

Nanoclay as New Tool for Discoloration of Dyed Denim Garment with Indigo

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ABSTRACT

Up to now, discoloration of the denim garment has been carried out through various methods including mechanical, chemical, physical and enzymatic treatments. In this study, the nanoclay was co-applied in bio stone washing of denim with cellulase to obtain denim garment with a new look and clear effluent. Acid and neutral cellulases along with nanoclay were applied on the dyed denim fabric with indigo and the properties of the treated sample and the obtained effluent were evaluated. The color changes of the denim fabric were investigated using colorimetric methods. The surfaces of the treated samples and montmorillonite in effluent were observed using SEM and TEM, respectively. According to the results, nanoclay as a new tool along with cellulase caused increasing the lightness, decreasing the back-staining, creating a new look and reducing the remained color in the effluent. Prog. Color Colorants Coat. 6(2013), 25-36. © Institute for Color Science and Technology.

1. Introduction

Denim fabric usually has a serge weaved with indigo-dyed warp and white weft yarns [1]. The abrasion process in stonewashing is done with pumice stone in washing machine (rotary drum washer), with or without an oxidizing agent such as potassium permanganate. This process results in dye removal and fabric strength loss to a desirable extent. The stonewashing or abrasion effect can be created on denim fabric either by using cellulase individually or along with the pumice stone [2, 3].

It was pointed out that the finishing by cellulase is intensified in mechanical motion processes. The balance between cellulase activity and mechanical process leads to removal of fuzz fiber and naps from the surface of the fabric without a remarkable strength loss. Moreover, using cellulase produces better results in contrast with stonewashing processes using pumice stone [4, 5].

Lightness, color change, and back staining increase with the cellulose content in bio washing. Back-staining

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depends on pH and type of enzymes. The staining of the acidic and neutral cellulases occurs at pH=5-6 and pH=6-7, respectively. Generally, neutral cellulases produce lesser staining compared to acidic cellulases [6, 7].

Discoloration of dyes was studied by a laccase from *Trametes modesta* immobilized on aluminium oxide pellets. Isatin (indole-2, 3-dione) is the product of indigo decomposition by laccase which changes into anthracitic acid. The kinetic of indigo decomposition by laccase shows that anthralinic acid would be as the end product in case of quick change of indigo into isatin and persistence of laccase activity. With regard to the dye-removal effect of laccase, it can be used along with cellulase on denim garment. Denim treated with laccase has more brightness and more laccase in cellulase-laccase mixture reduces back-staining in denim stone washing. The biowashing effluent is decolorized using laccases and can be reused for restonewashing [8-14].

Layer silicates are natural clay or synthetic silicate layers such as Magadiite, Mica, Saponite, Fluorohectorite and Montmorillonite. Montmorillonite is composed of smooth mineral poly-silicate groups with crystalline structure and its water content increases by water absorption. Montmorillonite or nanoclay with the chemical structure of $(\text{Na}, \text{Ca})_{0.33} (\text{Al}, \text{Mg})_2 (\text{Si}_4\text{O}_{10}) (\text{OH})_2 \cdot n\text{H}_2\text{O}$ includes silicate, magnesium, aluminium, calcium, and sodium. Altogether, clay can be used as an adsorbent for heavy metals, poisonous and hazardous chemical substances such as removed mercaptan sulphur from kerosene-oil. Different studies showed that activated clay has been successfully applied for the removal of dyes in the industrial textile waste water. Activated clay has proved its effectiveness as 98% of the dyes removed and the COD reduced with a neutral pH and an excellent decant ability [15- 21].

The morphology of nanoclay is platelet with a thickness of less than 1 nm and width between 100 nm and 1 μm . Due to the huge aspect ratio, nanoclay has a very large surface area of about 700 m^2/g . This unique morphological structure provides possibilities for excellent sorption capability. Nanoclay could be modified with organic quaternary ammonium to provide the required interaction between clay and other organic molecules. It has been indicated that the major contributive forces to dye sorption onto nanoclay were vander Waals forces and hydrophobic interaction. Ionic attraction also played an important role to dye adsorption [22- 24].

