Chiang Mai J. Sci. 2018; 45(1) : 492-504
http://epg.science.cmu.ac.th/ejournal/
Contributed Paper

Modification of Bentonite with Different Surfactants and Substitute as a Mordant in Wool Natural Dyeing

Hossein Barani
Department of Carpet, University of Birjand, Birjand, Iran.
*Author for correspondence; e-mail: barani@birjand.ac.ir

Received: 23 April 2016
Accepted: 30 July 2016

ABSTRACT

Surfactant-clay interaction is very important for the development of their applications in different industries. The aim of this work was to evaluate the use of modified bentonite as a promising substitute for metallic mordants in the natural dyeing process. Therefore, the domestic bentonite was modified with different surfactants types such as a non-ionic, amphiphilic, and cationic surfactant. After that, the wool fabrics were pretreated with surfactant modified bentonite and followed was dyed with madder as a natural colorants. The pretreated wool fabric samples were evaluated by scanning electron microscopy (SEM), moisture regain measurement, and reflectance spectrophotometry. The SEM images of pretreated wool fabric with surfactant modified bentonite were indicated that the modified bentonite platelets were well dispersed and settled on the wool fiber surface. The average size of dispersed bentonite particles was about 0.85 μm ± 0.41. Moreover, the pretreated wool sample with PEG modified bentonite presented the highest color strength.

Keywords: bentonite, alizarin, color strength, polyethylene glycol, lecithin

1. INTRODUCTION

Natural colorants have been used since ancient times for dyeing carpet, rug and cloth and nowadays, they are being reintroduced to use in the coloration of textile and food material due to growing attention on harmful effects of synthetics dyes, such as water pollution, sustainability of raw material, and environmental aspects. They are preferred to use compared to synthetics dyes because of their environment friendly nature, lower toxicity, antibacterial properties, biodegradability, and harmonizing natural shades. Natural colorants are usually obtained from animal (insect) or vegetable such as roots, stems, barks, leaves, berries and flowers source without chemical processing [1-2]. Natural colorants are mainly mordant dyes and usually have weak dye fastness when applied on fabrics. It is common to improve their affinity to substrate or color fastness by applying metal salts as a mordant [3-4]. Metal salt mordants such as alum, chrome, stannous chloride, copper sulphate and ferrous sulphate have negative impact on the environment and public health [5]. Therefore, the use of metallic mordants during natural dyeing often puts a question mark on the eco-friendliness of natural dyes [6]. Several studies have already been dedicated to developing natural mordants which are nontoxic and eco-friendly in place of metallic mordants [7-8].

The aim of this work was to evaluate the use of bentonite as a promising substitute for metallic mordants in the natural dyeing process. Bentonite is a rock with montmorillonite as the main clay mineral constituent and mostly used as an industrial raw material for many applications such as ceramics, adhesives, catalysts, desiccants, cosmetics and pharmaceutical uses. Bentonite is highly valued for its adsorptive properties because of its physical and chemical characteristics [9]. It is low-cost and abundant clay which is primarily composed of montmorillonite. Bentonite is an absorbent aluminium phyllosilicate that belongs to the class of 2:1 phyllosilicates and has negative charges on its surface. Surface charge of montmorillonite platelets is originated from isomorphic substitutions in the crystal lattice and pH-dependent charges of Al-OH (aluminol) and Si-OH (silanol) groups at the broken edges of octahedral and tetrahedral sheets, respectively. The inner layers of bentonite are composed of an octahedral sheet, which is situated between two tetrahedral sheets. These negative charges are balanced by the exchangeable cations (Na^+, Ca^{2+}, etc.) at the interlayer space of bentonite. The layered structure of the bentonite expands after wetting. Na^+ and Ca^{2+} are strongly hydrated in the presence of water, resulting in a hydrophilic environment at its surface. It is well known that the bentonite has been used as adsorbent for the removal of basic dyes and the modified bentonite is used as adsorbent for the removal acid, reactive and from aqueous solutions due to the fact that they are a very abundant and inexpensive material in the world. The adsorption capacities of basic dyes are larger than acid dyes and reactive dyes due to the electron interactions and hydrogen bridging with the bentonite surface [10]. The net negative surface charge of bentonite in water causes the repulsion interaction with anionic dyes.

Domestic bentonite is modified before the uses which are depending on the intended application. These treatment modifications are thermal, mechanical, acidic treatment, inorganic cations exchange, functionalization by organic molecules etc [11]. The modification of bentonite with surfactant is a method to obtain organobentonite by transforming organophobic to strongly organophilic surfaces and therefore increases the adsorption capacity for adsorption of organic compounds [12]. In order to obtain more efficient sorbent, bentonite can modify with cationic surfactant or polymer to replace the inorganic cations of bentonite with organic cations and change the bentonite surface property from hydrophilic to hydrophobic. The replacement of the natural inorganic cations with organic cations has been extensively studied with two objectives which are to remove the organic cations from the solution and the other is to alter the surface properties of swelling clays in order to improve their adsorption capacity [13].

