Energy-efficient dyeing of wool fabrics with sulfonic acid derivatives of aniline by oxidation polymerization

ABSTRACT

Traditionally, wool fibers are dyed with acid dyes at the boil, an energy-intensive process, which increases the cost of dyeing. The development of alternative energy-efficient dyeing processes is quite attractive to the textile industry to make textile dyeing sustainable. In this work, the feasibility of low-temperature dyeing of wool fabric with several aniline sulfonic acid (ASA) derivatives by oxidative polymerization method was investigated. The effect of dyebath conditions, such as monomer concentration, monomer to oxidant ratio, pH, temperature, and time on the shade produced and color strength was systematically studied. The treatment with various ASAs produced various yellowish-brown color shades with tonal change. The treatment conditions had a great effect on color strength and colorfastness to washing. The optimum treatment conditions were found to be pH 3, 30 °C, and 60 min. The excellent colorfastness to washing exhibited by the ASA-treated fabrics (colorfastness grades from 4 to 4-5) showed that the developed method could be used for the coloration of wool and other polyamide fibers.

Key-words: Polymeric dye; aniline derivatives; oxidative polymerization; wool fabric; coloration

1. Introduction

Wool fibers are dyed in various colors to make them aesthetically attractive for apparel and floorcovering applications. Acid dyes are the preferred class of dye for wool fiber dyeing because at acidic conditions the acid dyes not only can be easily exhausted into wool fiber but also can be electrostatically bonded to the fiber. The dyeing process is carried out at the boil, which not only makes the dyeing process energy-intensive but also damages the fiber to some extent due to hydrolysis and disulfide bond rearrangement [1,2]. The produced colored effluent also needs to be treated before discharging to watercourses [3]. In this regard, the energy-efficient low-temperature dyeing process is attractive as it not only minimizes the production cost but also reduces fiber damage [4,5].

Traditional textile dyes are organic compounds having various chromophores, such as azo, anthraquinone, cyanine, and nitroso. Recently, a new class of dyes called ‘polymeric dyes’ has emerged as an alternative to the classical dyestuffs, and they have chromophores like traditional dyes, but they are polymers rather than organic compounds. Sometimes, crosslink-forming compounds having chromophore groups are also included in the list of polymeric dyes, such as chromophore containing polyurethanes [6,7]. The synthesis of various n-arylmaleimides and thiadiazole-based polymeric dyes by the oxidative polymerization method was reported for the dyeing of textiles [8,9]. A range of polyurethane-based polymeric dyes has been investigated that can form a colored polymeric coating on the fiber surface [10]. A water-borne polyurethane polymeric dye synthesized by conjugating Disperse Red 11 into polyurethane backbone exhibited a gradual increase in fluorescence intensity with an increase in the concentration of dye [11–13]. The synthesis of polymeric dyes by binding anthraquinone derivatives onto carboxymethylated chitosan has also been reported [14]. Most of these polymeric dyes are not absorbed into textile fibers because of their larger molecular size than the conventional dyes and they form a coating on the fiber surface, which compromises their colorfastness to rubbing and washing.

Recently the synthesis of sulfonated polyaniline, a self-doped conducting polymer, has attracted attention [15–17] but it is difficult to synthesize high molecular weight sulfonated polyaniline because of the poor reactivity of sulfonic acid derivatives of aniline. This is due to the presence of an electron attractive sulfonic acid group at the opposite position of the amino group in aniline [18]. Therefore, the synthesis of sulfonated polyaniline is carried out either by sulfonation of polyaniline or by copolymerization with sulfonic acid derivatives of aniline [15,19–21]. Moujahid et al. studied in-situ polymerization of various sulfonated derivatives of aniline at mild conditions without using any oxidizing agent [22]. They found that the presence of the methoxy group at the opposite of the amino group in the benzene ring inhibited their polymerization and produced only dimers. Recently, Masdarolomoor et al. successfully synthesized poly(2-methoxyaniline-5-sulfonic acid) film by oxidative polymerization of 2-methoxyaniline-5-sulfonic acid but it was a mixture of low (M_n = 2436) and high molecular weight (M_n = 6869) components [20,23].

