

Single-step synthesis and energy-efficient coloration of wool textiles with poly(amino naphthalene sulfonic acid)-based dyes by oxidation polymerization

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Abstract

In the context of sustainability, energy-efficient low-temperature dyeing with non-toxic polymeric dyes is attractive. In this work, single-step synthesis of polymeric dyes of several non-toxic amino-naphthalene sulfonic acids (ANSAs) and energy-efficient coloration of wool

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fabrics by the oxidation polymerization method were carried out at moderate temperatures. The studied monomers are 7-amino-1,3-naphthalene monopotassium disulfonate (ANSA-1), 4-amino-1-naphthalene sulfonic acid (ANSA-2), and 5-amino-2-naphthalene sulfonic acid (ANSA-3). The prepared polymeric dyes were characterized by UV-vis, Fourier transform infrared (FT-IR), and mass spectrometry, and gel permeation chromatography (GPC). The mass spectra suggest that oxidation treatment of ANSA-1 formed only dimers but the other two ANSAs formed polymers, but the GPC data demonstrate successful polymerization of all three ANSAs. The treated fabrics were characterized by thermogravimetric analysis, and FTIR and reflectance spectroscopies. The treatment parameters, including the monomer and oxidant concentrations, treatment pH, temperature, and time, affected the color produced and its intensity. The optimum conditions for dyeing with ANSAs were 50 °C, 120 min, and a 1:1 monomer to oxidant ratio. The treatment with these amino naphthalene sulfonic acids produced various colors in the fabric including tonal changes. The colorfastness to washing increased with an increase in the treatment temperature and time. The shade produced and the color intensity were dependent on the position of the substituent sulphonate groups in the amino-naphthalene compounds. This developed treatment can be used for the energy-efficient dyeing of wool and other polyamide fibers with good colorfastness to washing.

Keywords: Sustainable dyeing; polymeric dyes; sulfonated amino naphthalene derivatives; oxidation polymerization; colorfastness properties

1. Introduction

Textile fibers are dyed with various classes of dyestuffs, which are organic compounds, and they can be divided into several classes, such as acid, basic, disperse, and reactive dyes depending on their functional groups. The textile dyes are mostly water-soluble or made water-soluble during the dyeing stage (except disperse dyes). They are either electrostatically or covalently bonded to the fiber or made water-insoluble inside the fibers. Of these, only the reactive class of dyes reacts with the hydroxyl groups in fibers and covalently binds to them whilst others are either bind to fibers electrostatically having opposite ionic functional groups or are made insoluble and thus locked inside the fiber. Textile dyes can be considered as virtually isolated chromogen molecules and when dissolved in a solvent every chromogen is available to absorb light. In contrast, polymeric dyes are colored polymers having chromophores in their macromolecular chains and can be used only for the coatings of fibers. Because of their large molecular size, they cannot be absorbed into the fiber. The primary target of the development of polymeric dyes was to overcome the deficiencies of both dyes and pigments as their physical properties are tunable and they have low toxicity (Wang et al, 2017). However, they can be exhausted into fibers like traditional dyestuffs because of their large molecular size (Miley, 1996). Many monomers (e.g., styrene, acrylamide, etc.) could be toxic and carcinogenic, but the polymers produced from them are harmless (Blanc-Lapierre et al., 2018; Kumar et al., 2018). Moreover, low-temperature dyeing is advantageous over traditional dyeing of wool with acid dyes at the boil which not only saves energy but also reduces fiber damage (Hassan and Carr, 2019; Hassan and Bhagvandas, 2017). Many dyes used in the textile industry could be toxic and the produced effluent needs expensive tertiary treatments.

In polymeric dyes, chromophores are introduced either by the monomer or the polymer. Dawson et al. prepared water-soluble polymeric dyes by attaching water-insoluble anthraquinone chromophores to the copolymer of N-vinyl acetamide and sodium vinyl sulfonate (Dawson et al., 1978). The synthesis of water-soluble polyamide polymeric dyes from

