Rendering viscose fabric dye-able with anionic dyes using plasma treatment technique and chitosan nanoparticles as an eco-friendly approach

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Abstract
Purpose – This paper aims at studying the oxygen plasma treatment and the previously prepared and fully characterized chitosan nanoparticles (CNPs) as a green and eco-friendly strategy for surface modification of viscose fabric. This was done to render viscose fabric dyeable with two types of acid dyes that do not have direct affinity to fix on it via improving the fabric wettability.

Design/methodology/approach – To achieve the goal, viscose fabric was activated with oxygen plasma at optimum conditions and coated with different concentrations of CNPs solution via conventional pad dry cure technique. The untreated and plasma-treated fabrics with CNPs were dyed with two types of acid dyes, namely, Acid Orange 7 and Methyl Red under determined conditions. The color strength (K/S), fastness properties to light, rubbing and perspiration, add on %, tensile strength, wettability and durability of the dyed samples were determined and compared.

Findings – The results divulged that oxygen plasma-treated fabric with CNPs and the aforementioned dyes in question could improve the following properties in comparison with untreated fabric: (a) the fabric wettability expressed as wetting area mm²; (b) the dye ability and fastness properties of viscose fabrics expressed as K/S and fastness properties; and (c) the strength properties and add on % of the treated fabric. On the other hand, the durability of the plasma-treated fabric decreased with increasing washing cycles.

Originality/value – The novelty addressed here was using plasma treatment as an eco-friendly pre-treatment approach for attachment of CNPs as a multifunctional green bio-nano polymer onto viscose fabric, which improved the dyeing properties of the fabric with acid dyes that do not have direct affinity to fix onto it.

Keywords Chitosan nanoparticles, Dyeing, Acid dyes, Fastness properties, Color strength

Paper type Research paper

1. Introduction
Surface modification of the textile fabrics without changing the bulk properties has been a conventional research topic for improving the dye ability of textile fabrics for many years. Such modification is used to designate a thoughtful change in composition, surface chemistry, wettability or structure leading to an improvement in different types of fiber properties. In this regard, different approaches for the modification of fibrous and non-fibrous textiles comprising crosslinking (Mostafa and Ameen, 2020; Mostafa and El-Sanabary, 2020, 2021), grafting (Mostafa et al., 2010a, 2010b; Amara et al., 2019), aminolysis (Brinker and Scherer, 1990), sol gel (Schramm and Rinderer, 2011; Yin et al., 2008), cationization (Ben Ticha et al., 2017), ionization radiations (Chan, 1994), UV and gamma radiation (Kim and Jang, 2010), UV/ozone irradiation (Kim and Bae, 2009), electron beam irradiation (Yip, 2002), UV excimer laser (Bide et al., 2006) and plasma treatment (Shishoo, 2006; Oktem, 2000; Peter, 1997; Javed, 2008; Hajj, 2016, 2017) have been deliberated, and their effects on the dye ability of different textiles have been explored. Plasma is the fourth state of matter in which a substantial part of molecules is dissociated and ionized via electromagnetic fields. It is composed of a high concentration of reactive species, including ions, electrons, neutrons, excited molecules, free radicals, metastable particles and photons that are capable of inducing physical and chemical alterations on the surface of textiles backbone structure. Besides, using plasma is a novel approach that reduces air, water and land pollution in comparison to conventional methods of wet chemistry (Graham, 2007). Plasma technology is quite promising for CO₂ conversion because of its high process versatility, low investment and operating costs, can be applied in a very modular setting and easily combined with various kinds of renewable electricity. However, more research is needed to further improve the capabilities of plasma-based CO₂ conversion in terms of energy efficiency, conversion and...
product selectivity (Bogaerts and Centi, 2020). Besides, laser-plasma acceleration promises compact sources of high-brightness relativistic electron beams. However, the limited stability often associated with laser-plasma acceleration has previously prevented a detailed mapping of the drive laser and electron performance and represents a major obstacle towards evolving laser-plasma acceleration for applications (Maier et al., 2020). Based on the above and because of the limiting use of the above types of plasma, we use what we called non-thermal plasma to treat textiles because of it is a partially ionized gas that enables substrate reactions to take place without its thermal degradation (Gorjanc et al., 2009; Cvelbar and Mozetič, 2001). Plasma is created and maintained at a low atmospheric pressure by using different systems of electrical power, such as the direct, radio-frequency and microwave systems (Fridman et al., 2008; Shishoo, 2007). This echo friendly process is surface-specific and modifies the highest part of the surface using minimum amounts of working gas. Specifically, oxygen plasma treatment may have several effects on the surface of the substrate, including cleaning, activation, grafting, etching and polymerization. The type and the extent of the impact depend on the nature of the gas used and the process parameters such as power, pressure, flow rate, frequency and duration (Dave et al., 2019). When plasma reacts with a substrate, new active species and functional groups are created on its surface. The longer we treat a substrate with plasma, the more we transcend into the sphere of grafting, etching and polymerization. The type and the extent of the impact depend on the nature of the gas used and the process parameters such as power, pressure, flow rate, frequency and duration (Dave et al., 2019). When plasma reacts with a substrate, new active species and functional groups are created on its surface. The longer we treat a substrate with plasma, the more we transcend into the sphere of grafting, etching and polymerization. The type and the extent of the impact depend on the nature of the gas used and the process parameters such as power, pressure, flow rate, frequency and duration (Dave et al., 2019). When plasma reacts with a substrate, new active species and functional groups are created on its surface. The longer we treat a substrate with plasma, the more we transcend into the sphere of grafting, etching and polymerization. The type and the extent of the impact depend on the nature of the gas used and the process parameters such as power, pressure, flow rate, frequency and duration (Dave et al., 2019). When plasma reacts with a substrate, new active species and functional groups are created on its surface. The longer we treat a substrate with plasma, the more we transcend into the sphere of grafting, etching and polymerization. The type and the extent of the impact depend on the nature of the gas used and the process parameters such as power, pressure, flow rate, frequency and duration (Dave et al., 2019).