The very low affinity of the basic dye to the nanoclay

indicated the existence of ionic repulsion between the nanoclay with cationic charge and the dye, both with positive charges in water. The strong affinity occurs between anionically charged acid and direct dyes and the cationic modified nanoclay. However relatively weak affinity of the anionically charged reactive dye suggested that ionic attraction was not as strong as the vander waals forces and hydrophobic interactions. Although the acid, direct and reactive dyes examined but the reactive dye with relatively high water solubility has relatively high water solubility and a low tendency to form strong vander waals and hydrophobic interactions with the clay. Furthermore, more reports indicated that dye sorption isotherms of nanoclay are followed Longmuir isotherm [25- 29].

There are different methods for stonewashing including conventional (using pumice stone) and modern (enzyme, laser ...) methods. A combination of these methods is usually applied.

The aim of this research was to study the usage of nanoclay on denim garment to discolour the indigo dyed denim garment. This research has also given special attention to the design of an environmentally friendly technique for discolouration of the textile waste-water.

Considering the increasing use of nano material compounds in textile and clothing particularly in finishing of textile products, we have contemplated the effect of nanoclay along with cellulase in denim stonewashing and investigated the properties of obtained garment.

2. Experimental

2.1. Materials

The denim fabric (blue jean) used was 100 % cotton with twill 2/1 weave construction, weft and warp count of 8 Ne with z twist, weft density of 20/cm, warp density of 26/cm, using open-end (OE) yarn weaving and fabric weight of 322 g/m^2 . In order to prepare experimental garment, samples of 20×30 cm^2 sewed from sides. A piece of white woven cotton pocket, with 26/cm of weft and warp density was sewed as the backside pocket using OE yarns with weft yarn count of 20 Ne and warp yarn count of 15 Ne and fabric weight of 166 g/m^2 (Figure 1). Enzymes used in this research were: (1) neutral cellulase (Denimax XT) with optimal solution of 40-50 $^{\circ}\text{C}$, pH=6-7, 1600 DAU/g activity, (2) acidic cellulase (Denimax 992 L) with optimal solution of 40-45 $^{\circ}\text{C}$, pH=5-6, 750 ACU/g activity, and (3) amylase (Hi-CONS) active in

range of 60-100 °C, pH=6-8, with 120 LAMU/g activity from Novozymes Co., Denmark.



Figure1: Denim sample with white pocket.

The nanoclay (Organo-montmorillonite) used was Cloisite® 10A from SCP, U.S.A.

2.2. Methods and instruments

Samples were desized using 3 g/L of amylase for 15 min, at pH=7 and 70 °C. In all experiments, the L:G was (Liquor to Goods Ratio) 70:1, dispersing agent to prevent back-staining was 3g/L and anti-creasing agent was 5g/L.

One desized sample was treated with 10 g/L of neutral cellulase (Nc) at pH=7 and 55°C for 1 h and other desized samples were washed under the same conditions along with 10, 20 and 30% nanoclay that were coded as 10C Nc, 20C Nc and 30C Nc, respectively.

One desized sample was treated with 10 g/L acidic cellulase at pH=5.5 and 55°C (Ac) for 1 h and also the other desized sample was washed under the same conditions along with 10, 20 and 30% nanoclay that were coded as 10C Ac, 20C Ac and 30C Ac, respectively.

A rotary drum washer with 100 g capacity, steel basket, 25 rpm, and temperature and mass control was used for different washing processes.

To determine spectrometric reflection values, a Data color spectrophotometer was used and colour values were calculated at 10° and D65 light source. Each sample is composed of 3 parts included face of the sample, back of the sample and white pocket. In order to prevent any possible errors, obtained colour data was repeated 5 times for every 3 parts of each sample and mean values of lightness (L^*), redness-greenness (a^*), yellowness-blueness (b^*), and colour difference with desized sample (ΔE) are reported. In addition, the whiteness index (W) for white pocket and back of fabric along with value of staining was recorded.

To measure the adsorption of stonewashing effluent, Camspec UV/Vis absorbance spectrophotometer (model

M-350, England), was used. Samples were diluted with water and estimated with blank sample (water).

Microscopic images were taken from the effluent of the treated sample using a Transmission Electron Microscope (TEM, model EM 208, Philips Co., Netherlands).

