Effect of Ozone Treatment on the Dyeing Properties of Mulberry and Tassar Silk Fabrics

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ABSTRACT
Ozone treatment has been carried out on silk fabrics and changes in the properties of the fabrics were reported recently. Further extending the work, in the present study, the dyeing studies of ozone treated mulberry and tassar silk fabrics were carried out using CI Acid Red 88. This type of study has not been carried out before. The results are quantified and expressed in terms of the dye uptake (DU), Equilibrium dye uptake (EDU) and half dyeing time ($_{t1/2}$). It has been found that the ozone treatment reduced the DU of silk fabrics irrespective of whether they were in a raw or degummed state. The DU was found to be the highest at pH 12. At other pH levels, it was lower and the DU increased as the pH increased from 4 to 7. The lowest DU of ozone treated fabrics was found to be 50% wet pickup (WP) compared to 10% and 100% WP. The higher the treatment time (TT), the lower the DU. the EDU of the treated mulberry and tassar silk materials were lower than the untreated materials.

Keywords: silk; acid dye; dye uptake; half dyeing time; Equilibrium dye uptake.

INTRODUCTION
The variance in the dyeing properties of different fibers has resulted in the production of a number of dyes by manufacturers. Though these dyes vary widely in chemical constitution, they possess similar dyeing properties within each range. For example, the acid dyes are more suitable for silk and wool, and the direct and vat dyes are more suitable for cotton and so on.

Dyeing and printing makes it possible to bring out the high-quality colors and shades on silk leading to an increased value for silk materials. Silk offers a wide range of possible colors covering almost the entire spectrum of colors and hues, because the nature of silk makes it easily dyed. The exceptional capacity to absorb moisture from the air, the comparatively simple and orderly arrangement of fibroin molecular structure, and the abundance of hydrogen and electrostatic bonds render silk fiber, an ideally suited substrate, with a very good dye affinity. Anionic dyestuffs, namely acid and direct dyes, form a 'Dye-Fiber' complex by electrostatic and hydrogen bonds. Silk can also be dyed with basic, metal-complex and reactive dyes. Acid dyes are widely used for dyeing silk. Using this class of dyestuff, a wide range of bright colors can be obtained. These dyes are composed of sodium salts of organic acids (mostly sulphonic acid) and are applied from an acidic medium.

It was found that the silk yarn and dye interact through complicated intermolecular actions generating a variety of intermolecular forces along with an ionic bond between them. The effects of dyeing time, temperature and pH of the dye bath on the adsorption of Acid violet 5B on tassar (Antheraea yamamai) and mulberry silk (Bombyx mori) were [1] reported. It was found that a difference in the dye adsorption by these fibers exists. They applied Langmuir and a non-ionic type of adsorption isotherms and an affinity constant of non-ionic type were found to be 0.586 and 0.534 for tassar and mulberry silk respectively. In terms of the color fastness to alkaline perspiration, the fibers showed no difference.

A study on the dyeing properties of the silk fibers spun by silkworms reared on artificial and mulberry leaf diets was reported [2]. The study was carried out on the raw and degummed states of silk fibers. The silk reared on an artificial diet had 26.0% sericin content whereas the other one had 23.7% sericin content. The results showed that the dye uptake of the former was higher than the latter, and the dyeing rate of the latter was found to be higher than the former. In the case of the degummed samples, the silk reared on artificial and mulberry leaf diets showed a similar equilibrium dye uptake and rate of dyeing. The authors have also described the isotherms for the raw and degummed samples. The isotherm for sericin was obtained mathematically from the above isotherms.

The dye uptake of sericin was found to be 3-4 times higher than the respective degummed samples. The silk reared on an artificial diet showed a 20% higher dye uptake than the silk reared on a mulberry leaf diet.

Researchers have known since 1785, the year in which Van Marum observed the formation of this gas in an electric spark discharge in oxygen, that Ozone is a highly active, allotropic form of oxygen. Schoenbein recognized ozone in 1840 as a new substance. Soret showed in 1866 that the chemical composition of ozone is that of triatomic oxygen [3] Ozone is relatively unstable and, hence, undergoes dissociation. It has powerful oxidizing and bleaching action as well.

