# ECO-FRIENDLY DYEING AND ANTIBACTERIAL TREATMENT OF COTTON

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Berberine, a natural cationic dye with excellent antibacterial activity, was extracted from the roots of *Berberis vulgaris* and applied on cotton fabric. Naturally, there is no affinity of cationic dyes for cotton fiber. To improve the dyeability of cotton fiber, plasma treatment and acrylic acid grafting, using plasma technology for pretreatment, were employed. The grafting of acrylic acid was confirmed using ATR-FTIR. The effect of pretreatments on the dyeability of cotton was evaluated. The antibacterial activity of the dyed samples was evaluated according to AATCC test method 100-2004. The samples dyed after acrylic acid grafting showed the highest antibacterial activity.

***Keywords***: plasma, grafting, cationic dye, dyeability, cotton, antibacterial

## INTRODUCTION

As renewable raw materials for textile industry, natural dyes and fibers, especially cotton, are gaining considerable importance due to recent environment conservation regulations.[1] Cotton is one of the most important natural fibers, which is used extensively in textile industry alone or in blends with synthetic fibers.[2] This fiber has great characteristics, such as good water and dye absorbency, comfort and stability. Synthetic dyes, such as direct, vat, sulphur, azoic and reactive dyes can be used simply to dye cotton fiber.[2-3] Today, due to environmental and health concerns, there is a great tendency to natural dyes.[2-8]

Natural dyes and pigments are found in some plants, animals, insects, bacteria, fungi and minerals. For example, alizarin is a very old and common red dye found in roots of madder, *Rubia tinctoria*. The development of synthetic dyes in the last century reduced the use of natural dyes in modern dyeing.[2-3,8-9]

Natural dyes can be used to dye protein fibers easily, but there are several problems in their usage on cotton fiber, mainly the low affinity and fastness properties of natural dyes toward cotton fiber.[8,10] To overcome these drawbacks, several studies have been carried out. Vankar *et al.* have used mineral and bio-mordants, besides ultrasound energy, to improve dyeability of cotton fiber with an extract of *Rubia cardifia.*[11] Pretreatments of cotton with chitosan, anionic and cationic active compounds, cross-linking agents and enzymes have been used to improve the dyeability of cotton with natural dyes.[4-6,8,12]

The prevention of microbial attack on textiles has become increasingly important to consumers and textile producers.[13] Natural dyes are considered to give advantages to applications, such as non-toxic functions, specific medical actions and environmentally friendly finishes.[3] Several natural dyes have been reported to be effective antimicrobial agents. Tannin-rich extract from *Quercus infectoria* was found to have good activity against gram-positive and gram-negative bacteria. Colorants extracted from onion pulp and onion skins were grafted onto cotton fabrics and the antimicrobial activity was evaluated. Also, curcumin-treated cotton and wool fabrics showed good antimicrobial activity to both *E. coli* and *S. aureus*.[13-14] Berberine, a natural cationic dye was applied on wool and nylon fabrics and the dyed samples showed good antibacterial activity.[2,15-19] *Berberis vulgaris* is a shrub, which is extensively planted in Southern Khorasan, Iran, and many other places all over the world, for its valuable fruit, barberry. In the previous studies, the roots of this plant were used as a source of a natural colorant to dye wool fibers.[18-19] There is a natural cationic yellow dye (natural yellow 18) in these roots named Berberine (Figure 1).[18] The amount of the dye is lower in the wood of the plant. This natural cationic dye was extracted and applied on cotton fiber.

Because of the low affinity of cationic dyes to cotton fiber, the fabric was pretreated with oxygen plasma and grafted with acrylic acid to create acidic groups on the surface of cotton fibers. The grafted samples were dyed with natural cationic dye. The color strength, fastness properties and antibacterial activity of the dyed samples were evaluated.

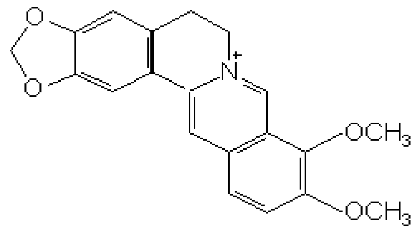


Figure 1: Chemical structure of berberine

## EXPERIMENTAL

### Materials

In this work, scoured and bleached cotton fabric (142 g/m$^2$) was supplied from Mazandaran Textile Company, Iran. Before being used, the fabric was treated with a solution containing 1 g/L non-ionic detergent and 1 g/L sodium hydroxide at 95 °C for 30 min. Then the fabric was thoroughly washed with water and air-dried at room temperature.

*Berberis vulgaris* roots were first washed and dried and then powdered. To prepare the original solution of the dye, each 100 gram of powder was added to 1 liter of distilled water and boiled for 2 hours and then filtered. Before filtration, the volume of the solution was adjusted to the initial amount by adding distilled water. The concentration of the resultant solution is 10% w/v. All chemicals used were analytical grade reagents from Merck.