0.5 × 0.5 cm² pieces of fabric were cut out and then covered with gold using sputter coater machine from BAL-TEC Co. (model SCD00S, Switzerland). Microscopic images were taken from each sample using SEM (Philips, Netherlands, model XL30 with 500X).

3. Results and discussion

3.1. Color changes of denim garment

The results of chromaticity indices and color changes of treated samples with cellulases and cellulase along with nanoclay and the colorimetric properties of face, back and white pocket of treated samples with nanoclay/cellulases were given in Table 1.

The enzymatic process with cellulase (bio washing) increased the lightness (L^* in Table 1) in comparison with the desized sample. Also, the denim treated with neutral cellulase was lighter than the acid cellulase, which justified the higher activity of natural cellulase than the acid cellulases. The samples treated with the cellulase along with nanoclay were also lighter than the one treated with cellulase alone.

Thus, nanoclay absorbed indigo dye from denim surface, in other word nanoclay discoloured the denim and increased the lightness of the treated samples. With increasing the nanoclay concentration in bio washing, lightness of the treated denim was increased. It seems that the discoloration of the denim is increased with the nanoclay concentration.

The a^* values of the denim treated with cellulase along with nanoclay showed that using nanoclay with absorbing indigo from denim surface reduced the redness and increased the greenness compared to the denim treated with cellulases alone and the desized sample. Also with increasing the nanoclay concentration, the redness of the treated denim reduces but the greenness increases. The b^* values of the treated denim showed that samples treated with nanoclay along with cellulases were yellower than denim treated with cellulases alone because of the absorbed indigo on denim surface by nanoclay. With increasing the nanoclay concentration, the discoloration of the indigo on denim surface is increased because of the nanoclay absorbency.

Table 1: The colorimetric properties of face, back and white pocket of treated samples with nanoclay/cellulases.

Sample	Face				Back			White pocket			
	L*	a*	b*	ΔE	L*	a*	b*	L*	a*	b*	W
Desized	23.2	1.1	-8.7	0	44.6	-1.3	-4.2	80.9	-1.9	4.9	31.5
Nc	25.3	0.9	-9.8	1.3	45.8	-1.7	-5.5	79	-2.8	2.4	28.5
10C Nc	26.2	0.8	-8.6	2.9	46.5	-1.3	-4.2	81.5	-3.6	3.8	34.9
20C Nc	27.7	0.5	-6.6	5	48	-1.1	-3.4	83.1	-4.5	5.9	38.1
30C Nc	30.1	0.2	-3.6	8.6	50.6	-0.8	-1.8	85.1	-6.2	8	44.6
Ac	25	0.9	-9.7	1.2	45.5	-1.8	-5.4	80.6	-2.8	2.9	29.3
10C Ac	26.1	0.8	-8.2	2.9	46.3	-1.5	-4.1	82.9	-3.5	4.1	35.1
20C Ac	27.4	0.6	-7.1	4.5	47.9	-1.2	-3.2	84.8	-4.6	5.9	40.4
30C Ac	29.8	0.3	-5.1	6.9	49.4	-0.9	-1.6	86.5	-6.5	8.3	45.8

L*, lightness; a*, redness–greenness; b* yellowness–blueness; ΔE, color difference with desized sample; W, whiteness

The ΔE values (i.e. the color difference of the treated samples with desized sample) indicated the color changes of treated samples with cellulase and that nanoclay along with cellulases and using more nanoclay increased ΔE values. Thus, nanoclay resulted in enhanced color changes, increased lightness and blueness and also decreased redness in comparison with applying the cellulase alone.

Using cellulases increases the lightness of the back of the sample as indicated by L* values in Table 2. The b* of the denim back indicated that nanoclay reduced back-staining of treated sample with nanoclay along with cellulase compared with denim treated with cellulases alone. b* of treated denim back decreases because of indigo absorbency by nanoclay. Thus, back-staining decreased and lightness increased due to the discoloration of denim back by nanoclay. Overall, bio washing with cellulases increases back-staining but adding nanoclay in bio washing furthermore increases the lightness of bio washed denim and the back staining was decreased.

Acid and neutral cellulase decreased the whiteness of the white pocket and turned it to blue because of redeposition of indigo dye (blue color) on the white pocket and denim back (according to b* and W values of the pocket material). Introducing the nanoclay to bio washing decreased the indigo staining on pocket material because of the indigo absorption by nanoclay and with increasing nanoclay and nanoclay along with cellulases in treated sample back-staining and staining on pocket is

decreased.