The possibility of using bentonite instead of metallic mordant in natural dyeing process was assessed [14]. It is stated that the bentonite-pretreated wool samples presented higher dyeing properties compared with untreated wool. Moreover, their color strength improved with an increasing amount of clay in the pretreatment bath. In addition, it was reported that Nano-clay coating on cotton fibers [15] reduces flammability, thermal degradation, and wrinkle-ability of cotton fabric. According to the authors' knowledge, there are a several literatures on the modifications of montmorillonite with surfactants, but there is no specific comparative study on their adsorption properties of modified bentonite with different surfactant types such as a non-ionic, amphiphilic, and cationic surfactant. In the present paper, wool fabric was pretreated with bentonite that was modified with different types of surfactant, followed dyed with madder as a natural colorants. The pretreated wool fabric samples were evaluated by scanning electron microscopy (SEM), moisture regain measurement, reflectance spectrophotometry.

2. MATERIALS AND METHODS

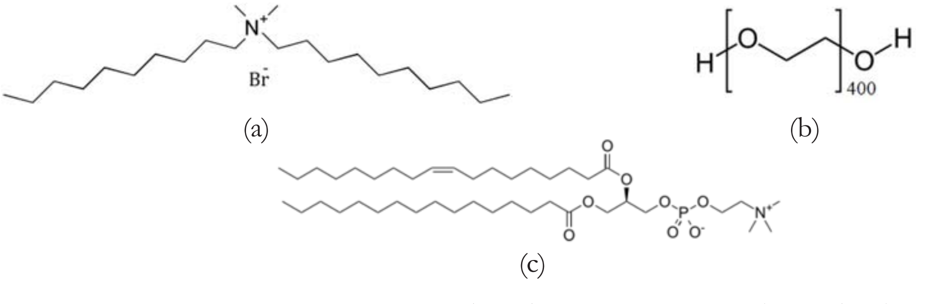
2.1 Materials

A plain wool fabric structure (100% wool yarn; 48/2 Nm) with a warp and weft density of 17 ends/cm was supplied by Iran Merinos Co, Iran. In order to remove the wool impurities, it was washed with a non-ionic detergent (1 g/L) for 30 min at 50 °C (Liquor to goods ratio or L: G = 40:1), then rinsed with tap water and dried at room condition. Bentonite was obtained from Birjand city which is located at South Khorasan, Iran. Firstly, the domestic bentonite was milled and passed through a 100 mesh screen. Moreover, the mass percentage of chemical compositions of domestic bentonite obtained by X-ray fluorescence (XRF) and is listed in Table 1. The other chemical materials were used at this study were in an analytical grade.

According to the literature, the cation exchange capacity (CEC) of the sodium-bentonite is 90 mequiv./100g [16]. Didecyldimethylammonium bromide (DDAB) was selected as a cationic surfactant (Figure 1a) with a molar mass of 462 g/mol, and a density of 0.95 g/ml at 20 °C (obtained from Sigma-Aldrich). It has a valence of one, thus it has one molar equivalent. Polyethylene glycol 400 (PEG 400) is a low-molecular-weight grade of polyethylene glycol. It was selected as non-ionic surfactants (Figure 1b) with an average molar mass of 400 g/mol, and a density of 1.128 g/ml at 20 °C (obtained from Sigma-Aldrich). Lecithin is amphipathic lipid (Figure 1c) which has different affinities for oil and water [17]. It was received from Lipoid Co. (Lipoid® S 75; Germany).

Table 1. Chemical composition of domestic bentonite.

Chemical composition	Fe_2O_3	CaO	K_2O	Al_2O_3	SiO_2	MgO	Na_2O
Mass percentage	1.98	0.98	0.35	11.23	65.43	2.86	6.12



(a) (b)

(c)

Figure 1. Chemical structure of (a) Didecyldimethylammonium bromide, (b) Polyethylene glycol (PEG) and (c) Phosphatidylcholine which is the main component of Soybean lecithin (contains 70% phosphatidylcholine).

2.2 Bentonite Modification

The domestic bentonite powder was dispersed at 2.5 wt% in distilled water, and stirred (approximately 1500 rpm) on a hotplate stirrer for a period of 24h at room temperature and finally followed by careful decanting of the supernatant suspension. The stock bentonite suspension is used at the further process. The domestic bentonite was modified at 1, 2, and 4 CEC by adjusting the molar quantity of DDAB, PEG400, and lecithin. According to the CEC of the bentonite [16], 1 CEC meant 90 mmol surfactant per 100 g of bentonite. Therefore, appropriated stock bentonite suspension was added drop wise to an aqueous solution of prepared surfactant with heating (60 °C) and stirring (approximately 1500 rpm) for at least 60 min. This colloidal solution was used at further pretreatment process of wool fabric.

2.3 Bentonite Pretreatment of Wool

The process was carried out using the prepared colloidal solution of bentonite and acetic acid buffer solution for adjusting the pH 5 at L:G of 40:1. The wool fabric sample was introduced to the prepared colloidal solution (Table 2), while its temperature was around 40 °C. The temperature was raised gradually to the boiling point (95 °C at the laboratory condition) with gradient of 3 °C min^{-1}, and followed at this temperature for 1h. Finally, the treated wool fabrics were rinsed with distilled water and dried at the room condition.

Table 2. Characteristics of bentonite colloidal solution that was pretreated on wool fabric samples.