Ozone reacts directly on organic matter to form carbonyl groups by acting as a dipole agent on >C=C< bonds, an electrophilic agent on aromatic compounds to form ring hydroxylated products and a nucleophilic agent on >C=N- bonds. Ozone converts objectionable compounds to unobjectionable reaction products during the water treatment [4].

A study on the action of the ozone on the chemical modifications of cellulose, namely cotton, jute and flax, and animal fibers, namely wool and silk, reported that, in the presence of water, silk fibers are powerfully attacked by ozone. They also become acidic and sticky and, on drying, are yellowish, harsh and without lustre [5].

A study on the progressive action of ozone on different kinds of cellulose, namely normal cellulose, mercerized cellulose, hydrocellulose, oxy cellulose and fibrous cellulose triacetate, and the influence of water content and temperature on the oxidation of cellulose were reported [6]. In the presence of water, ozone strongly attacked cellulose and modified cellulose to form products, which reduced their volume and had a comparatively small affinity for methylene blue. The action of the ozone on cellulose therefore resembles that of oxidizing agents, which work in an acidic solution. It was also reported that the dry ozone had very little action on dry cellulose. The extent of oxidation, both for normal and mercerized cellulose, was very small when the water content was below 15%, but rose rapidly with an increase of water content and reached a maximum, in both cases, at about 45-50% of water. The influence of the temperature at a constant water content of 55% showed that the rate of oxidation increased with the rising temperature, but the solubility of ozone and, possibly the hydration of the hydroxyl group, was diminished. The second factor counteracted the first at 40° C. The reactivity of the ozone rose with the temperature up to 40° C and then decreased. Another study [7, 8] was awarded a patent for bleaching cotton with ozone. Various systems were also developed to shrink resist wool fabrics, garments with the ozone-steam process.

In one report [9, 10], a single stage process, steam is mixed with ozone enriched air or oxygen and passed through or over a fabric. In this system, the steam had the following four functions: It caused liquid water, needed for optimum, rapid treatment, to condense on the wool; it increased the reaction rate by elevating the gas temperature to about 65-85°C; the reaction times were from 2- 10 minutes, depending on the ozone concentration and the fabric structure; it made a pre-wetting stage and it eliminated the final drying stage. Wool treated under this process had an excellent shrink resistance and improved dyeability; in some cases, the yarn tensile strength was also increased.

A study [11] reported on the modified shrink resist process, in which garments are continuously moved through an open-ended funnel; the ends are sloped downwards to confine the hot gases. In this process, the ozone was injected at the centre, so that nearly all of it was consumed during its movement towards the ends. This system claimed the following advantages; No pre-wetting or post drying stages were required; it was a continuous, single stage process; excellent, uniform shrinkage control was attained without significantly impairing fiber properties, and treatment costs were low.

Dye uptake is a very sensitive index of fiber irregularity, which may happen between different batches of fiber or occur due to uneven pre-treatment processes. The problem is more acute with yarn formed from continuous filaments if the variation in the chemical constitution or physical property occurs. The dyeing rate determines the magnitude of inequalities in dye distribution throughout the fiber mass. In order to better understand, the dyeing process was carried out under suitable conditions and the amount of dye on the fiber or remaining in solution was estimated at intervals using a suitable method. The results were commonly expressed in terms of the percentage of the exhaustion of the bath, which was the percentage of the dye originally present adsorbed on the fiber at the given time.

The time/adsorption curves of the above type gives a better understanding of the properties of individual dyes or to help compare and select dyes of similar properties. Curves of this shape, in which an initially rapid reaction tends asymptotically towards an equilibrium position, were of common occurrence and may be described in terms of two factors, namely equilibrium position and the rate at which equilibrium was achieved. In order to give numerical values to this rate, a parameter called 'half dyeing time' was used. This was the time required for the fiber to adsorb half as much dye as it will absorb in the equilibrium state.