Overall, nanoclay was effective in increasing the whiteness and decreasing the staining. It also increased lightness of the white pocket and decreased the blueness. Nanoclay absorbed indigo dye from the effluent and then decreased the staining. As a result, the nanoclay can be used as discolour agent to denim stonewashing.

3.2. Color evaluation of effluent

The absorption spectra of the effluent from samples treated with cellulase, 10% nanoclay along with cellulase and 30% nanoclay along with cellulases after 30 min and complete precipitation are shown in Figure 2.

The curve relates to treated sample with cellulase indicated absorption at 650 nm in Figure 2. This demonstrates the existence of indigo in colored effluent (Figure 2). Absorption spectrum of the effluent including 10% nanoclay shows less absorption at 650 nm and effluent of the treated sample with 30% nanoclay along with the cellulases exhibited no absorption at 400–800 nm. It can be proposed that this effluent is free from indigo and the indigo absorption during bio washing by nanoclay in the processing bath.

It can be observed from absorption spectra of the effluents of the treated sample with 30% nanoclay that effluent of reused baths for biowashing has no peaks. Overall, because of indigo absorption by nanoclay is caused discoloration of surface denim and decrease of back-staining.

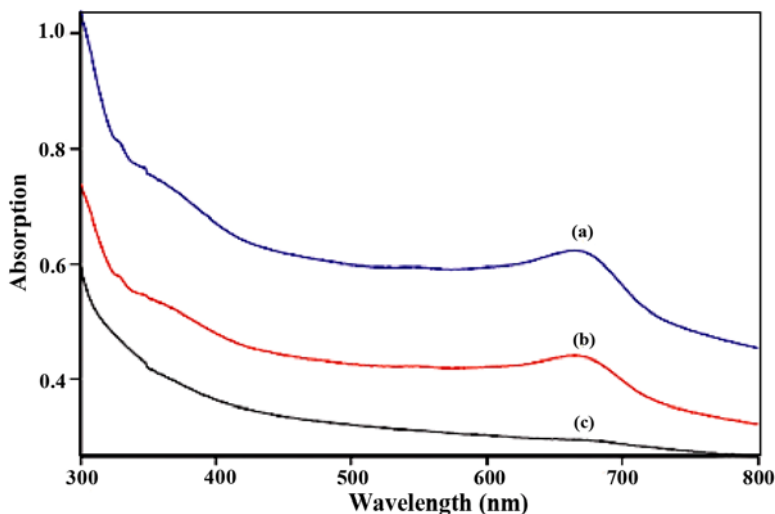


Figure 2: Absorption spectra of the effluents of the sample treated with cellulases (a); treated sample with cellulase along with 10% nanoclay (b); treated sample with cellulase along with 30% nanoclay (c).

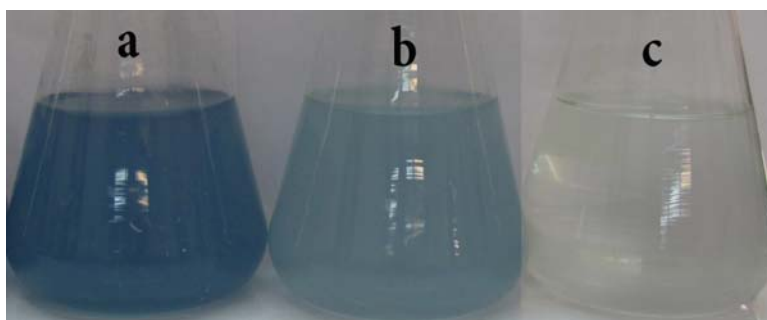


Figure 3: (a) Selected effluents of sample treated with cellulases; (b) treated sample with cellulase along with 10% nanoclay; and (c) treated sample with cellulase along with 30% nanoclay.

As Figure 3 showed while effluent of treated sample with cellulases is colored illustrating indigo in the effluent, the effluent of treated sample with 10% nanoclay is less colored and also effluent of treated sample with 30% nanoclay with cellulases are not colored due to using more nanoclay, which absorbed indigo from effluent and denim surface.