Concentration (OWF%)	CEC	Surfactant Type	Sample code
5	0	-	Bent
5	2	Polyethylene glycol	Bent-PEG
5	2	Didecyldimethylammonium bromide	Bent-DDBr
5	2	lecithin	Bent-Lec

2.4 Dyeing Procedure

To extract the dye from the madder, the well-milled parts of roots were boiled in water for 60 minutes and stirred simultaneously. After that, the dyestuff solution was cooled to the room temperature and filtered through a whatman No. 1 filter paper. The dyeing process was carried out using the madder solution (100% on weight of fabric sample) and acetic acid for adjusting the pH 5 at L:G of 40:1. The pretreated wool fabric sample with bentonite was introduced to the dyeing bath solution at around 50 °C. The temperature was raised gradually to the boiling point with gradient of 2 °C min^{-1}, and followed at this temperature for 1h.

2.5 Surface Morphology of Wool Fibers

The surface morphology of the wool fibers were characterized by scanning electron microscopy (SEM) (Zeiss, Merlin Series). This microscope was equipped with Energy Dispersive X-ray Spectroscopy (EDS). The EDS can provide rapid qualitative, and quantitative analysis of elemental composition with a sampling depth of 1-2 microns. Firstly, a piece of wool fabric sample was coated with a gold layer and then observed by SEM. The average diameter of bentonite particles were determined using Digimizer.4.1.1.0 software through measuring at least 20 measurements were taken.

2.6 Color Coordinates and Color Strength Measurement

The spectral reflectance of all wool fabric samples was measured using a Color-Eye spectrophotometer from Gretag Macbeth in the visible region. In order to evaluate the color characteristic of dyed wool fabric samples, the CIE color coordinates, namely, L^*, a^*, b^*, and C^*, were measured under illuminant D65 and 10° standard observer. Color strength (K/S) values of the dyed wool samples were calculated using Kubelka-Munk equation (1) as follows:

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

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

2.7 Fastness Properties Assessment on Dyed Samples

The color fastness of dyed wool samples to wash and light was tested according to ISO standard test method. Color fastness to wash was according to ISO105-CO2:1989, and color fastness to light was assessed according to ISO105-B02:1994.

2.8 Moisture Regain and Water Absorption Evaluation

Moisture regain of the samples were tested under standard conditions (RH 65% and 25 °C). Moisture regain was calculated using the following equation:

$$\text{Moisture Regain } \% = (M_1-M_2)/M_2 \times 100 \quad (2)$$

Where M_1 is the weight (g) of the wool fabric sample after conditioned for 24h at standard conditions, and M_2 is the weight (g) of the wool fabric sample was dried in the oven at 105 °C for 30min.

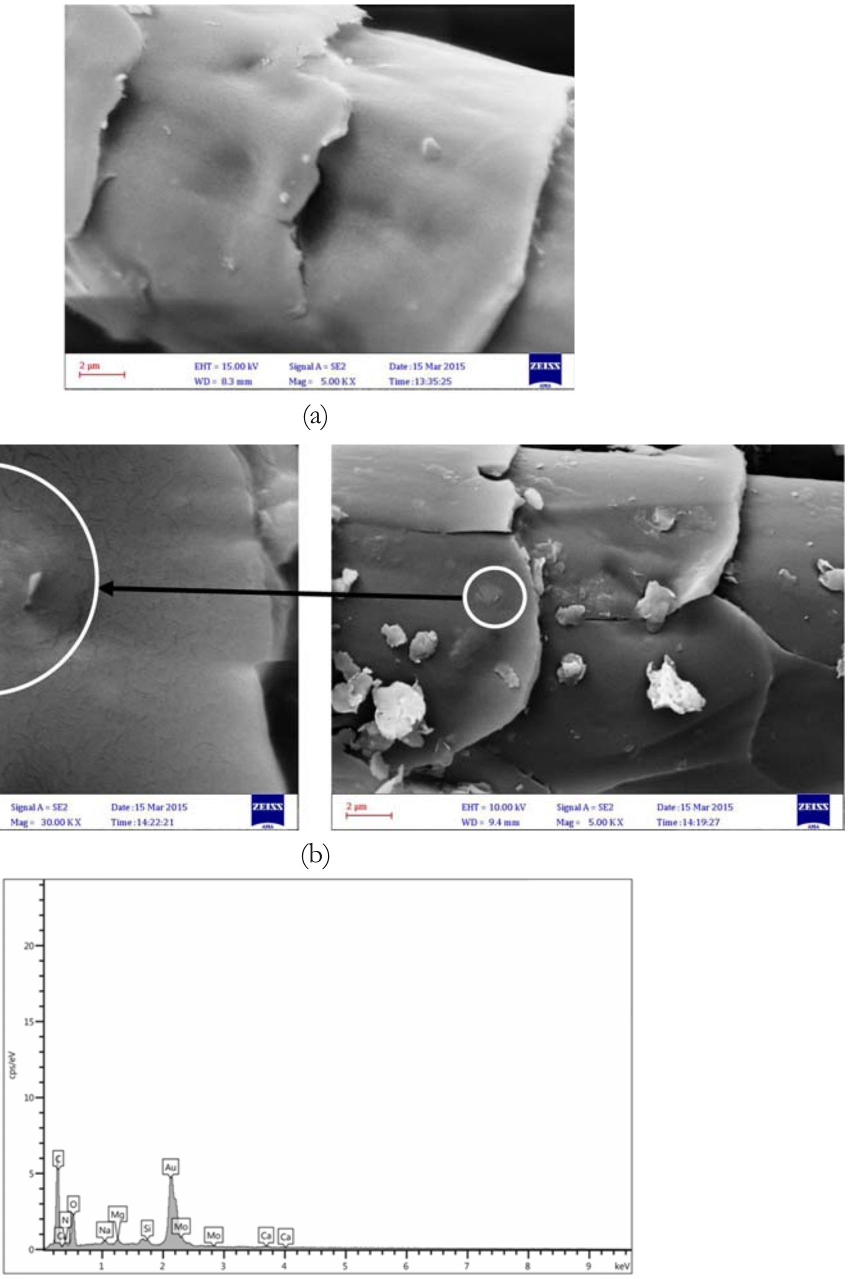
In order to determine the wettability of treated and untreated wool fabrics, a drop of distilled water (17 μl volume) from specific distance, was placed on the surface of fabrics. After that, the required time for a drop to be completely absorbed by the fabric was measured. For each sample, at least 5 measurements were taken and average absorbance time values were calculated.