2. Materials and methods

2.1 Fabric

Mild scoured and bleached plain weave 100% viscose fabric (76 picks × 61 ends/inch, 127 g/m²) was kindly supplied by El-Nasr Company for Spinning, Weaving and Dyeing, El-Mahalla, Egypt. The fabric was washed for 5 min with diluted acetone (reagent grade of 99% purity) and subsequently completely dried in oven at 50 °C. Samples were conditioned at 20 ± 2 °C temperature and relative humidity of 65 ± 2% for at least 24 h before use. The reference values of untreated viscose fabrics with respect to tensile strength (N), weight (%) and wettability were 386.4 ± 2.98, 6.10 ± 3.44 and 215.7 ± 3.88, respectively.

2.2 Dyes structure

Anionic dyes (acid) used were Acid Orange 7 (C.I. 15510) and Methyl Red (C.I.1305) (Sigma-Aldrich) and their structures are shown in Scheme 1.

2.3 Preparation of freeze drying chitosan nanoparticles

CNPs were prepared according to the reported method published by Morsy et al. (2019) with some modification. Unless otherwise indicated, a known weight of chitosan (0.8 g) was dissolved in an aqueous methacrylic acid solution (0.5%, w/v) for 24 h under magnetic stirrer for homogenization. Then, 0.02 mol/L of potassium permanganate as initiator was added to the above solution under continuous stirring at 60 °C for 2 h, leading to the formation of CNPs, which were then cooled in an ice bath. The suspension was centrifuged at 6000 rpm for 45 min and the supernatant was removed and the settled CNPs obtained from the centrifugation process were further subjected to freeze-drying process at −60 °C for 6 h and ice crystals of pure water were formed. Details of the conditions used and main characteristics for CNPs with respect to source, preparation, properties and characterization after freeze drying are found in the recent report published by Morsy et al. (2019).

Scheme 1 Chemical structure of Acid Orange 7 (C.I. 15510) and Methyl Red dyes (C.I. 13020) as two different types of anionic dyes
2.4 Plasma treatment of viscose fabrics
Plasma treatment technique of the viscose fabrics was performed using radio-frequency (13.56 MHz) low-pressure plasma equipment (model: Tetra 30 PC LF-40kHz). After plasma treatment, the treated fabrics were conditioned at 20 ± 2 °C temperatures and relative humidity of 65 ± 2% for at least 24 h before used.

2.5 Chitosan nanoparticles treatment
Plasma-treated fabric samples were instantaneously soaked in different concentrations (20–100 g/L) of CNPs solution (1% w/v) containing 1% v/v acetic acid for 15 min. Then, the samples were padded through two dips and two nips to 100% wet pick up and dried at 90 °C for 3 min. The fabric was then water rinsed and dried at ambient conditions before use.