3.3. Mechanism of discoloration of denim by nanoclay

Nanoclay (Montmorillonite) is composed of two silicate tetrahedral and one aluminium octahedral sheets with aluminium sheets sandwiched between the two silicate

layers with modification by quaternary ammonium salt caused a net positive charge as shown in Figure 4 [18, 19].

When modified-nanoclay is used in nanoscale, the adsorptive characteristics improve because of large surface area of the nano-particles. Thus, the aromatic structure of the nanoclay sorbent because of modification with organic modification could substantially increase the sorption of an aromatic material. During denim biowashing with nano clay, clay layers are opened thus, surface area of nano clay increases (based on the interaction of the dyes on surface of the denim and in the effluent) and indigo dyes is absorbed into nanoclay. Finally, the discoloration of the surface denim and the

effluent is happened. Figure 5 shows mechanism of discoloration by nanoclay

Nanoclay and indigo dye (as an insoluble dye in water) have aromatic rings, so it can be concluded that the major contributive forces to dye sorption onto nanoclay were vander waals forces and hydrophobic

interaction. Furthermore, another possible mechanism is ionic attraction between the nanoclay modified with quaternary ammonium (positive charge) and indigo dye (negative charge).

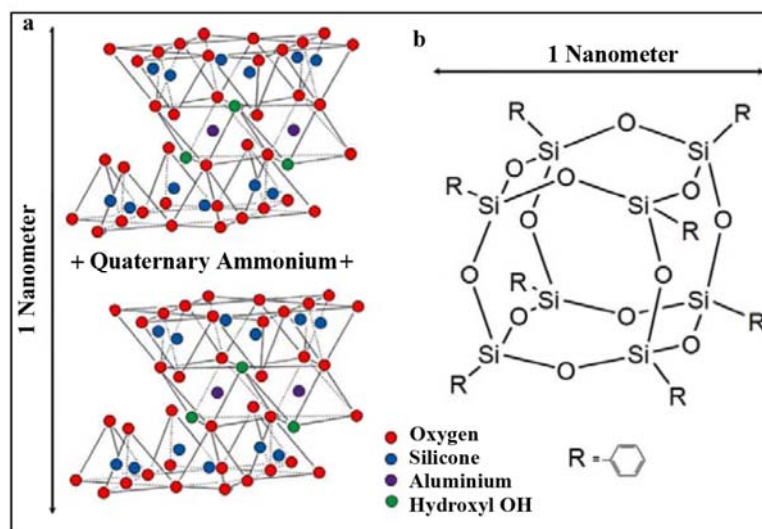


Figure 4: Chemical constitution of montmorillonite (nano clay)[18, 21].

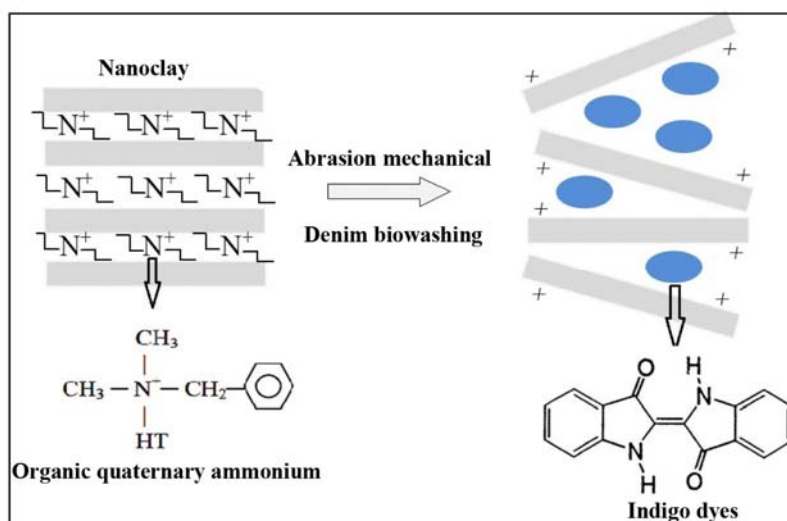


Figure 5: Schematic of the discoloration mechanism of denim by nanoclay.