3. RESULTS AND DISCUSSION

3.1 Surface Morphology Characterization

SEM was used to probe bentonite platelets on the surface of pretreated wool fabric samples and to observe the change in morphological features of wool fibers. Figure 2 shows the SEM micrographs of untreated and treated wool samples with modified bentonite. The outer layer of wool surface is covered with scales from the cuticle (Figure 2a). Overlapping structure of these scales in one direction is the characteristic feature of wool fibers and the untreated and treated samples presented this specific feature of wool fibers. However, the scale surface morphology of the bentonite treated wool sample was different from the untreated. The smooth scales surface is converted to the rough surface due to treating with bentonite platelets (Figure 2b). Moreover, The SEM images of treated wool fabric with modified bentonite indicated that the bentonite platelets were partially dispersed and settled on the wool fiber surface. The average size of dispersed bentonite particles was about 0.85 μm ± 0.41.

The elemental analysis of pretreated wool fabric with bentonite is presented in Figure 2c that confirmed samples included calcium, sodium, silica, and magnesium on their surface. This is indicated that elements on the surfaces of wool fiber sample relates to bentonite particles. The presence of gold element at the EDS spectra is related to the gold coating before capturing SEM images.



(a)

(b)

(c)

Figure 2. SEM images of wool fiber samples a) untreated wool fiber b) wool fiber treated with surfactant modified bentonite c) EDS spectra of the sample treated with surfactant modified bentonite.

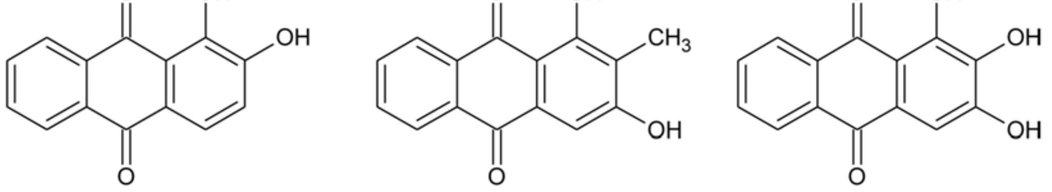
3.2 Colorimetric Characteristics of Dyed Wool Samples

In order to find out the effect of surfactant type on the color strength (K/S) of dyed wool fabric, the bentonite was modified with different types of surfactant (cationic, non-ionic, and amphipathic) and wool fabric was treated with them before natural dyeing process. As it can be seen in Table 3, the average color strength of dyed wool sample that pretreated with bentonite was higher than the untreated one. Therefore, the presence of bentonite was enhanced the dye absorption in to the wool structure fiber and led to higher color strength.

Table 3. The K/S Value of different wool fabric samples dyed with madder.

Sample code	Average Reflectance	Average Color Strength
Untreated	0.19	1.72
Bent	0.18	1.86
Bent-PEG	0.14	2.65
Bent-DDBr	0.16	2.21
Bent-Lec	0.15	2.4

The main chemical coloring constituent of madder are alizarin, rubiadin, and purpurin (Figure 3) [18-19]. Madder is mordant natural colorant, it produces brightly colored insoluble complexes or lakes with metal ions present on the mordanted fabric. Metal ions capable to form a bridge between the functional groups of the dye and the wool protein and led to higher dye exhaustion as well as enhance fastness [20]. When using bentonite as mordant, the colorant molecules might not be adsorbed on the bentonite surface due to net negative charge on bentonite surface platelets owing to substitutions of trivalent aluminium and magnesium within the lattices [9]. However, these negative charges are balanced by the presence of exchangeable cations (Na^+, Ca^{2+}, etc.) that occupy the interlayer space of bentonite [21]. The adsorption of uncharged organic component on bentonite minerals is generally considered to entropy driven, but several factors can influence the extent of adsorption [22]. It has been proposed that the hydroxyl groups at broken edges of bentonite platelet serve as the principal adsorption sites for anions [23]. Therefore, the adsorption of coloring constituent of madder was occurred by the following mechanisms; (I) hydrogen bonding that occurs between hydroxyl groups of coloring constituent of madder and Al-OH (aluminol) and Si-OH (silanol) groups at the broken edges of octahedral and tetrahedral sheets, respectively [23], (II) the multivalent hydrated cations in interlayer position may also be involved in the adsorption of dye molecules and acting as bridges to the bentonite structure (Figure 4) and (III) the van der Waals forces.