monomers having anthraquinone chromophore groups (1,5-bis(2-hydroxyethyl-amino)anthraquinone and 1,5-bis(2-hydroxyethoxy)anthraquinone) by condensation polymerization have been reported (Meng et al., 2002). A range of polyurethane-based polymeric dyes has been investigated that can form a colored polymeric coating on fiber surfaces (Mao et al., 2015). Another type of polymeric dye is based on crosslinking of bi or multifunctional organic compounds containing chromophore groups (Tang et al., 2015). The synthesis of polymeric infrared emissive dyes has also been studied (Donuru et al., 2010). Synthesis of coumarin chromophore-containing polymeric fluorescent dyes also has been reported (Ma et al., 2013). The synthesis of water-borne polyurethane polymeric dye by conjugating Disperse Red 11 into the polyurethane backbone exhibited a gradual increase in fluorescence intensity with an increase in the concentration of dye (Hu et al., 2018). 4,4'-difluoro-4-bora-3a,4a-diaza-s-indacene-based polymeric dyes were investigated as biochemical labeling, fluorescent switches, and electroluminescent devices (Squeo et al., 2017). Polymeric dyes also can be synthesized by binding anthraquinone derivatives onto carboxymethylated chitosan (Lv et al., 2017). UV curable chromophores containing waterborne polyurethane dyes have been investigated for the coloration of textiles (Mao et al., 2017; Hu et al., 2013). The synthesis of a new class of polymeric dyes containing difluoroboraindacene chromophore within the main chain also has been reported (Alemdaroglu et al., 2009). However, polymerization initiators used for the polymerization of many monomers are highly toxic and the reaction is complicated, and the polymerization needs special equipment as the reaction needs to be carried out at ultra-low or high temperatures. Nevertheless, the oxidative polymerization method is highly advantageous as the initiators used are oxidative, generally non-toxic, and the polymerization can be carried out between room temperature and 50 °C.

The synthesis of n-arylmaleimides and thiadiazol-based monomers and the polymeric disperse dyes produced from them by oxidative polymerization has been reported (Maradiya and Patel, 2000a; Maradiya and Patel, 200b; Maradiya and Patel, 2001; Maradiya and Patel, 2002). Kaya et al reported the synthesis of a polymeric dye from tris(4-aminophenyl)-methanol by oxidative polymerization (Kaya et al., 2013). The synthesis of polymers from sulfonated derivatives of amino naphthalene by electrochemical oxidation polymerization has been studied for sensing applications (Doğan et al., 2016; Amare and Admassie, 2020; Geto and Brett, 2016). Recently, we reported the sustainable coloration and multi-functionalization of wool fabrics with sulfonated derivatives of aniline by a single-bath oxidation polymerization (Hassan, 2020; Hassan, 2021). Sulfonated amino naphthalene derivatives are relatively non-toxic and biodegradable (Usha et al., 2010; Nachiyar and Rajakumar, 2006; Song et al., 2005), and therefore could be a sustainable alternative to environmentally unfriendly traditional dyes. Successful polymerization of sulfonated derivatives of amino naphthalene by oxidative polymerization has been reported (Atkinson et al., 2000). To the best of our knowledge, the application of oxidative polymerized sulfonated derivatives of amino naphthalene as a colorant has not been reported for the coloration of textile fibers.

In this work, for the first time, we are reporting a single-step synthesis of ANSA-based dyes and coloration of wool fabric at room temperature to moderate temperatures by oxidation polymerization, which not only saves energy but also made dyeing eco-friendly as they are relatively non-toxic. Several ANSAs with sulfonate substituents at various positions of the naphthalene ring were exhausted into wool fibers by varying treatment pH, temperature, and time, and they were polymerized inside the fiber by oxidation polymerization.

2. Experimental methods

2.1 Materials

A complex woven wool fabric of 220.0 g/m² having 20 ends/cm and 20 picks/cm made from merino wool fibers of an average of 18 μ m was used throughout this work. ANSA-1 (molecular weight = 341.42), ANSA-2 (molecular weight = 223.25), and ANSA-3 (molecular weight = 223.25) were purchased from Sigma-Aldrich Limited (USA). Sodium peroxydisulfate (SPS), acetic acid, and sodium acetate were also purchased from Sigma-Aldrich Limited (USA) and were of analytical reagent grade. Sandozin MRN (a non-ionic wetting agent), Sandoclean PC (a non-ionic detergent) were purchased from Arkema Chemicals, Switzerland. Albegal FFA (a leveling agent) was purchased from Huntsman Chemicals, USA. For MALDI-MS, trifluoroacetic acid, $\geq 99\%$, was obtained from Sigma Aldrich (France). Peptide calibrant II and α -cyano-4-hydroxycinnamic acid were obtained from Bruker Daltonics (Germany), Optima®LC/MS water, absolute ethanol, and HPLC grade acetone were obtained from Fisher Chemicals (USA).