The literature survey revealed that though a number of studies were carried out on the dyeing behavior of both mulberry and tassar silk fibers in raw and degummed states, studies on dyeing behavior of ozone treated silk fabrics have not been carried out by researchers. Therefore, an elaborate work was carried out to understand the effect of the ozone treatment on the properties of mulberry and tassar silk fabrics and the results have been reported and published [12, 13]. In addition to the previous study, and to understand dyeing behavior of the ozone treated silk fabrics, a study has been conducted for ozone treated mulberry raw (MR), Mulberry degummed (MD), Tassar raw (TR) and Tassar degummed (TD) silk fabrics, using an Acid fast red A (C.I. Acid red 88) and the results were expressed in terms of Dye uptake (DU), Equilibrium dye uptake (EDU) and Half dyeing time ($t_{1/2}$).

EXPERIMENTAL

Materials

Commercial grade plain woven silk fabrics were used. Mulberry silk fabric, 100x88 yarns/cm, 22-denier single yarn in warp and weft and 40g/m^2, and tassar silk fabric, 80x65 yarns/cm, 30-denier untwisted single yarn in warp and weft and 45g/m^2 were used. All the chemicals, namely sodium carbonate, tartaric acid, hydrogen peroxide (35% w/v) and formic acid, used in the various experiments were laboratory grade reagents and supplied by Qualigens Fine Chemicals Limited, India. Glauber's salt (Na_2SO_4. 10 H_2O) and soap solution, commercial grade agents, were used. An enzyme, namely Silkenz DGM, used was supplied by Rossari Biotech Pvt. Limited., India. A dye, namely Acid fast red A (C. I. Acid Red 88) having a molecular weight of 400.4 ($C2OH_{14}N2O_4S$•Na) and λmax at 505.2 nm, was supplied by Atul Limited, India. The commercial dye sample was used as received. The structure of the dye used is given in *Figure 1*.

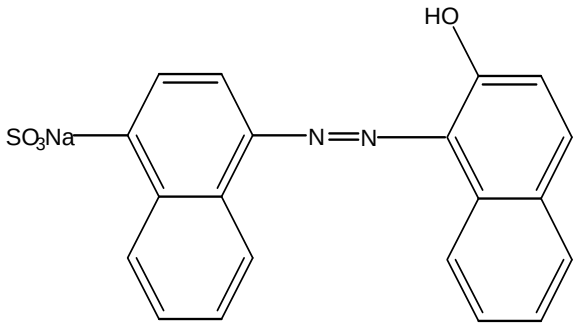

FIGURE 1. Chemical Structure of Acid fast Red A (C.I Acid Red 88).

Methods

Fabric Preparation and Ozone Treatment

The preparation of the raw and degummed mulberry and tassar silk fabrics, using soap and treatment by te ozone (with apparatus), were reported earlier [12, 13]. To explain briefly, Ozone treatment was carried out as follows: Fabric strips cut in the warp direction with various Wet pick up (WP) levels (10, 50, and 100%), and the pH (2, 4, 6, 7, 8, 10, and 12) were vertically hung inside the applicator of the ozonation apparatus and the treatment time of (TT) 10, 20 and 30 min was used to carry out the treatment. A concentration of 60 g/m^3 of ozone, with a flow of 0.5 L/min, was used. The treated materials were washed with water and then soaked at 85°C, for 10 minutes, using 2 g/L solution followed by washing, drying, and conditioning.

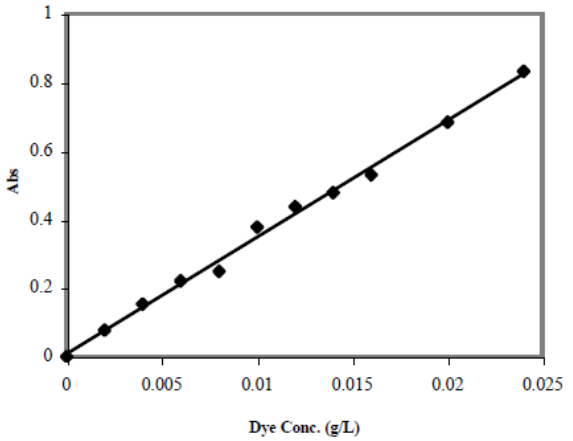

FIGURE 2. A standard calibration curve for Acid fast red A (C.I. Acid Red 88).

