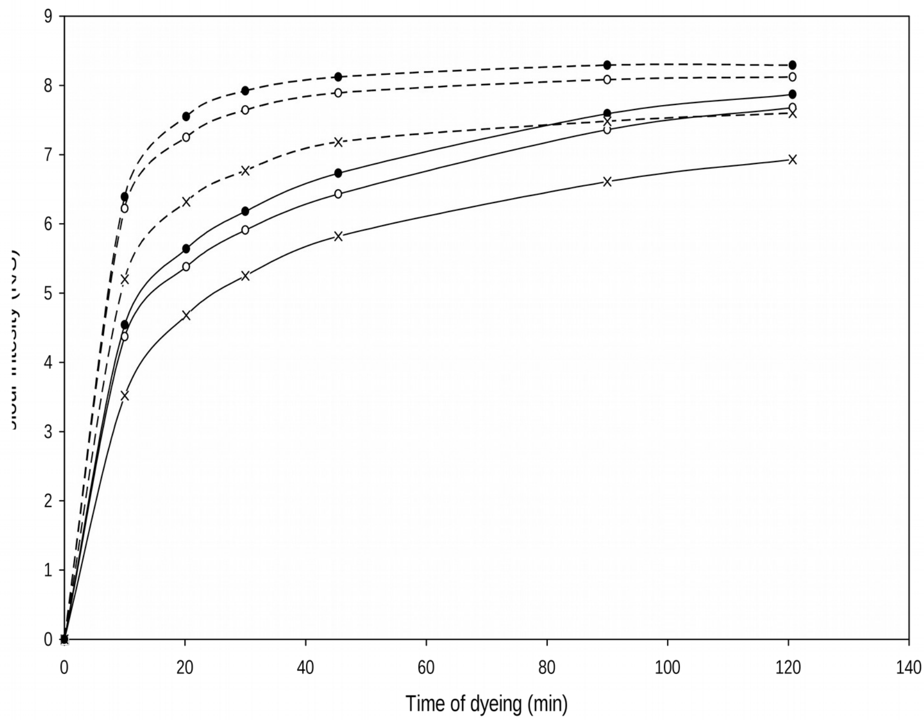


**Fig.7: Effect of time of dyeing with acid dye on the colour intensity of pretreated wool fibre with copper sulphate at different temperatures.**

Treatment: 1.5 % (o.w.f.) copper sulphate, 30 min., pH4.5, liq. ratio 1:30

x-x untreated wool , o-o treated wool at 40ºC , ●-● treated wool at 60ºC.

Dyeing: 2 % (o.w.f.) C.I. Acid Blue 221, pH 4.5, liq. ratio 1:50

_____85º C, _ _ 95ºC

## Conclusion

Wool has an accessibility to take metal ions from its salt solutions. The metal ions uptake by wool was found to be a function of the pH value. The influence of these acquired metal ions (copper, iron, aluminum, cobalt and nickel) on the dyeability of wool with both reactive and acid dyes was investigated. The dyeability of wool with acid dye is markedly enhanced in the form of dye uptake and colour intensity as well as fastness properties. Kinetic investigation of dyeing process showed an increase in the dyeing rate constant and the diffusion coefficient and a decrease in the half dyeing time. These results may reflect on saving energy consumption in the dyeing process with keeping the good quality of dyed wool.

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