Alizarin
(1, 2- dihydroxyanthraquinone)

Rubiadin
(1,3-dihydroxy-2-methylanthraquinone)

Purpurine
(1,2,4-Trihydroxyanthraquinone)

Figure 3. The main chemical components coloring constituent of madder.

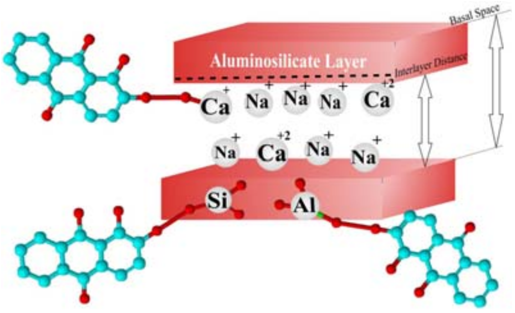


Figure 4. The proposed adsorption mechanism process of madder dye molecules on bentonite sheets.

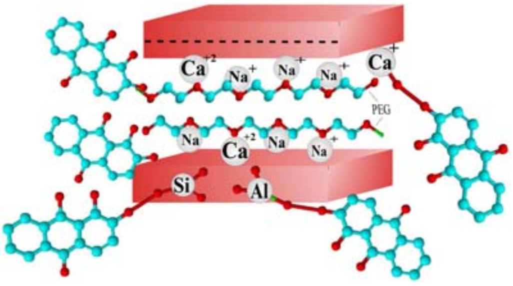


Figure 5. The proposed adsorption mechanism process of madder dye molecules on PEG modified bentonite sheets.

Moreover, the average color strength of dyed wool sample that pretreated with surfactant modified bentonite was higher than the sample pretreated with unmodified bentonite. The obtained results were in agree with other literatures that reported the anion exchange capacity of bentonite can be enhanced using surfactants [23]. The pretreated wool sample with PEG-bentonite presented the highest color strength, because the adsorption on the modified bentonite depends on the kind of surfactant, and pH of the solutions [24]. Plamondon et al [16] reported that the basal spacing of montmorillonite can be adjusted with the use of a surfactant. The extent of intercalation depends on the type of surfactant and its concentration. They stated that the non-ionic surfactant causes only a crystalline expansion of bentonite interlayer (Figure 5), while the cationic surfactant induces an osmotic intercalation. The amphiphilic lecithin derivatives intercalate more extensively with the bentonite matrix. Therefore, can conclude that the lower basal spacing interlayer due to pre-treat with nonionic surfactant resulted to higher adsorption of madder dye molecules as well as higher color strength.

The color coordinates of dyed wool fabric which was pretreated with different value of CEC are presented in Figure 6. The a* value represents the red-green coordinate (+ve= red, -ve = green), and b* represents the yellow-blue coordinate (+ve = yellow, -ve= blue), and the c* represents chroma or 'saturation'. This ranges from 0 at the center, which is completely unsaturated (i.e. a neutral grey, black or white) to 100 or more for very high Chroma (saturation) or 'color purity'. It is clear that the pretreated wool sample with CEC of 1 resulted to highest Chroma (35.01) as well as lower hue angle (38.5 °). Poly(ethylene glycol) (PEG) derivative additives have been used to reduce clay swelling which can arrive to the surface with minimum dispersion and disintegration [25]. Therefore, it seems that the higher poly (ethylene glycol) concentration resulted to the lower dispersion of modified bentonite that was affected on its loading efficacy into the wool fabric and dye molecules adsorption.

The color strength of dyed wool fabric sample which was pretreated with different concentration of PEG400 is presented in Figure 7. This results, also confirmed that the sample pretreated with PEG400-Bentonite at CEC of 1 presented higher color strength. PEG is polar and miscible in water; it is compatible with aqueous bentonite mineral suspensions and interacts at the molecular level [22]. It is stated that the hydroxyl groups present on edge sites of montmorillonite and the water bound to the exchangeable cations readily form hydrogen bonds with the hydroxyl groups terminating the PEG chains. Moreover, there is a competition between poly (ethylene glycol) and water molecules for the adsorption sites on the bentonite and it is able to reduce the hydration water of the bentonite complexes. Therefore, the higher absorption of poly (ethylene glycol) resulted to the lower absorption of water molecules as well as dye molecules. Moreover, when high levels of PEG were offered to Na-bentonite only a bilayer of PEG (Figure 5) could be accommodated in the clay interlayer [22] that can affect the dye molecule adsorption.