Studies on Dyeing

A standard calibration curve was prepared by plotting the absorbance against the dye concentration (*Figure 2*). The correlation coefficient was found to be 0.99. The values were determined using a Hitachi UV-vis Spectrophotometer U-3210. The prepared and ozone

treated mulberry and tassar silk fabrics were used to carry out studies on dyeing properties.

Determination of DU

The dye bath was prepared using the necessary quantity of dye required for the production of 2% (o.w.f) shade using a liquor ratio of 80:1. The pH of the bath was adjusted to 3.5 with a formic acid. Pre-wetted material was introduced in the above dye bath at 40ºC for 15 minutes. The temperature of the dye bath was gradually raised to 85°C for another 15 minutes. 5% Glauber's salt (o.w.f) was added in two installments during the process. The dyeing was continued for another 30 minutes, and the material was removed and washed thoroughly with distilled water. The collected wash liquor was added to the dye bath in order to account for an unfixed dye in the material. The DU of the dyed fabrics was determined using the following formula.

$$\% \text{ DU} = [(A-B)/ A] \times 100 \quad (1)$$

where,

A - absorbance value of initial concentration of the dye bath and

B - absorbance value of final concentration of the dye bath.

Determination of EDU and $t_{1/2}$

Pre-wetted material was introduced in a 0.15 g/L dye solution at 40ºC taken in a reflux condenser. Agitation in the solution was achieved with the help of a magnetic stirrer and the temperature of the dye bath was raised to 60°C for 10 minutes. A 0.5ml dye solution was removed from the dye bath every 5 minutes until 30 minutes had passed and then every hour up to 24 hours. The DU of the fabrics was determined. Plots were prepared between DU (%) and the time (minutes) and the EDU of the fabrics was determined after confirming that the curve had become parallel to the x-axis. From these curves, t1/2 values were found out by determining the time taken for 50% of EDU.

RESULTS AND DISCUSSION

Effect of Ozone Treatment on DU

The DU control samples of the raw and degummed mulberry silk fabrics were found to be 94.6% and 89.2%, whereas the raw and degummed tassar silk fabrics were 88.3 and 82.6% respectively. The DU of the raw silk fibers was higher than that of the degummed silk fibers because of the higher DU by sericin [2, 14]. The DU (% reduction) of the ozone treated raw and degummed mulberry and tassar silk fabrics are given from *Figures 3-5*.

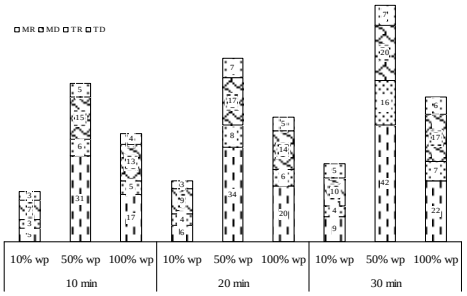

FIGURE 3. Effect of ozone treatment at pH 4 and various WP and TT levels dye uptake of silk fabrics.

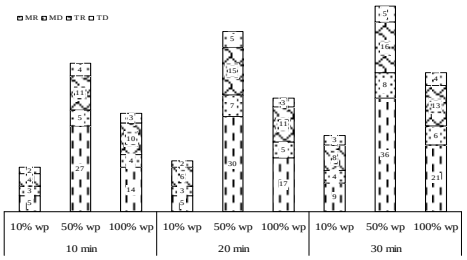

FIGURE 4. Effect of ozone treatment at pH 7 and various WP and TT levels dye uptake of silk fabrics.

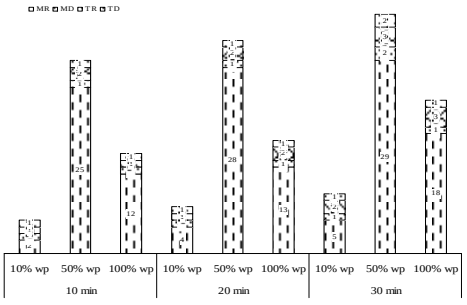

FIGURE 5. Effect of ozone treatment at pH 12 and various WP and TT levels dye uptake of silk fabrics.