Nanoclay, enormously abundant natural inorganic material, has been considered as a potential adsorbent for removing pollutants from water and effluent. Nonetheless, the effective application of nanoclay for water and wastewater treatment is limited due to small surface area and the presence of net negative surface charge leading to its low adsorption capacity for dyes and pollutants, so nanoclay should be modified to enhance the surface area, adsorption capacity and the range of applicability.

The modification of nanoclay which is itself a low-cost adsorbent drives the need for the development of a modification technique that is simple and cost-effective. Moreover, nanoclay is used in a powder form and when it is used in washing machine, some problems may happen for device due to nanoclay precipitation. The remaining nanoclay in garment has also allergic effect for people especially for children, so it needs serious washing cycles.

This is an easy, rapid, cost effective and environment friendly method. It provides high durability because the dye is chemically binding with clay structure. It seems that such findings are valuable for industry and also for those who respect the environment.

3.4. SEM & TEM images

The microscopic images of the surface of the samples are shown in Figure 6. In these images, the surface of the fibers is clearly observed. The fibers on desized samples (Figure 6(a)) are completely unchanged without any damage on their surface. However, on the cellulose

treated samples (Figure 6 (b) and (c)) the fibres on the fabric surface are damaged and some of them are ruptured remarkably while the inner fibers are remained unchanged without any damage.

Comparing samples treated with nanoclay/cellulase with cellulase, it can be seen that nanoclay particles have settled on the fiber surface and also have penetrated into the yarn bunches. As a result of enzymatic treatment in the washing machine using mechanical action and abrasion caused nanoclay layers to be opened and distributed on the fiber surface.

The microscopic images of the treated fibres are shown in Figure 7. SEM images of treated fabrics with cellulase and nanoclay in comparison with cellulase indicated loading of nano particles on fibre surface, thus during the washing process, the nanoclay layers are opened and well dispersed on the fibres also penetrated into the yarns bunches.

Figure 7 indicates the clear loading of nanoclays on the fabric surface. In all samples, the dimensions of particles were at nano-scale with ranging around 60 nm.

Figure 8 shows the TEM images of the nanoclay in the bio washing effluent of samples treated with cellulase along with nanoclay. As it can be seen, nanoclay layers are opened, separated and getting far from each other. The image of dispersed nanoclay before washing indicates that layers are not separated from each other and are placed in aggregated form. Overall, opened layer of nanoclay is increased the available surface of nanoclay caused increase in indigo absorption by nanoclay and enhanced discoloration of denim surface and effluent.

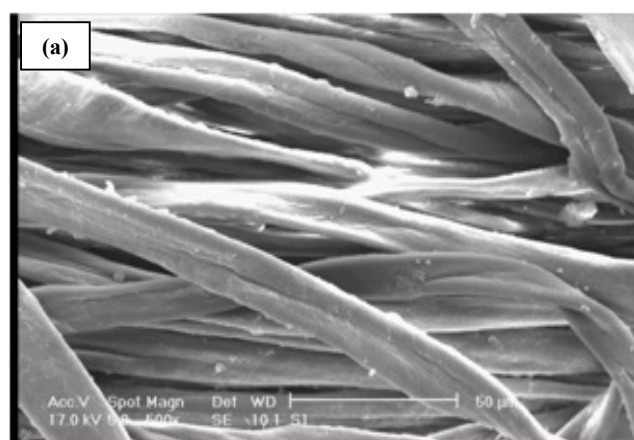


Figure 6: SEM images of desized sample (a); treated sample with cellulases (b); treated sample with cellulases along with 30% nanoclay.