The color strength of dyed wool fabric sample which was pretreated with PEG400 at different concentration of hydrated potassium aluminium sulfate (Alum; $KAl(SO_4)_2{\cdot}12H_2O$) is presented in Figure 8. It is clear that adding Al^{+3} in to the bentonite complex structure was resulted to obtain higher color strength. Polyvalent metal cations (Al^{3+}) specifically adsorbed on edges of octahedral and tetrahedral sheets, contributing to the positive surface charge and form bridges between the bentonite particles and organic anions[23]. Therefore, the presence of Al^{3+} in the bentonite structure was enhanced the dye molecules adsorption as well as color strength of dyed wool fabric. Figure 9 shows the SEM micrographs of pretreated wool sample with PEG modified bentonite in presence of Al^{3+}. The SEM images of pretreated wool fabric with PEG-Al-bentonite compared with only PEG-bentonite (Figure 9b) indicated that the bentonite platelets were well dispersed and settled on the wool fiber surface.

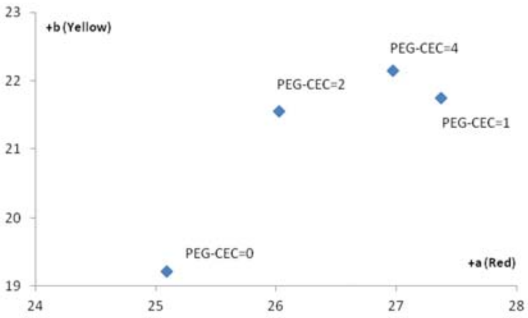


Figure 6. The color coordinates of dyed wool fabric that pretreated with different value of CEC.

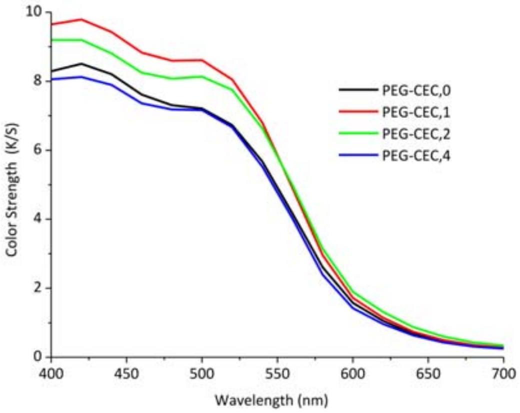


Figure 7. The color strength of dyed wool fabric sample which was pretreated with different concentration of PEG400.

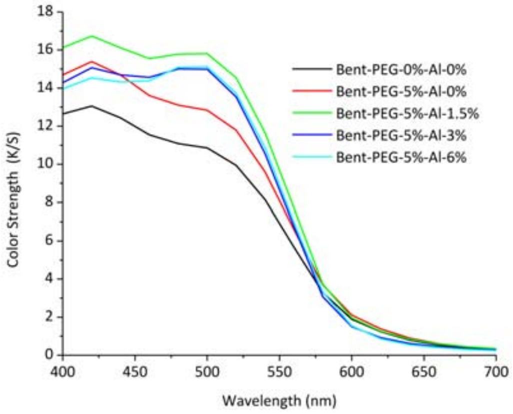


Figure 8. The color strength of dyed wool fabric sample which was pretreated with PEG400 at different concentration of hydrated potassium aluminium sulfate.

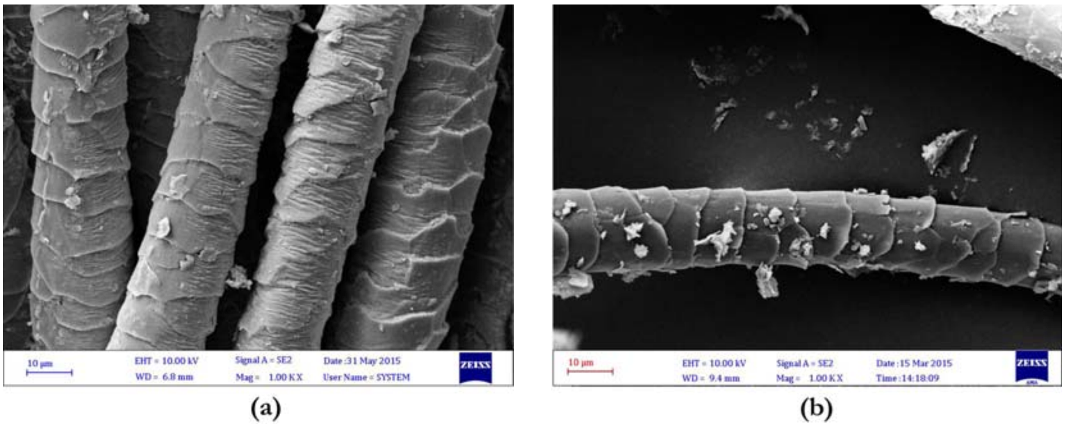


Figure 9. The SEM micrographs of wool fabric sample which was pretreated with modified bentonite a) PEG-Al b) PEG.

3.3 Fastness Assessment

The obtained results from the wash and light-fastness tests are presented in Tables 4. For the wash fastness tests of the colored wool fabric, a piece of dyed sample was sewn together with white pieces of wool and cotton fabric and washed. The wash fastness of madder-dyed wool fabric was not improved, when pretreated with bentonite and PEG-bentonite, which might be due to the hydrogen bonds between alizarin molecules and the bentonite outer layers not being strong enough to immobilize dye molecules[14]. But, madder dyed wool fabric that was pretreated with PEG-Al-bentonite presented a good wash fastness due to formation of insoluble complexes or lakes [20].