The ozone treated raw and degummed silk fibers also showed that the DU was higher in raw silk than the degummed silk fabrics. Both the silk fibers, irrespective of whether they were in a raw or degummed state, resulted in reduction in DU at all the process variable combinations used due to the ozone treatment. This above behavior of treated fabrics is explained below.

In the dyeing of silk with acid dyes, the dye anion bonds with NH_3^+ radicals produced from NH_2 groups, which are available at the side chains and terminals of the silk molecules and the bulk of the dye adsorption occurs at the side chains [15]. It was found from the results that the ozone treatment

resulted in an increase in the amino group content of the raw and degummed mulberry and tassar silk fabrics [12, 13]. Hence, the introduction of the amino groups in the silk during the ozone treatment should have resulted in an increase in DU. On the contrary, the treatment resulted in a reduction in DU, which indicated that the dye absorbing sites in the side chains were affected and the reaction seemed to be complex. The reduction in DU may also be due to the attack of ozone in the non-protonated free amino (NH_2) group [16] present in the silk. Further, it could be observed from the figure that the process variables (pH, WP and TT) used in the treatment play an effective role in the DU of both the raw and degummed mulberry and tassar silk fabrics. The DU increased when the pH used in ozone treatment was increased from 4 to 12 .This kind of behavior of the DU of treated fabrics depended on the ozone decomposition at various pH was reported earlier [12, 13] and the following points were considered for this study:

At pH 4, ozone acted on the silk having the following structure [15].

$$^{+}NH_3\text{---}S\text{---}COO^{-} \quad (2)$$

Ozone did not react with the protonated group, $^{+}NH_3$ [16]. Hence, the DU at these sites was unaffected. The reduction in DU compared to the control sample was due to the action of the ozone at the accessible non-protonated free amino (NH_2) group [16] present in the silk. COO^{-} was converted into CO2 and escaped [17]. When the sample was washed after the treatment, NH_3^{+} would have undergone a conversion into the NH_2 group. Because of these actions, the side chain lost its potential to form an ionic bond with the dye molecules and showed a higher reduction in DU than the other pH, since the study [12, 13] showed that the action of the ozone was maximized at pH 4. Since the efficiency of the ozone treatment was maximized at pH 4, the efficiency of the ozone treatment maximizes up to pH 4 and then decreases, irrespective of its availability as ozone or OHº.

At pH 7, the silk also had the same structure as above, but showed a smaller reduction in the percentage of DU. The reason for such behavior was due to the reduction in severity of the action of ozone arising because of the reduced solubility of ozone at the higher pH levels [17].

At pH 12, silk had the following structure during the ozonation.

$$NH_2\text{----}S\text{----}COO \quad (3)$$

But, it showed a smaller reduction in the percentage of DU than the other levels pH. It is explained as follows.
In the above structure, NH_2 was reactive towards the ozone and was converted into nitrates [17]. The nitrates so formed were removed during subsequent washing.

A simple experiment was carried out to find the presence of nitrates in the wash liquor. 5 ml of wash liquor was placed in a beaker along with 0.5 ml of diluted sulphuric acid (1% w/v) and a little quantity of ferrous sulphate. Then, a few drops of conc sulphuric acid were added to the mixture. The formation of a brown ring confirmed the presence of nitrates. The other group in the structure, COO^{-} was also reactive towards the ozone and was converted into CO_2 and escaped. But, due to the inhibition action of bicarbonate ions (HCO_3^{-}) and carbonate ions (CO_3^{-}) produced from the sodium carbonate, which was used in the treatment for the adjustment of the required pH, the NH_2 and COO^{-} groups were less affected by the ozone. This resulted in an increase in DU (less reduction of DU) of the fabrics treated at pH 12 over the other pH levels.