2.6 Dyeing
The dyeing of the plasma-treated viscose fabrics in presence of CNPs with acid dyes in question was done using 0.5%, 1.0% and 1.5% of the dye solution. Material to liquor ratio of 1:40 was used, and pH value was set at 3. The temperature was slowly raised to 98 °C and dyeing was continued for 30 min. The samples were dried at ambient temperature after the rinsing step. Finally, these samples were dried and evaluated for color strength and overall fastness properties.

2.6.1 Color strength (K/S)
It was measured using color matching spectrophotometer (model color Eye 3100 – SDL England) according to the standard test method (AATCC 110-2000).

2.6.2 Fastness properties
All dyed samples were tested for color fastness to light according to ISO 105 B02 test method using xenon arc light fastness tester for 24h, and colorfastness to rubbing and perspiration using (ISO 105x12:1987) and (ISO 105-E04: 1989), respectively.

2.6.3 Durability (washing fastness)
The durability to washing was done on dyed plasma-treated fabric with CNPs, then washed at 40 °C in a small washing machine using a solution containing 2 g/L nonionic wetting agent. Then, 1, 3 and 5 washing cycles (home domestic laundering washing), 2min each, were given followed by a water rinse in the same washing machine in accordance with EN ISO 69330 (2005) to test laundering durability. Finally, the fabrics were dried, conditioned and examined for different properties.

2.7 Wettability (drop test)
After 24 h conditioning, 20 μm of Methylene Blue dye solution was dropped on fabric surface perpendicularly by an auto pipette. The area of dispersion of the Methylene Blue dye solution absorbed in fabric was measured after no further spreading was observed for untreated, plasma-treated fabrics with CNPs. Five measurements were obtained for analyzing the wetting area (mm²). As a reference point, the wetting area for untreated cotton fabric is 215.7 mm².

2.8 Mechanical properties
2.8.1 Tensile strength (N)
The tensile strength (N) of the untreated and plasma-treated samples with CNPs in the warp direction was analyzed according to En ISO 13934-1:1999 standard.

2.9 Add on %
Add on % of the samples treated in presence of CNPs and the aforementioned dyes were estimated according to the reported method (Mostafa and El-Sanabary, 2021).

2.10 Statistical analysis and metrological precision
All of the experiments were conducted in triplicate. The data were analyzed and expressed as mean values ± standard deviations. This was done to insure about the high precision of metrological measurements all over the work when using our calibrated instruments in our institute either by primary standard apparatus or certified reference materials used, especially for this purpose.

3. Results and discussion
Oxygen plasma treatment enables surface chemical activation of textiles by introducing new functional groups such as

![Scheme 2](image_url)
carbonyl (\(-\text{C}=\text{O}\))

carboxylic acid (\(-\text{COOH}\))

drastically increase the surface energy of the fabric via surface activation (Briggs et al., 1980).

Generally, plasma treatment and CNPs coating introduce hydroxyl and amine groups on the viscose fibers which lead to the better attraction of the dye molecules by the fiber via absorption (fixation) as shown below in Scheme 2.

\[ \text{Acid Orange 7} - \text{Methyl Red} \]

3.1 Tentative mechanism

Surface functionalization by plasma exposure occurs via the chemical interactions between gas phase species and activated radical on the viscose fabric surface. For this reason, functionalization is directly dependent on the type of working gas. In our case, when using reactive gas like oxygen, atoms or molecular portions are added to the fabric surface at which a visible increase in the ratio of oxygen to carbon as new oxygen-containing functional groups are introduced (Kan and Man, 2018). These groups were \(-\text{OH}\) and \(-\text{COOH}\) which dramatically increase the surface energy of the fabric via surface activation (Briggs et al., 1980). Generally, plasma treatment and CNPs coating introduce hydroxyl and amine groups on the viscose fibers which lead to the better attraction of the dye molecules by the fiber via absorption (fixation) as shown below in Scheme 2.

3.2 Wettability

Generally, the plasma treatment can further enhance viscose fabric wettability expressed as wetting area mm². In textiles processing, wettability of fabric plays a key role in enhancing the plasma treatment was not effective on the dye ability of viscose fabrics with acid dyes in addition to the untreated fabric as we mentioned above as shown by the lower \(K/S\) (−1) and fastness properties (very poor). So, we can use only the plasma-treated fabric with CNPs for studying the different performances related to the dye ability of viscose fabric like color strength, fastness properties, durability as well as wettability. The latter was studied to see the effect of plasma treatment on the degree of wettability of plasma-treated fabric in comparison with untreated one. The obtained results along with appropriate discussion are presented below.