Polyaniline is one of the most explored polymers for making textiles electro-conductive [24–27] but the treatment also produces strong color. However, its monomer, aniline, is not only highly toxic with an LD50 (rat) value of 100 mg/kg but it is also a possible carcinogen [28]. Polyaniline degrades to carcinogenic benzidine in the environment [29]. Moreover, aniline is a cationic monomer and soluble only in highly acidic conditions affecting its absorption into wool fiber as the wool fiber and the monomer both are cationic at these conditions. However, its sulfonated derivatives, such as aniline sulfonic acid (ASA), have very low toxicity with an LD50 (rat) value of 12300 mg/kg, and they can be easily absorbed into wool fiber because the dye and the fiber have opposite ionic charge [30]. Although ASA polymers may not provide electrical conductivity like doped polyaniline [31], they produce strong stable colors and therefore, can be used for the coloration of textile fibers. They can be polymerized at ambient conditions like aniline [30,31]. Our previous research shows that ASA dimers can be used for the functionalization of wool fibers [32]. In this work, wool fabrics were treated with three sulfonic acid derivatives of aniline by the oxidative polymerization method, and the effects on color produced, the intensity of color and the colorfastness to washing were systematically assessed. No published literature until present reported the application of ASA polymers and dimers as a polymeric dye for the coloration of textile fibers. For the first time, we are reporting the application of ASA polymers and dimers as a polymeric dye for the coloration of wool fabric.

2. Experimental methods

2.1. Materials

A knitted fabric of 126 g/m^2 having 15 courses/cm and 12 wales/cm made from 19 μm average diameter merino wool fiber supplied by Levana Fabrics (Levin, New Zealand) was used in this work. Aniline-3-sulfonic acid (ASA-1), aniline-4-sulfonic acid (ASA-2), and 4-methylaniline-2-sulfonic acid (ASA-3), potassium peroxydisulfate (PPS), acetic acid, and sodium acetate were of analytical reagent grade and supplied by Sigma-Aldrich Limited (USA). Sandozin MRN and Sandoclean PC were purchased from Arkema Chemicals, Switzerland. Albegal FFA was supplied by Huntsman Chemicals, USA. The phosphate-free standard detergent used for the assessment of colorfastness to washing was supplied by the

Society of Dyers and Colorists, UK. Softly®, a domestic wool textile washing detergent made by Pental Products Limited (Australia) was purchased from a local supermarket.

2.2. Coloration of fabrics with ASA by oxidative polymerization

The wool fabric was scoured with 1 g/l non-ionic detergent (Sandoclean PC) and 0.25 g/l Sandozin MRN (wetting agent) at 50 °C for 20 min, which removed any oil and dirt remained in the fabric after the knitting process. The treatment of wool fabric with ASA was carried out in an Ahiba Turbomat laboratory dyeing machine (Model 1000, Datacolor International, Switzerland) using materials to liquor ratio of 1:30. Wool fabric samples were placed in the treatment bath prepared with the required quantity of pre-dissolved ASA, 1 g/l Albegal FFA (antifoaming and leveling agent), and 0.25 g/l Sandozin MRN. The pH of the bath was set at 3, 4, or 5 with acetic acid and sodium acetate, or 8 with sodium bicarbonate. The temperature of the bath was then slowly increased to 30, 50, or 75 °C at 1 °C/min, held for 15 min, and then PPS (oxidizing agent) pre-dissolved in water was added and held for various times. After the completion of the polymerization treatment, the bath was cooled to 30 °C at 2 °C/min and the liquor drained. The treated fabric samples were then washed with 1 g/l Sandoclean PC at 50 °C for 15 min, rinsed with cold water several times, and dried at 60 °C for 30 min.

2.3. Measurement of color and colorfastness to washing

The color strength (K/S) values of the fabrics treated with various ASAs were measured at the wavelength of maximum absorption using a Datacolor reflectance spectrophotometer (Model: DC 550, Datacolor International, Switzerland) interfaced to a personal computer. All the samples were measured under illuminant D65, using a 10° standard observer with the UV component excluded and specular included. Each sample was folded four times and one measurement was made at five different positions giving a total of five measurements. The *CIE L*, a*, b** values of wool fabrics treated with various concentrations of ASA also were measured under illuminant D65, using a 10° standard observer by a Mahlo hand-held spectrophotometer (Model 45/0, Mahlo GmbH, Germany). The colorfastness to washing of the ASA-treated fabrics was measured according to the ISO Test Method 105-C03 1987: *Textiles – Tests for colorfastness – Part C03: Colorfastness to washing: Test 3* by washing them in a Gyrowash (Model 415/8, James Heal, Halifax, England) using the phosphate-free standard detergent. The fastness grades were determined by comparing with the 3M Grey Scale.