Table 4. Fastness evaluation of untreated and bentonite pretreated wool fabric and dyed with madder.

Sample	Wash fastness	Staining on cotton	Staining on wool	Light fastness
Pristine sample	4	4-5	4-5	6-7
Bent	4	4-5	4-5	7
Bent-PEG	4	4-5	4-5	7
Bent-PEG-Al	5	5	5	7

It was observed that bentonite pretreatment of madder dyed wool fabric improved the light fastness compared with the untreated sample. As stated earlier, there is an intermolecular attraction between alizarin, wool, and bentonite layers. Amino acids are able to transfer UV radiation to alizarin molecules, can reduce the light fastness of dyed fabric, followed by further transmittance to the bentonite surface via π-interactions of the dye. This phenomenon might inhibit the degradation of the dye molecules and enhancing the light fastness of the samples. This result was further confirmed by other research groups [14].

3.4 Moisture Regain and Water Absorption

Wool is a protein fiber that composed of keratin. The outer surface wool fiber is covered by a fatty acid layer that creates a hydrophobic surface and preventing water drop absorption and sweat venting [26]. It is well known that the chemical composition and surface topography affect the fabric wettability. Several techniques were applied to create hydrophilic wool fiber surface, which can be classified into two major types: decomposing the fatty surface layer and coating the fatty surface layer of wool fibers with hydrophilic materials or nano-materials [27]. It is stated that water molecules are intercalated into the interlamellar space of bentonite in aqueous solutions and it is inherently hydrophilic in nature because of the hydration of metal ions [28]. Therefore, the pretreatment of wool fabric with bentonite or modified bentonite covered the hydrophobic components of wool fiber surface and resulted to hydrophilic surface and reduced the water drop absorption time (Table 5). On the other hand, the pretreated wool fabric presented the lower moisture regain compared with untreated wool fabric. Therefore, it can be asserted that pretreatment with hydrophilic bentonite did not lead to increase moisture absorption of treated wool fabric.

Table 5. Water drop absorption times and moisture regains of dyed wool fabrics that pretreated with different type of bentonite.

Sample	Pristine sample	Bent	Bent-PEG	Bent-PEG-Al
Time of water drop absorption (s)	2054	73	27	56
Moisture Regain (%)	12.5	5.9	5.3	5.1

4. CONCLUSIONS

The aim of this work was to consider the use of domestic bentonite or surfactant modified bentonite as a mordant in the natural dyeing process of wool fibers with madder. Therefore, the wool fibers were pretreated with domestic bentonite solution or modified one with different surfactants types and followed dyed with madder as a natural colorant.

The SEM images of pretreated wool fabric with surfactant modified bentonite indicated that the bentonite platelets were partially dispersed and settled on the wool fiber surface. The average size of dispersed bentonite particles was about 0.85 μm ± 0.41. Although, the SEM images of pretreated wool fabric with PEG-Al modified bentonite compared with only PEG modified bentonite indicated that the bentonite platelets were well dispersed. Therefore, the presence of Al^{3+} ion enhanced the dispersion and settlement of bentonite on the wool fabric sample. Moreover, the elemental analysis of pretreated wool fabric with modified bentonite was indicated that this sample included calcium, sodium, silica, and magnesium on its surface which is related to bentonite particles.

Madder colorant is a mordant colorant and it is common to improve its affinity to fibers or color fastness by applying mordant. The color strength of dyed textile has a direct correlation with its colorant concentration. The obtained results indicated that pretreatment of wool fibers with bentonite resulted to higher dye molecules absorption due to color strength of dyed sample. The average color strength of dyed wool sample that pretreated with bentonite was higher than the untreated one and the PEG (CEC= 1) modified bentonite presented the highest color strength. It can be concluded that the presence of bentonite was enhanced the dye absorption into the wool fiber structure that led to higher color strength.

In addition, the adding of Al^{3+} into the bentonite structure was enhanced the dye molecules adsorption as well as color strength of dyed wool fabric.

The pretreatment of wool fabric with bentonite or modified bentonite covered the hydrophobic components of wool fiber surface and resulted to hydrophilic surface and resulted to reduce the water drop absorption time. On the other hand, the pretreated wool fabric presented the lower moisture regain compared with untreated wool fabric. Therefore, it can be concluded that the pretreatment with bentonite did not lead to increase absorption of moisture in the wool fabric.

ACKNOWLEDGEMENT

The author is grateful to the Birjand University Research Council for the financial support.

REFERENCES

[1] Lichtfouse E., Schwarzbauer J. and Robert D., *Green Materials for Energy, Products and Depollution*, 2013: Springer. DOI 10.1007/978-94-007-6836-9.

[2] Meena C.R., *J. Text. Assoc.*, 2011; **72(3)**: 193-194.

[3] Barani H., Nasiri Broumand M. and Haji A., *J. Nat. Fibers*, 2012; **9(2)**: 73-86. DOI 10.1080/15440478.2012.681485.

[4] Haji A., *Mater. Sci.*, 2012; **18(3)**: 267-270. DOI 10.5755/j01.ms.18.3. 2437.