### Methods

#### *Plasma treatment*

The fabric samples were treated using radio frequency (13.56 MHz) low pressure plasma equipment (model: Junior plasma, Europlasma, Belgium). In all treatments, oxygen was used as the processing gas. The system was evacuated to 100 mTor and oxygen was introduced into the chamber at a flow rate of 20 sccm (standard cubic centimeters per minute). The chamber pressure was subsequently maintained at 100 mTor and plasma was generated at 100 W for a predefined period of time. Subsequently, air was introduced into the chamber and the sample was removed for the grafting reaction. The time between the plasma treatment and the beginning of the grafting reaction was 5 min to ensure the formation of peroxide radicals necessary to initiate the grafting reaction.[20]

#### *Grafting*

The plasma-treated cotton sample was placed into a reaction flask containing 50 mL of solutions of different acrylic acid (AA) concentrations in distilled water. Nitrogen was purged into the flask to remove the air trapped inside the reaction mixture. The reaction flask was heated for different times at different temperatures. Then the fabric sample was drained and Soxhlet extracted with distilled water for 60 min to remove any non-reacted acrylic acid and homopolymers adhered to the sample surface. The samples were then dried in an oven at 50 °C for 2 h, cooled over a silica-gel desiccator and weighed. The grafting percent was calculated according to the following equation:

$$G\% = [(W_1 - W_2)/W_1]*100 \quad (1)$$

where $W_1$ and $W_2$ are the weights of the conditioned cotton fabric (25 °C, 60% RH) before and after the grafting process, respectively.

#### *FTIR analysis*

Fourier transform infrared measurements were carried out using a Nicolet 670 with a resolution of 4 cm$^{-1}$. An average of 40 scans was recorded in the ATR mode.

#### *Dyeing*

50 cc of the original dye solution was mixed with 50 cc of distilled water for each 2 gram of cotton (L:G = 50:1). The dyeing was started at 40 °C and the temperature was raised to boil at the rate of 2 °C per min. The samples were allowed to remain in that condition for 45 min, and then were rinsed and air-dried. All dyeing processes were carried out using a laboratory dyeing machine made by Rissanj Co., Iran.

#### *Color measurements*

The reflectance of the dyed samples were measured on a Color-eye 7000A spectrophotometer, using illuminant D65 and 10° standard observer. The color strengths (K/S) of the dyed samples were calculated at the maximum absorption wavelength, using the Kubelka-Munk equation:

$$K/S = (1-R)^2/2R \quad (2)$$

where R is the observed reflectance, K is the absorption coefficient and S is the light scattering coefficient.

***Color fastness tests***

Color fastness to washing, light and rubbing was measured according to ISO 105-C01: 1989(E), ISO 105-B02: 1994(E) and ISO 105-X12: 1993(E), respectively.

***Antibacterial test***

The antibacterial property of the dyed samples was quantitatively evaluated according to AATCC 100-2004. The bacterial species used were *Klebsiella pneumoniae* (gram-negative) and *Staphylococcus aureus* (gram-positive). Before and after incubation on the agar plate, the colonies of both bacteria were counted by microscope. The percent reduction in the number of bacteria, which was calculated using equation (3), shows the efficacy of the antibacterial treatment.

$$E\% = [(N_1 - N_2)/N_1]*100 \quad (3)$$

where $N_1$ is the number of bacterial colonies at the beginning of the test (0 hour), and $N_2$ is the number of bacterial colonies after 24 hours of contact with the dyed samples.

## RESULTS AND DISCUSSION

### Effect of plasma treatment on grafting efficiency

Cotton samples were plasma-treated at different times (power = 100 W) and grafted with a 20% V/V of AA for 1 hour at 60 °C. Table 1 shows the effect of plasma treatment time on graft yield of AA on cotton. As can be seen, the graft efficiency increases with the increase in plasma treatment time. The reason is the creation of more free radicals and active sites as the plasma treatment time increases. When the plasma treatment time extends beyond 120 s, the grafting degree decreases. This decrease can be due to over-etching of the fiber surface and reducing the accessible free radicals on the surface. So, a plasma treatment time of 120 s seems to be the optimum time for plasma treatment to reach the maximum grafting yield.

Plasma treatment can lead to the production of some radical sites. These radical sites will be oxidized with oxygen molecules in air and produce peroxides, and graft reaction will take place between cellulose and AA monomer. There are already some explanations regarding the optimal plasma treatment time. Before the optimal time, plasma treatment mainly produces radical sites; after the time, some existing radicals will disappear due to chemical degradation and finally reach a dynamic equilibrium. Besides, long-time plasma treatment can lead to the cross-linking between some radicals.[21] The grafting percent on the blank sample (grey cotton fabric) is approximately zero, which confims the positive effect of plasma treatment on grafting yield.