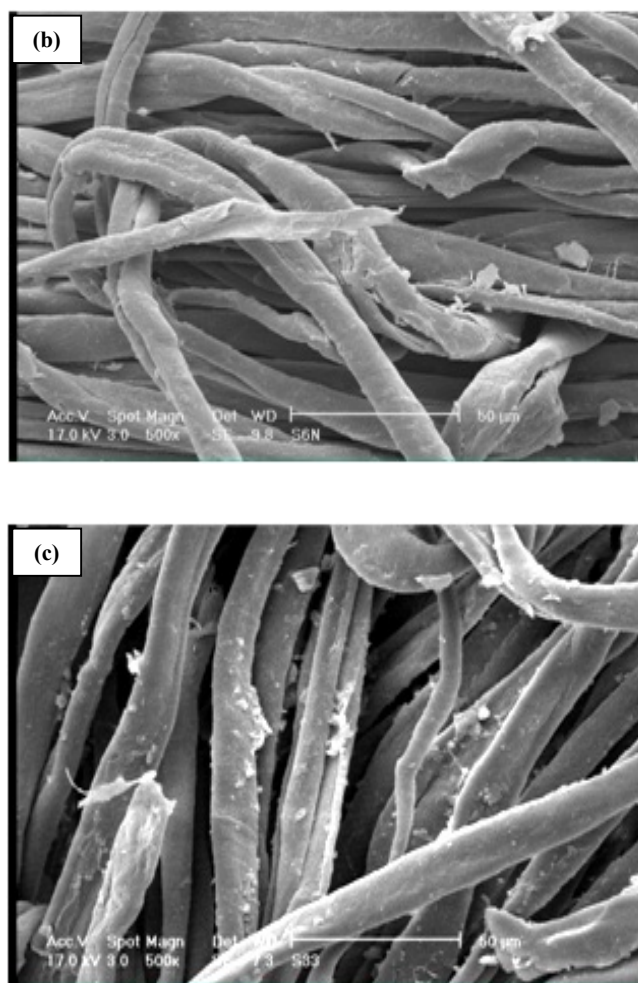


Figure 6: Continued.

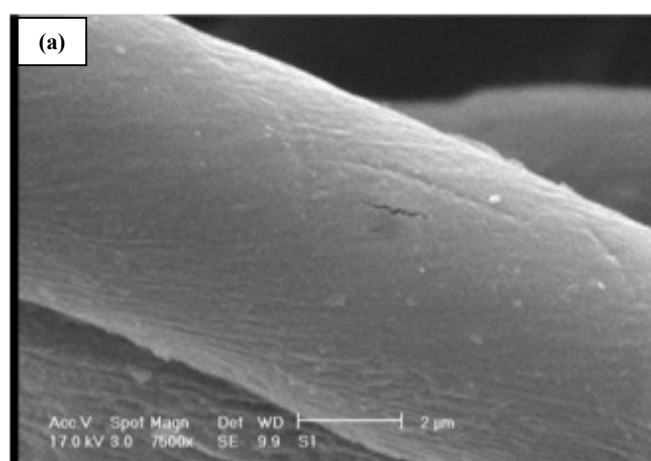


Figure 7: SEM images of the treated fiber with cellulases (a); treated sample with cellulases along with 30%nanoclay (b); nanoclay on fibres surface (c).

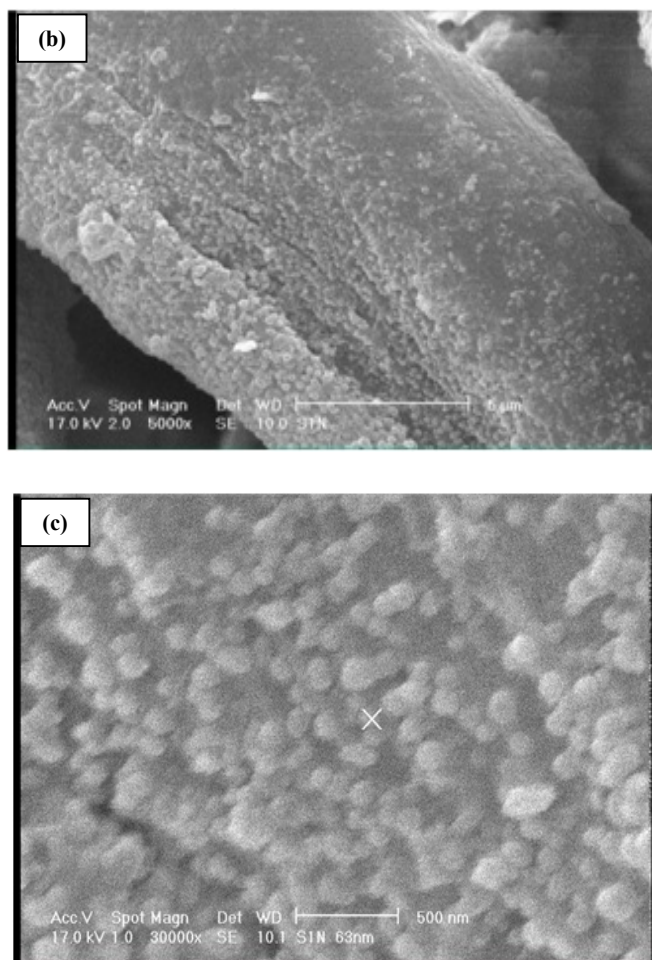


Figure 7: Continued.