2.5. Surface characterizations of fabrics treated with various ASAs

To observe the surface morphology, the surface of fabric samples was scanned on a Hitachi scanning electron microscope (Model: TM3030 Plus, Hitachi Corporation, Japan) at an accelerated voltage of 15 kV without any conductive coating. The elemental analysis of C, O, N, and S was carried out by an energy dispersive X-ray (EDX) using the same SEM equipped with Quantax75 energy dispersive X-ray attachment (Bruker Nano GmbH, Germany). The wool fabrics dyed with ASAs were characterized by a Fourier transform infrared (FTIR) spectroscope equipped with an attenuated total reflectance (ATR) attachment

(Model: Nicolet Summit Pro, ThermoFisher Scientific, USA) at a resolution of 4 cm^{-1} in the range from 600 to 3600 cm^{-1} by using a diamond crystal and 64 scans were signal-averaged.

3. Results and discussion

3.1. Polymerization of ASAs and the effect of substituent groups

ASAs are similar to aniline but with 1–3 sulfonic acid groups. The introduction of these sulfonic acid groups increases their water- solubility. Because of their similarity with aniline, they can be polymerized in the same manner as aniline by the oxidative polymerization method. The reaction mechanism of the formation of ASA dimers/polymers by oxidative polymerization is shown in Fig. 1. Of the ASAs investigated, ASA-1 readily polymerized, similar to the polymerization of 2-methoxyaniline-5-sulfonic acid observed by Masdarolomor et al. [20]. On the other hand, ASA-2 and ASA-3 mainly produced dimers because of the steric hindrance produced by the $–SO_3$ and $–CH_3$ groups respectively as these functional groups stopped the growth of polymer chains as observed by others for the other sulfonated aniline derivatives [18, 22].

3.2. Effect of dyeing parameters on the shade produced and color strength

It is necessary to study the effect of dyeing conditions on the shades produced, color strength, and *CIE L*a*b** values to determine the best dyebath conditions for producing the deepest color. Generally, dye concentration, dyebath pH and temperature, and dyeing time have effects on the shade produced on the fabric. The effect of dyeing parameters on the various dyeing characteristics of the treated wool fabrics are discussed below:

3.2.1. Effect of pH

It is necessary to study the effect of dyebath pH, which not only affects the dye adsorption but also causes damage to wool fiber [1]. The change in dyebath showed a great effect on the shades produced, and the color intensity of the wool fabric treated with various sulfonated derivatives of aniline. ASA-1 produced dark yellowish-brown color and the color intensity decreased with an increase in the dyebath pH as shown in Fig. 2. On the other hand, ASA-2 and ASA-3 produced bright yellowish-brown and dull yellowish-brown colors respectively. Compared to ASA-1, pH had a great effect on the shade produced and the intensity of color, which decreased with an increase in the dyebath pH for the other two ASAs. For the wool fabric treated with ASA-1, the color strength only considerably changed when the dyeing was carried out at neutral to alkaline conditions. The change in dyebath pH only changed the color strength and caused tonal change for the fabric treated with ASA-1 but for ASA-2 and ASA-3, a shade change was observed. It is evident that the adsorption of ASA by wool fiber is dependent on the dyebath pH as the color of the fabric became lighter with an increase in the treatment pH. Fig. 2 also shows the effect of pH on the color strength of wool fabric treated with various ASAs and detailed results are provided in Tables S1-S3 (Supplementary Material). For all the ASAs, the wool fabrics treated at pH 3 showed the highest color strength. In the case of ASA-1, the change of pH from 3 to 5 had a little effect on the color strength but for the other two ASAs, a considerable change in color strength was observed. Of them, ASA-2 produced the deepest color and ASA-3 the lightest color. The color strength of the fabric treated with ASA-1 at pH 3 was 2.91 which decreased to 0.57 for the fabric treated at pH 9. Similarly, for the fabric sample treated with ASA-2 and ASA-3, the color strength decreased from 3.45 and 1.86 to 0.46 and 0.49 respectively when the treatment pH changed from pH 3 to pH 9.