### Effect of AA concentration on grafting efficiency

Plasma-treated cotton samples (2 min, 100 W) were grafted using different concentrations of AA. Figure 2 shows that grafting percent increased as the AA concentration increased from 10% to 40%, and thereafter decreased with a further increase in AA concentration. This decrease can be due to more chances for AA monomers to form homopolymer, instead of copolymer, with cellulose at increased concentrations.[20] So the viscosity of the reaction medium increases significantly, which causes the monomer depletion and hence diminishes monomer accessibility to the grafting sites.[20]

Table 1
Effect of plasma treatment time on grafting percent

| Plasma treatment time (s) | Grafting, % |
|---|---|
| 0 (blank) | 0 |
| 30 | 0.81 |
| 60 | 1.74 |
| 90 | 2.66 |
| 120 | 3.54 |
| 150 | 3.47 |

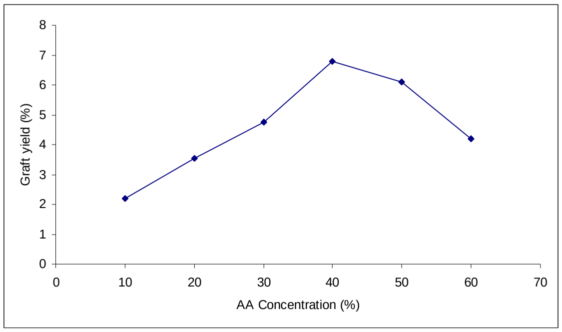


Figure 2: Effect of AA concentration on graft yield

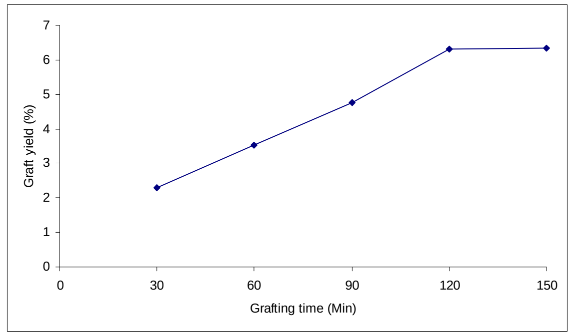


Figure 3: Effect of grafting time on graft yield (plasma treated, 20% AA, 60 °C)

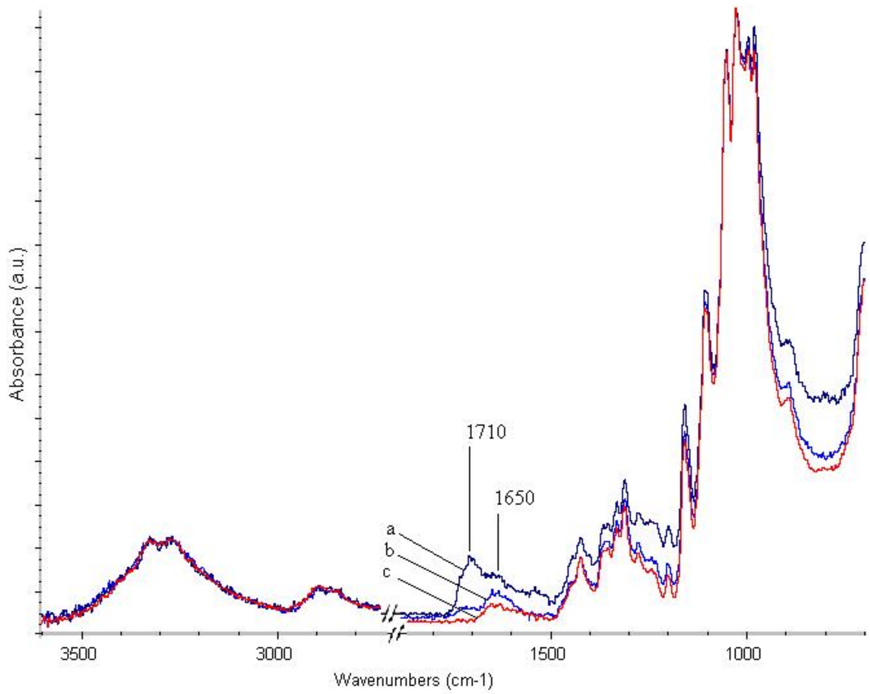


Figure 4: ATR-FTIR spectra of (c) raw, (b) plasma-treated (2 min, 100 W) and (a) acrylic acid grafted cotton fibers (G % = 3.54)

**Effect of grafting time on graft yield**

As can be noted from Figure 3, the grafting yield increases with the increase of grafting time from 30 min to 120 min, thereafter any further increase in grafting time has no significant effect on grafting yield. It can be explained by the reduced amount of AA monomer in the solution and the free radicals at the fiber surface after prolonged time. It may be stated that the growing chains are exhausted within 2 h and lead to the equilibrium degree of grafting.[20]