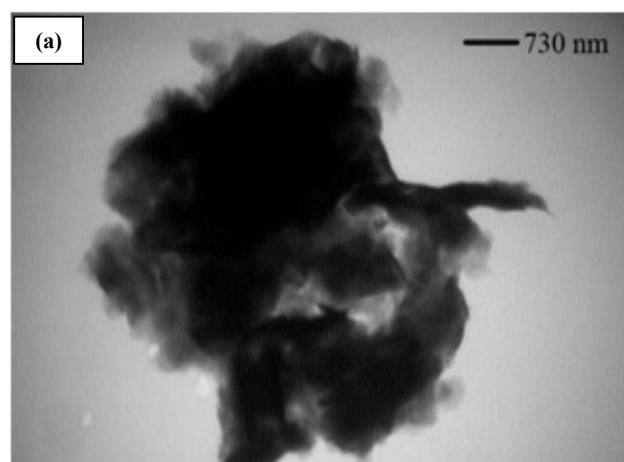


Figure 8: TEM images of nanoclay before biowashing (a); in disperse form after biowashing (b), (c).

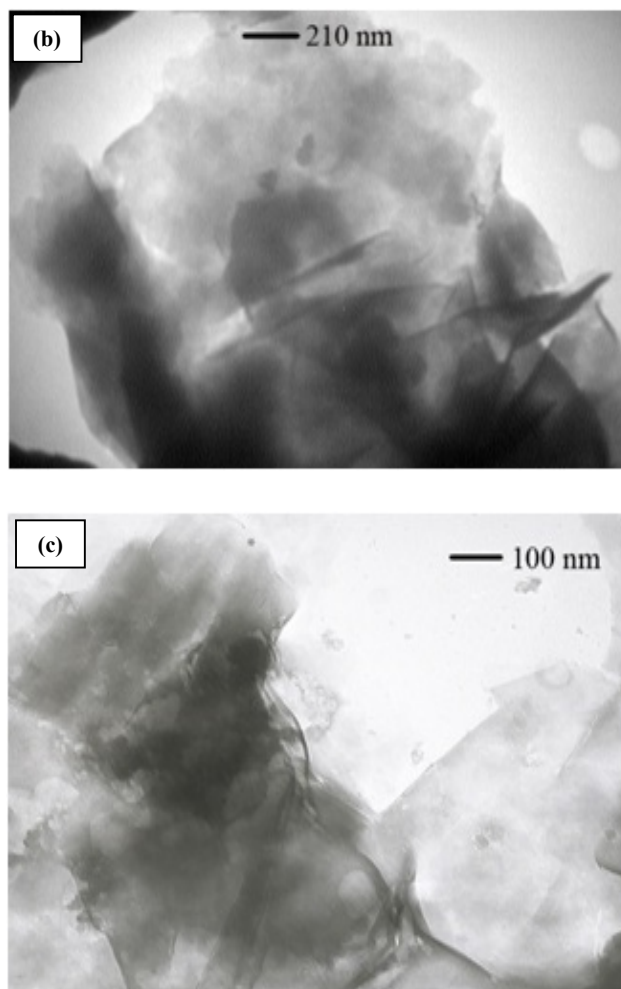


Figure 8: Continued.

4. Conclusions

In this study, the new discoloration method based on silicate nanoclay on denim garment was explored. In this method of denim stone, nanoclay (montmorillonite) along with common enzymes (cellulases) was applied. As a result, adding nanoclay enhanced lightness of the denim garment due to the absorbency of indigo by nanoclay and discoloration of the indigo on denim surface that is caused color change and decreased back staining. Also, the remaining

effluent of stone washing has been discolored through this method.

Besides, microscopic images are the evidence to the low damage of treated sample and nanoclay settle down on fiber surface of treated sample. Moreover, based on TEM images, it was proved that the nanoclay layers are opened, hence the absorbency of the indigo increases.

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