Tables S1-S3 (Supplementary Material) show the effect of pH on the lightness value ($L*$) of wool fabric treated with various ASAs. The value of $L*$ increased with an increase in pH for all the ASA-treated fabrics investigated, i.e. the color became lighter with an increase in the treatment pH. The reddish and yellowish tone of the color decreased with an increase in pH as the values of $a*$ and $b*$ decreased with an increase in pH.

The redox reactions started as soon as PPS was added to ASA solution as observed for aniline oxidation polymerization by other researchers [33]. It was reported that for aniline, the acidity of the aniline solution (i.e. the pH of the aniline solution) had a great effect on the oxidation of aniline [34]. A conducting polymer with high conductivity is produced only in strongly acidic conditions, pH >2.5, i.e. full oxidation only occurs at low pHs [34,35]. The effect of pH on the polymerization of various ASAs is consistent with the polymerization of aniline. The zeta potential measurement of wool fiber surface showed that the isoelectric point of the wool fiber surface is at pH 4.5, i.e. the zeta potential of wool fiber is positive at pH below 4.5 and negative at pH over 4.5 [36]. The color strength is related to the quantity of dye absorbed by the fiber, i.e. the color strength of fiber increases with an increase in the adsorption dyes. At pH 3, the protonation of most of the amino groups of wool keratin peptides increased the number of positively charged sites in the fiber resulting in an increase in the attraction of negatively charged ASA molecules into the fiber. The increase in the pH slowly decreased the color strength of ASA-treated wool fabrics up to pH 5 and then a very high decrease was observed when the pH was increased from 5 to 9, which decreased the color strength to only 0.57, 0.46, and 0.49 in the case of ASA-1, ASA-2, and ASA-3 respectively. Similar observations were observed for the other two ASAs. Above the isoelectric point of wool, i.e. above pH 4.5, the ASAs are repelled by the fiber. The absorption of ASA into the wool fiber at pH below 4 is mainly electrostatically driven but at pH higher than 5, the adsorption of ASA is governed mainly by the weak hydrogen bonding and van der Waal’s force. Therefore, wool fiber repels negatively charged ASA with an increase in the pH resulting in a gradual decrease in the absorption of ASA into the wool fiber, and the formation of ASA polymer mainly occurred in the bath outside of the fiber. The treatment of wool with ASA polymer was carried out without using any salt but still, the exhaustion was almost 100% when the treatment was carried out at pHs below 4 as the produced effluent was colorless.

3.2.2. Effect of ASA concentration

Fig. 3 shows the effect of the concentration of ASAs on the color strength and shade produced. The color strength of the fabric increased with an increase in the concentrations of ASAs. In the case of ASA-1, the color turned from light yellowish-brown to a dark yellowish-brown with an increase in the monomer concentration. For the ASA-2, the color of the treated fabric turned from lighter yellowish-brown to darker bright yellowish-brown. On the other hand, the color of the ASA-3 treated fabric turned from lighter dull yellowish-brown to a slightly darker dull yellowish-brown. The effect of monomer concentration on the color strength (K/S) of wool fabric over the visible wavelength of light is also shown in Fig. 3. The color strength increased with an increase in ASA concentration. In the case of the wool fabric treated with ASA-1, the color strength increased from 0.57 to 2.91 when the applied dosage of ASA-1 was increased from 1 to 4% owf, and the corresponding values for the ASA2- and ASA-3 are 5.01 and 2.63 increased from 0.94 and 0.69 respectively.

Tables S1-S3 show the effect of the monomer concentration on the lightness value ($L*$) of wool fabric treated with various ASAs. The value of $L*$ decreased with an increase in the monomer concentration for fabrics treated with various ASAs, i.e. the color became darker with an increase in the ASA concentration. The reddish and yellowish tone of the color increased with an increase in the ASA concentration as the values $a*$ and $b*$ increased with an increase in the ASA concentration.

It is known the color strength of fabric increases with an increase in the concentration of dye. The increase in the dosage of ASA increased the color strength of wool fabrics treated with various ASAs suggesting increased absorption of ASA into the wool fiber. The highest color strength was exhibited by the fabric treated with ASA-2 and the poorest by the fabric treated with ASA-3. The ASA-3 has a methyl substituent group and the presence of this group probably affected the shade produced and color intensity of ASA-2 dimers. The color strength produced by the fabric treated with ASA-1 was quite similar to the color strength of fabric treated with ASA-2. Both ASA-2 and ASA-3 produced dimers and had the same number of the sulfonic acid groups, but ASA-3 has a hydrophobic methyl group which probably affected its color intensity and the shade produced.