Figure 6 shows the effect of WP on the degree of action of the ozone was at a maximum of 50% WP followed by 100% and 10% WP. Since the ozone affected the dye absorbing sites to a maximum extent at 50% WP level, the DU of these fabrics showed the lowest value followed by 100% and 10% WP treated fabrics. In the ozone treatment on the silk fabrics, the effect on the physical and chemical properties, such as yellowness index, breaking strength, breaking elongation, weight, amino group content and flexural rigidity, showed a higher change in value at 50% WP compared to 100% WP of both the mulberry and tassar silk fabrics in the raw and degummed states. At 10% WP, the water content was low and the ozone did not decompose and did not act much on the fiber/dye site. At 100% WP, the water content was at a high level and the ozone dissolved before reaching the fiber/dye site and fewer were affected. The ozone was more effective at 50% WP, since the fiber contained a medium level of water content and the fiber/dye sites were easily accessible and easily affected [12,13]. Since the fiber/dye sites were affected, the dye uptake was low at 50% WP. The results also showed that, as the time of treatment increased, the reduction in dye uptake increased.

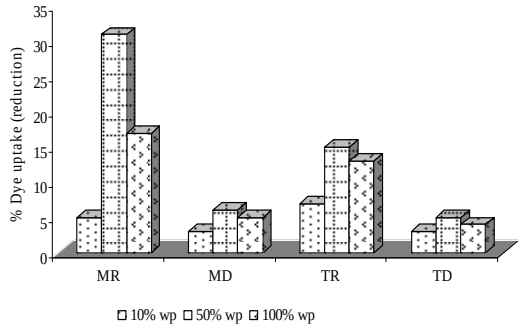

FIGURE 6. Effect of WP on dye uptake of silk fabrics on ozone treatment pH 4, 10 min and various WP levels.

Effect of Ozone Treatment EDU and $t_{1/2}$

Table I shows the EDU, as well as $t_{1/2}$, determined from EDU. It could be observed that the ozone treatment resulted in a reduction of EDU, which was due to the attack on the dye sites during the treatment. The rate of dyeing and $t_{1/2}$ at pH 12 values were closer to the control samples and indicated fewer fiber/dye sites were affected. The dye uptake was high or the % reduction of dye uptake was low, whereas, at pH4, the values showed that the fiber/dye sites were greatly affected indicating the dye uptake was less or the % reduction of dye uptake was high compared to pH 12 during the ozone treatment. The EDU of fabrics treated at pH 12 was more than that at pH 4 and the same reasoning could be applied. The $t_{1/2}$ was the lowest for the fabrics produced at a pH 4, followed by fabrics produced at a pH 12 and the control sample. It brought out an important point that the lower $t_{1/2}$ of ozone treated fabrics over the control sample did not reflect a higher rate of dyeing of the treated fabrics. When a decision on the rate of dyeing of the ozone treated fabrics is made based on $t_{1/2}$ values, due consideration for the EDU should be given.

TABLE I. Equilibrium dye uptake and $t_{1/2}$ of ozone treated samples with 50% WP and 30 min TT at pH 4 and 12.

Silk samples	Equilibrium dye uptake (%)			Half dyeing time (s)		
	Control sample	Ozone treated samples		Control sample	Ozone treated samples	
		pH 4	pH 12		pH 4	pH 12
MR	71.1	44.9	61.1	1050	966	1032
MD	67.2	53.8	61.8	1110	1062	1092
TR	48.9	36.6	43.6	1182	1128	1146
TD	43.0	31.0	38.0	1260	1140	1224

CONCLUSIONS

The study clearly indicated that the ozone treatment resulted in the reduction of the dye uptake of the mulberry and tassar silk fabrics. This occurred regardless of whether these materials were in a raw or degummed state, due to the destruction of the dye absorbing sites present in the side chain of the silk molecules by the ozone. The dye uptake of both the silk fibers in raw and degummed states were found to be higher at a pH 12 because of the inhibiting action of the bicarbonate and carbonate ions produced from sodium carbonate, which was added for achieving the required pH in the treatment. At other pH levels, the dye uptake increased when the ozone treatment pH was increased from 4 to 7. The dye uptake of the ozone treated samples were the lowest for 50% WP treated samples compared to samples treated at 100% and 10% WP because of the maximum deteriorating effect that this condition produced during the treatment. Further, the higher the treatment time, the lower was the dye uptake. The equilibrium dye uptake and the rate of dyeing of the treated mulberry and tassar silk materials were lower than that of the untreated materials. The treatment of materials carried out at pH 12 gave a higher equilibrium dye uptake than the pH 4 treated fabrics.

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