**FTIR Analysis**

The raw, plasma-treated and acrylic acid grafted fabrics have been characterized in order to validate the grafting (Figure 4). The small peaks at 1650 and 1710 $cm^{-1}$ in the FTIR spectrum of the plasma-treated fabric confirm the creation of carbonyl groups after the oxygen plasma treatment. The FTIR spectrum of the grafted fabric, when compared to that of the raw fabric, clearly indicates the peak for the –COOH group at 1710 $cm^{-1}$, which is due to the introduction of poly(acrylic acid) graft onto the cotton fibers.[1]

**Effect of plasma treatment and grafting on color strength of dyed cotton sample**

Raw, plasma-treated and AA-grafted cotton samples (with different graft percents) were dyed by the above-mentioned process. As noted from

Table 2, the raw sample absorbed a very low amount of the berberine dye, because of the low affinity of the dye towards cotton fiber. The plasma-treated sample showed a little improvement in dye absorption due to the creation of some oxygen-containing chemical groups on the fibers surfaces due to plasma treatment, as evidenced by the FTIR analysis. The K/S of the samples increases as the graft yield increases. This is due to the creation of more acidic sites after grafting of AA on cotton. Cellulose has no active site to react with cationic dye, berberine (Figure 1). After grafting of AA on cotton, the acidic COOH groups will appear on cotton surface, which will promote more absorption of cationic dye to it. Cationic dyeing of cellulose is generally done by pre-mordanting it with tannic acid, as cellulose lacks the groups required for the attachment of cationic dye molecules. Grafting of cellulose with acrylic acid is another technique for making cellulose anionic and, hence, cationic dyeable, as the carboxyl groups introduced as a result of grafting act as sites for the attachment of cationic dye molecules.[1]

**Fastness properties**

As mentioned in Table 3, the fastness properties of the samples dyed after AA grafting were also found to improve. Cationic dyes are known for inferior fastness properties on cellulose; hence the improvement in fastness properties of the grafted product may be attributed to the increase in the content of carboxyl groups, which provides a better attachment of the dye molecules to the sites, offering resistance against removal through washing or rubbing. The improvement in light fastness is due to a larger amount of dye being adsorbed onto the fiber, as compared to the experiment with no grafting.

Table 2
Effect of plasma treatment and grafting on color strength of dyed cotton sample

| Graft yield (%) | K/S |
|---|---|
| 0 (Untreated cotton) | 0.577 |
| 0 Plasma-treated cotton) | 0.765 |
| 2.3 | 2.15 |
| 3.54 | 3.17 |
| 4.76 | 4.56 |
| 6.32 | 5.98 |

Table 3
Fastness properties of dyed samples

| Sample | Washing fastness | Rubbing fastness | Light fastness |
|---|---|---|---|
| Raw | 1 | 1 | 3-4 |
| Plasma treated | 2 | 1-2 | 3-4 |
| AA grafted (3.54%) | 4 | 3-4 | 6 |

Table 4
Antibacterial activity of different samples (% reduction of bacteria after 24 h incubation)

| Bacterium / Sample | *Staphylococcus aureus* | *Klebsiella pneumoniae* |
|---|---|---|
| Raw (Undyed) | 0% | 0% |
| Raw-Dyed | 0% | 0 % |
| Plasma treated-Dyed | 0% | 0% |
| AA grafted (3.54%)-Dyed | 99.2% | 99.1% |

**Antibacterial activity**

Table 4 shows the reduction (%) in number of two bacteria after 24-hour incubation on the surface of different samples. Only the cotton sample dyed after plasma treatment and acrylic acid grafting showed good antibacterial activity. Berberine colorant is a quaternary ammonium compound, containing a positive charge on the N atom that could destroy the negatively charged cell membrane of the bacteria by disturbing the charge balances of the cell membrane. Other detrimental effects of quaternary ammonium compounds on microbes are denaturizing of proteins and disruption of the cell structure.[18] The samples dyed without plasma treatment or only after plasma treatment showed no antibacterial activity, because the amount of antibacterial dye on the fabric seems to be less than the minimum inhibitory concentration of the compound needed to inhibit the growth of bacteria.

## CONCLUSION

Oxygen plasma treatment of cotton fabric, as described in this study, improves the graft yield of acrylic acid on the fiber. Grafting of acrylic acid on cotton fiber is affected by time of plasma treatment, AA concentration and grafting time. Grafting of acrylic acid onto cotton fiber improves the absorption of berberine natural dye on it, because of ionic interactions between the dye and the modified fiber. The dyed fabric showed good fastness properties, besides excellent antibacterial activity against both gram-negative and gram-positive bacteria.

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