3.2.3. Effect of monomer to oxidant ratio

Fig. 4 shows the effect of the monomer to oxidant ratio on the shade produced and the color strength of the treated fabrics. For all the ASAs, the color of the treated fabric became darker to lighter with a decrease in the monomer to oxidant ratio. Similarly, the color strength also decreased with a decrease in the monomer to oxidant ratio. In the case of the fabric treated with ASA-1, the color strength decreased from 3.68 to 2.02 when the monomer to oxidant ratio was decreased from 1:1.5 to 2:1. For the ASA-2 and ASA-3, the color strength decreased from 4.95 and 2.78 to 1.67 and 1.13 respectively. The effect of monomer to oxidant ratio on the *CIE* $L^*a^*b^*$ values of the fabric treated with various ASAs is shown in Tables S1-S3. It is evident that the increase in ASA to PPS ratio decreased the value of L^*, i.e. the color of the fabrics became darker with an increase in ASA to PPS ratio but the yellowness and redness of the fabric increased with an increase in the ASA to PPS ratio. The probable reason for the color strength of the fabrics increased with an increase in the ASA to PPS ratio could be due to the increase in oxidation levels by the increase of ASA to PPS ratio.

3.2.4. Effect of dyebath temperature

The effect of dyebath temperature on the color strength for the treated fabric was studied only for ASA-2 as it produced the deepest color. The increase in the dyebath temperature had little effect on the color strength of the fabric treated with 3% on the weight of fiber (owf) ASA-2 as shown in Fig. 5(a). The increase in color strength by increasing the dyebath temperature from 30 to 75 °C was very negligible as the color strength only increased from 3.40 for the fabric treated at 30 °C to 3.45 for the fabric treated at 75 °C. The value of L^* decreased from 63.95 to 63.66 when the treatment temperature increased from 30 °C to 75 °C (Table S2 in Supplementary Material). In the case of dyeing with acid dyes, the dye molecules are first adsorbed into the fiber surface and then slowly diffuse into the fiber by jumping from one dyeing site of the fiber to the other dyeing sites towards the center of the fiber. The equilibrium between the dye adsorbed onto the fiber surface depends on the relative magnitudes of the activation energies for adsorption and desorption. If the activation energy for adsorption is lower than the activation energy for desorption, then rapid adsorption of dye occurs. The diffusion of negatively charged acid dye molecules into wool fiber occurs due to the constant thermal motion of atoms, and molecules depending on the energy available. The diffusion of negatively charged dye molecules into wool fiber occurs due to the constant thermal motion of atoms, and molecules depending on the energy available. The increase in temperature provides heat energy, which increases the molecular motion of dye molecules and drives their diffusion into the wool fiber. As ASA is anionic like acid dyes, therefore the adsorption and diffusion of ASA into wool fiber also can be described by the same mechanism. The increase in dyebath temperature provided the heat energy, which increased the molecular motion of ASA molecules and drives their diffusion into the wool fiber. After the formation of dimers, they are bonded to the fiber by the electrostatic attraction resulting in increased colorfastness to washing. In the case of low-temperature dyeing, the dye adsorption and diffusion take longer, but at higher temperatures, the dye adsorption and diffusion become quicker. As the dyeing time was long for the treatment with ASA-2 (120 min), the ASA molecules had enough time to absorb and diffuse into the fiber. Therefore, the increase in dyebath temperature did not show any effect on color strength and colorfastness to washing of the treated fabrics.

3.2.5. Effect of treatment time

The treatment time also had a great effect on the color strength of wool fabrics treated with 4% owf of ASA-2 at pH 3.0 as shown in Fig. 5(b). The color strength of the treated fabric increased from 2.56 for the fabric treated for 30 min to 3.37 for the fabric treated for 60 min. Further increasing the treatment time to 120 min only increased the color strength to

3.45. The fabric also became darker with an increase in the treatment time as the value of L^* decreased from 65.76 to 62.80 when the treatment time increased from 30 min to 120 min. The adsorption and diffusion of dye molecules is a slow process and highly depends on the treatment time [37]. Short treatment time (30 min) did not permit diffusion of many ASA molecules into the fiber and therefore most of them formed dimers on the fiber surface instead of inside the fiber and washed out during washing resulting in low color strength. On the other hand, 120 min treatment time allowed the absorption and diffusion of ASA molecules to reach equilibrium, and polymerization of dye molecules mostly occurred inside the fiber, which considerably increased the colorfastness to washing.