[5] Moiz A., Ahmed M.A., Kausar N., Ahmed K. and Sohail M., *J. Saudi Chem. Soc.*, 2010; **14(1)**: 69-76. DOI 10.1016/ j.jscs.2009.12.011.

[6] Uddin M.G., *J. Text.*, 2014; **2014**: 1-8. DOI 10.1155/2014/405626.

[7] Haji A., *Iran. J. Chem. Chem. Eng.*, 2010; **29(3)**: 55-60.

[8] Vankar P.S., Shanker R. and Verma A., *J. Clean. Prod.*, 2007; **15(15)**: 1441-1450. DOI 10.1016/j.jclepro.2006.05.004.

[9] Zhang F., Wu X., Chen Y. and Lin H., *Fiber. Polym.*, 2009; **10(4)**: 496-501. DOI 10.1007/s12221-009-0496-8.

[10] Leodopoulos C., Doulia D. and Gimouhopoulos K., *Sep. Purif. Rev.*, 2014; **44(1)**: 74-107. DOI 10.1080/15422119. 2013.823622.

[11] Djowe A., Laminsi S., Njopwouo D., Acayanka E. and Gaigneaux E.M., *Plasma Chem. Plasma Procs.*, 2013; **33(4)**: 707-723. DOI 10.1007/s11090-013-9454-8.

[12] Wang C., Jiang X., Zhou L., Xia G., Chen Z., Duan M. and Jiang X., *Chem. Eng. J.*, 2013; **219(0)**: 469-477. DOI 10.1016/j.cej.2013.01.028.

[13] Bilgiç, C., Yazycy D.T., Karakehya N., Çetinkaya H., Singh A. and Chehimi M.M., *Int. J. Adhes. Adhes.*, 2014; **50(0)**: 204-210. DOI 10.1016/j. ijadhadh.2014. 01.033.

[14] Parvinzadeh Gashti M., Katozian B., Shaver M. and Kiumarsi A., *Color. Technol.*, 2014; **130(1)**: 54-61. DOI 10.1111/ cote.12065.

[15] Yuen C., Kan C.W., Wong W.K. and Lee H.L., *J. Appl. Polym. Sci.*, 2006; **99(6)**: 3700-3707. DOI 10.1002/app.23170.

[16] Ouellet-Plamondon C.M., Stasiak J. and Al-Tabbaa A., *Colloid. Surface. A: Physicochemical and Engineering Aspects*, 2014; **444(0)**: 330-337. DOI 10.1016/j. colsurfa.2013.12.032.

[17] Barani H. and Montazer M., *J. Liposome Res.*, 2008; **18(3)**: 249-262. DOI 10.1080/ 08982100802354665.

[18] Muthu S.S., *Roadmap to Sustainable Textiles and Clothing: Environmental and Social Aspects*

of Textiles and Clothing Supply Chain, 2014. DOI 10.1007/978-981-287-065-0.

[19] Ghaheh F.S., Mortazavi S.M., Alihosseini F., Fassihi A., Nateric A.S. and Abedi D., *J. Clean. Prod.*, 2014; **72(0)**: 139-145. DOI 10.1016/j.jclepro.2014.02.050.

[20] Barani H. and Maleki H., *J. Disper. Sci. Technol.*, 2011; **32(8)**: 1191-1199. DOI 10.1080/01932691.2010.505525.

[21] Epstein M. and Yariv S., *J. Colloid Interf. Sci.*, 2003; **263(2)**: 377-385. DOI 10.1016/S0021-9797(03)00339-4.

[22] Mongkholrattanasit R., Saiwan C., Rungruangkitkrai N., Punrattanasin N., Sriharuksa K., Klaichoi C. and Nakpathom M., *J. Nat. Fibers*, 2016; **13(1)**: 65-76. DOI 10.1080/15440478.2014.984056.

[23] Errais E., Duplay J., Elhabiri M., Khodja M., Ocampo R., Baltenweck-Guyot R. and Darrag F., *Colloid. Surface. A: Physicochemical and Engineering Aspects*, 2012; **403(0)**: 69-78. DOI 10.1016/j.colsurfa.2012.03.057.

[24] Díaz-Nava M.C., Olguín M.T. and Solache-Ríos M., *J. Incl. Phenom. Macro. Chem.*, 2012; **74(1-4)**: 67-75. DOI 10.1007/s10847-011-0084-6.

[25] Tork M.B., Nejad N.H., Ghalebaghi S., Bashari A., Shakeri-zadeh A. and Kamrava S.K., *J. Ind. Text.*, 2016; **45(6)**: 399-1416. DOI 10.1177/1528083714560255.

[26] Montazer M., Pakdel E. and Moghadam M.B., *Colloid. Surface. A: Physicochemical and Engineering Aspects*, 2011; **375(1-3)**: 1-11. DOI 10.1016/j.colsurfa.2010.10.051.

[27] Barani H., Montazer M., Calvimontes A., and Dutschk V., *Text. Res. J.*, 2013; **83(12)**: 1310-1318. DOI 10.1177/0040517512464290.

[28] Ikhtiyarova G.A., Özcan A.S., Gök Ö. and Özcan A., *Clay Miner.*, 2012; **47(1)**: 31-44. DOI 10.1180/claymin.2012.047.1.31.