Figure 1  Effect of changing discharge power of untreated fabric and plasma treated fabric with CNPs on fabric wettability (mm²)

Notes: Reaction conditions: [CNPs], 50 g/L; chamber base pressure: 5 Pa; oxygen flow rate: 0.3 L/min; discharge power: 170 W; duration: 7.5 min

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Figure 2  Effect of varying acid dyes concentration on the color strength (K/S) of plasma-treated fabric with CNPs with Acid Orange 7 and Methyl Red dyes

Notes: Reaction conditions: [CNPs], 50 g/L; chamber base pressure: 5 Pa; oxygen flow rate: 0.3 L/min; discharge power: 170 W; duration: 7.5 min
different processes such as dyeing, finishing and printing. As a reference point, the wetting area for untreated viscose fabric measured is 215.7 mm². In this manner, to study the wettability of plasma-treated fabric with CNPs; different discharge power (140, 150, 160 and 170 W) are used in this experiment. Figure 1 shows the effect of changing discharge powers on wetting area (mm²) of untreated viscose fabric and plasma-treated fabric in presence of CNPs under the optimum conditions used, i.e. CNPs concentration: 50 g/L; chamber base pressure: 5 Pa; oxygen flow rate: 0.3 L/min; and duration: 7.5 min. It is seen from the figure that wetting areas of plasma-treated fabric with CNPs are higher than those of untreated samples and the higher discharge power would lead to a larger wetting area. For more elaboration, a high discharge power generally induces a formation of plasma active species at a higher rate which increases the etching and oxidation effect on the substrate surface (Kan et al., 2014). Moreover, active plasma species possess a higher energy that can interact with the viscose fabrics because high discharge power can supply more energy to the plasma species to approach the substrate surface.

3.3 Color strength (K/S)
Figure 2 designates the effect of changing acid dyes concentration (0.5%, 1.0% and 1.5%), namely, Acid Orange 7 and Methyl Red on the color strength (K/S) of plasma-treated fabric with CNPs. Details of the conditions used are given in the text. Results from Figure 2 reveal that as the concentration of anionic dyes increased, the color strength (K/S) values of the dyed plasma-treated fabric with CNPs increased evocatively. The samples treated using highest concentration of dyes, i.e. 1.5%, presented high upsurge in K/S values in comparison with other lower concentrations, i.e. 0.5%. With the increase in the concentration of dyes, the latter is getting selectively absorbed with the free amine groups resulted from the plasma-treated fabric with CNPs as shown in Scheme 2. In other words, the ionic interaction and/or hydrogen bonding between the protonated amine groups of CNPs and the functional groups of anionic dye molecules (SO₃H) or COOH was effective in increasing the dye absorption and enhancing the color strength values. This can be explained as shown under: Oxygen plasma treatment creates oxygen-containing groups and reactive radicals on the surface of viscose fabrics. These radicals turn into functional groups in contact with the oxygen in the air. Therefore, the wettability and dye ability of the fabrics are improved after plasma treatment (Kan and Man, 2018).

However, if impregnate the plasma-treated fabrics in a CNPs solution instantly, the radicals react with the functional groups of CNPs (−OH and/or −NH₂) via coating and the CNPs are grafted on the surface of the fabrics permanently (Vrabič Brodnjak et al., 2018).

3.4 Fastness properties
It is well known that color fastness is considered as one of the important factors for buyer for measuring the quality of a textile product. As shown in Table 1, plasma treatment and CNPs coating generally improved the fastness to light, rubbing and perspiration of viscose fabrics dyed with different concentration of acid dyes in question. This is because of the hydrogen bonding and/or ionic interactions between the dye molecules −SO₃H or −COOH and the functionalized fibers coated with CNPs containing −NH₂ and/or −OH groups as shown in

Figure 3 (a) Tensile strength (N), (b) Add on % values for plasma-treated fabric with different concentration of CNPs

Table 1 Colorfastness to light, rubbing and perspiration of the plasma-treated fabric with CNPs 50 g/L