3.3. Effect of treatment conditions on colorfastness to washing

The colorfastness to washing of the ASA-treated wool fabric was affected by the treatment conditions, especially by the change of monomer to oxidant ratio. Table S1-S3 (Supplementary Material) shows the effect of pH on the colorfastness of the wool fabrics treated with various ASAs. Overall, the fabrics treated with all the ASAs produced quite similar but good colorfastness to washing. The fabrics treated with ASA-3 produced only slightly poor colorfastness to washing than the fabrics treated with ASA-1 and ASA-2. The fabric treated with 1% owf of ASA-1 and ASA-2 showed excellent colorfastness to washing as the change in color grade was 4-5, but the increase in the concentration of the ASAs slightly decreased the colorfastness. The pH had a little effect on the colorfastness of washing as all fabrics treated at different pHs showed quite a good colorfastness to washing and the change of color grade was 4 to 4-5 except for the ASA-3. The increase in the concentration increased the saturation of ASA inside fibers. Therefore, some ASA dimer and polymer molecules formed near to the surface of the fibers, and during the washing test, they were removed resulting in a slight decrease in colorfastness. The effect of the ratio of PPS to showed a negative effect on their colorfastness to washing, which decreased as the rate of oxidation of ASA increased resulting in reducing the diffusion of the ASA into wool fiber and ASA dimer/polymer formed before totally diffusing into the fiber, which removed during the washing test. The increase in the treatment temperature and time had little effect on colorfastness to washing as the colorfastness to washing only slightly increased with an increase in the treatment time and temperature.

3.4. SEM

SEM scanning was carried out to observe the effect of treatment time on the surface of wool fibers whether the increase in dyeing time increases the absorption of ASA dimers/polymer into wool. Fig. 6 shows the SEM images of wool fabrics treated with 4% ASA-1, ASA-2, and ASA-3. The SEM micrographs of the control fabric surface exhibited the typical scaly structure of the wool fiber as shown in Fig. 6(a). The deposition of some polymer is visible in the case of wool fabric treated with ASA-1, which suggests the formation of a polymer by the polymerization of ASA-1. The ASA-1 polymer formed a thin coating on the surface of wool fibers. However, for wool fabrics treated with ASA-2 and ASA-3, no deposition or coating formation was observed on the surfaces of fibers suggesting dimer formation rather than polymer formation and diffusion of dimers into the interior of wool fiber. As dimers cannot form any coating, the fiber surfaces are clean, and the scaly structure of wool is still visible.

3.5. Elemental analysis

Elemental analysis of wool fabrics treated with various ASAs was carried out to determine the absorption of various ASAs into the wool fiber. Fig. 7 shows the EDX spectra and elemental compositions of C, N, O, and S of wool fabrics treated with 4% owf various ASAs. The corresponding elemental mappings are shown in Fig. S1 (Supplementary Material). The composition of C, O, N, and S of untreated fabric was 51.85, 26.61, 18.79, and 2.75% respectively. The treatment with various ASAs caused a considerable change in the elemental composition of wool fabric, especially the S content. The wool fabric treated with ASA-3 had the highest S content and the wool fabric treated with ASA-2 had the lowest suggesting that the absorption of ASA-3 into the wool fabric was the highest but the color strength of the treated fabric was considerably lower than the fabrics treated with ASA-2 and ASA-3, suggesting that the presence of methyl groups in the formed ASA-3 dimers affected the color intensity. The absorption of ASA-1 into wool fabric was also quite good as the sulfur content of the ASA-1 treated wool was almost near to the S content of the fabric treated with ASA-2. On the other hand, the S content of the ASA-2 treated wool was almost similar to the wool treated with ASA-1, but the color intensity of the treated fabric was slightly higher than the fabric treated with ASA-1 suggesting that the position of the sulfonate moiety also affected the color produced and the color intensity of the produced polymer/dimer. Of the treated fabrics, the fabric treated with ASA-3 showed the lowest O content (even lower than the control fabric) and higher C content due to the presence of the methyl group in ASA-3. The elemental analysis suggests that the position of the substituent groups in the ASA structure affects the color intensity of the produced polymers/dimers. Elemental mapping shows that C, O, N, and S elements are uniformly distributed in all the treated fabrics indicating the uniform treatment of wool fabrics occurred for all ASAs investigated in this work.