<table>
<thead>
<tr>
<th>Dye concentration (%)</th>
<th>Colorfastness to light (Acid Orange 7)</th>
<th>Colorfastness to rubbing (Acid Orange 7)</th>
<th>Colorfastness to rubbing (Methyl Red)</th>
<th>Colorfastness to perspiration (Acid Orange 7)</th>
<th>Colorfastness to perspiration (Methyl Red)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1−2</td>
<td>2−2</td>
<td>1−2</td>
<td>2</td>
<td>1−2</td>
</tr>
<tr>
<td>1.0</td>
<td>2−3</td>
<td>2−3</td>
<td>2−3</td>
<td>2</td>
<td>2−3</td>
</tr>
<tr>
<td>1.5</td>
<td>3</td>
<td>3</td>
<td>2−3</td>
<td>3−2</td>
<td>2−3</td>
</tr>
</tbody>
</table>

Note: Reaction conditions: chamber base pressure: 5 Pa; oxygen flow rate: 0.3 L/min; discharge power: 170 W; duration: 7.5 min
The concentration of CNPs increases from 389 to 390 N for Acid Orange 7 and from 3.44 to 7.10 K/S for untreated fabric. This may be accounted for by the good to very good fastness properties to light, rubbing and perspiration are another evidence for coloration of the dyed fibres. Light fastness is also affected by the amount of the dye molecules absorbed on the fibers. As the plasma-treated and chitosan-coated samples absorbed more dye molecules, the light fastness properties of these samples were also improved. In other words, the good to very good fastness properties to light, rubbing and perspiration are another evidence for coloration of viscose fabric by anionic dyes in question.

3.5 Tensile strength (N) and add on (%)  
Figure 3(a) and (b) denotes the variation of tensile strength (N) and add on % of the plasma-treated fabrics with different concentrations of CNPs. Details of the conditions used are given in the text. It was shown from the above figure that the tensile strength and add on % of the plasma-treated fabric in presence of CNPs showed relatively higher values than that treated with lower CNPs concentration. For more explanation, tensile strength of plasma-treated fabrics at different concentrations of CNPs increases from 389 ± 2.12 to 425 ± 3.12 N for Acid Orange 7 and from 390 ± 2.44 to 430 ± 3.88 N for Methyl Red by increasing the CNPs concentration from 20 to 100 g/L. This is against 386 ± 2.12 N for untreated fabric. On the other hand, the add on % (weight) of the plasma treated fabric with CNPs increases from 6.20 ± 3.44 to 6.98 ± 2.88 for Acid Orange 7 and from 6.20 ± 3.44 to 7.10 ± 3.22 for Methyl Red, respectively, by increasing the CNPs concentrations from 20 to 100 g/L. This is against 6.10 ± 3.44 for untreated fabric. This may be account on the basis that, the highly reactive CNPs with smaller particle size (60–100 nm) and larger surface area can easily penetrate inside the bulk of the viscose fiber and reinforce the fabric structure via coating process and accepts the load to a great extent. Furthermore, the amount of CNPs and dye absorbed inside the fabric structure increased considerably (Morsy et al., 2019).

3.6 Durability (washing fastness)  
Table 2 shows the significance of durability (fastness to washing) on the foremost technical properties of plasma-treated fabrics with CNPS (50 g/L) at optimum conditions after 1, 3 and 5 washing cycles. Details of the conditions used are given in the text. It is seen (Table 2) that the tensile strength, color strength and add on % decrease after washing. The plasma-treated fabric with CNPs and dyed under investigation seems to involve certain amount of unfixed anionic dyes and/or CNPs which are lightly attached to the fabric surface and, therefore, are liable to washing. The latter depends on the number of washing cycles which, in turn, reflects the severity of washing.

4. Conclusion  
In this work, viscose fabrics were modified with oxygen plasma and CNPs as two environmentally friendly processes. The untreated, plasma-treated and plasma-treated fabrics with CNPs were dyed with two different anionic dyes, namely, Acid Orange 7 and Methyl Red. The obtained results of the plasma-treated fabric with CNPs reflect the following findings:

- the results and experimental trials revealed that plasma treatment itself could not improve the dye ability of viscose fibers;
- certain notable enhancement in the fabric wettability expressed as wetting area was obtained;
- improvement in the dye ability and overall fastness properties of viscose fabrics in comparison with untreated fabric;
- the strength properties and add on % of the treated fabric is higher than that untreated one; and
- the durability of the plasma-treated fabric decreased with increasing the number of washing cycles.

Finally, the attachment of CNPs on viscose fibers using plasma pre-treatment activation can be an excellent alternative to replace the use of harsh chemicals and toxic solvents in the dyeing of such fiber with aforementioned anionic dyes.

References


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