3.6. ATR-FTIR

The ATR-FTIR spectra of control and wool fabrics treated with 4% owf various ASAs are shown in Fig. 8. The spectrum of control wool fabric shows typical IR bands of wool fiber, such as wool keratin-related IR bands of amide III, amide II, and amide I peak at 1227, 1350, 1540, and 1635 cm^{-1} respectively [38]. The peak at 1506 cm^{-1} could be attributed to the C–N stretching and to the N–H in-plane bending vibrations (amide II). The broad IR band at 3270 cm^{-1} could be attributed to the hydroxyl groups of wool fiber. On the other hand, the spectra of wool fabrics treated with various ASAs show a new IR band at 1040 cm^{-1}, which can be attributed to the sulfonate groups of various ASAs [39,40]. It is interesting to notice that the intensity of the sulfonic acid band at 1040 cm^{-1} for wool fabric treated with ASA-3 is slightly higher than the wool fabrics treated with the other two ASAs, but it showed the lowest color strength. The high intensity of the sulfonic acid band at 1040 cm^{-1} observed for the fabric treated with ASA-3 suggests that its color intensity of fabric decreased not because of the decreased absorption of ASA-3 but because of the presence of methyl group in its chemical structure which probably affected the color and color intensity of the treated fabric. The intensity of sulfonate bands observed for wool fabrics treated with various ASAs is consistent with the S contents measured by elemental analysis. The intensity of hydroxyl peaks at 3270 cm^{-1} also highly decreased for the wool fabrics treated with various ASAs compared to the control wool fabric suggesting that the hydrophobicity of wool fabrics treated with various ASAs increased compared to the control fabric. The results are consistent with our previously published work, which showed that the hydrophobicity of wool fabric considerably increased by the treatment with p-aminobenezenesulfonic acid [32]. Of the wool fabrics treated with various ASAs, the fabric treated with ASA-1 showed the lowest hydroxyl band intensity suggesting that wool fabric treated with ASA-1 made the fabric most hydrophobic. The presence of sulfonate band at 1040 cm^{-1} in the spectra of wool fabrics treated with various ASAs suggests the presence of ASA dimers/polymer in the treated fabric.

3.7. Energy and water consumption

Energy calculations were carried out to evaluate the sustainability of the developed method. Wool dyeing is carried out at the boil using materials to liquor ratio of 1:30 for 60 to 120 min depending on the depth of the shade required. It is reported that the dyeing carried out at the boil by the jet dyeing machine consumes 4.4 kWh/kg with heating and 1.0 kWh/kg without heating [41], i.e. the energy saving for each kilo of wool by the developed method is only 3.4 kWh, which is less than 25% of the energy consumed in the traditional dyeing of wool fibers. Because of the low toxicity of ABSA, the effluent produced by this treatment may not need any further treatment to discharge to watercourses, unlike other synthetic dyes. Therefore, the developed method will be highly sustainable over traditional methods.

4. Conclusions

This work has demonstrated that ASAs can be used as a polymeric dye for the coloration of textile fabrics, which not only produced deep to light yellowish-brown colors with various tonal differences but the dyeing also could be energy-efficient as the dyeing can be carried out at room temperature. ASA-2 produced the deepest color and the ASA-3 the weakest. ASA-1 produced dark yellowish-brown colors, but the ASA-2 and ASA-3 produced bright and dull yellowish-brown colors respectively. The intensity of the color was dependent on the applied concentration of ASA, treatment pH, and time. The increase in pH to alkaline conditions drastically reduced the absorption of ASA into wool fiber resulting in poor color strength. The colorfastness to washing is affected by the oxidant to monomer ratio and treatment temperature. The treated fabrics showed excellent colorfastness to washing, especially when treated at pH 3 at 75 °C for at least 120 min. The developed treatment could be used in industry for the energy-efficient coloration of wool and other polyamide fibers.

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