2.2. Synthesis and characterization of ANSA dimers/polymers

For various characterizations, ANSAs were polymerized by oxidative polymerization at 30 °C for 2 h at pH 3 using ANSA to SPS ratio of 1:1. the same conditions used for the treatment of wool fabric, but without the fabric. The low molecular weight fractions of the dyes were removed by dialysis with a 2k MWCO dialysis membrane against Milli Q water. The UV-vis spectroscopy of aqueous solution of polymerized ANSA was carried out on a Thermo Fisher Scientific UV-vis spectrophotometer (Model: Evolution 220, Thermo Fisher

Scientific Inc., Waltham, USA) using 10 mm path length. The mass spectroscopy of the dyes was carried out on an Ultraflex III matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF/TOF MS) made by Bruker Daltonics GmbH and Co KG (Bremen, Germany), in positive ion reflectron mode with an m/z range of 500–4000 m/z . For this purpose, solutions of each dye, with a concentration of 20 mg/mL, were prepared in 0.1% v/v trifluoroacetic acid. The matrix was prepared by taking 1 part of the supernatant of a saturated solution of α -cyano-4-hydroxycinnamic acid in acetone and 9 parts of a matrix solvent containing 6:3:1 ethanol:acetone:0.1% trifluoroacetic acid (in water). For mass spectrometry analysis, aliquots of the samples were diluted 10x, 20x, and 50x in 0.1% trifluoroacetic acid. Initially, 0.5 μ L of the diluted samples were spotted onto a steel plate (Bruker Daltonics). Once dry, 0.5 μ L of the prepared matrix was spotted over the sample and left to dry. The plate was inserted into an Ultraflex-III-TOF-TOF MALDI instrument (Bruker Daltonics). The instrument was first calibrated with the peptide calibrant II (Bruker Daltonics). Samples and calibrant were analyzed with the same method in positive reflectance mode between 500 to 4000 m/z . The smart beam parameters were set to 4-large and a frequency of 200 Hz. Voltages were set as follows, 25 kV for source one, 21.3 kV for source two, 26.3 kV for reflector one, 13.75 kV for reflector two, and 9.8 kV for the lens. The sampling rate of 1.00 GS/s and detection gain of 1687 V. A total of 1600 shots were used for each of the sample spectra.

The molecular weight was determined using a Waters GPC system (Model e2695, Waters Corporation, Milford, USA) with PSS Win GPC software using 3x PSS Suprema 100 Å, 1x Suprema Guard column held at 30 °C in a column oven with a mobile phase consisting of 0.1M NaNO₃ at a 1 ml/min flow rate. Chromatograms were recorded using a refractive index detector (Waters 2414 RI detector). All molecular weight calibrations were determined via relative calibration against Pullulan standards.

2.3. Treatment of wool fabric with ANSAs

Any spinning oil and dirt present in the fabrics were removed by scouring with 1 g/L Sandoclean PC and 0.25 g/L Sandozin MRN at 50 °C for 20 min as their presence may affect the absorption of ANSAs into the fabric producing uneven dyed fabric. All the treatments were carried out using Milli-Q water in an Ahiba Turbomat laboratory dyeing machine (Model 1000, Datacolor International, Switzerland) using a 1:30 materials to water ratio.

The bath was dosed with the required quantity of pre-dissolved ANSAs, 1 g/L Albegal FFA, and 0.25 g/L Sandozin MRN. The applied dosage of ANSA was varied from 1 to 4% of the weight of fiber (owf). 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 raised to 25 °C, 50 or 75 °C at 1 °C/min, the required quantity of sodium peroxydisulfate (SPS) was added to the bath and held at different times interval. After completion of the treatment, the bath was cooled to 25 °C at 2 °C/min, and the liquor drained. The treated fabric samples were then soaped with 0.5 g/L Sandoclean PC at 45 °C for 15 min and rinsed with cold water several times after which they were dried at 60 °C in an oven for 30 min. The treatment was carried out using various concentrations of ANSAs and SPS at various pHs and temperatures for various times. The mechanism of the formation of dimers and polymer of sulfonated amino naphthalene derivatives is presented in Fig. 1.

2.4. Measurements of color and colorfastness to washing

The color measurements of fabrics dyed with ANSAs were carried out according to published literature (Hassan, 2018). The K/S values (at the appropriate wavelength of maximum absorption for each dyeing) of the dyed samples were measured using a Datacolor DC 550 spectrophotometer interfaced with a personal computer. Samples were measured under D65 illuminant, using a 10° standard observer with UV component excluded and specular included. Each sample was four times folded and four measurements were made at four different places of each sample. The average value is reported here. The $CIE L^*$, a^* , b^* values of each fabric sample 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 yarns was measured according to the ISO Test Method 105-C03 1987: *Textiles – Tests for colorfastness – Part C03: Colorfastness to washing: Test 3* by washing in a Gyrowash (Model 415/8) using the phosphate-free standard detergent. In both cases, fastness grades were assessed by comparing with the 3M Grey Scale.

2.5. Surface characterizations

The surface of the treated wool fabrics was characterized by using a Thermo Fisher Scientific FT-IR (Model: SUMMIT Pro, Thermo Fisher Scientific Inc., Waltham, USA) equipped with an attenuated total reflectance (ATR) attachment at a resolution of 4 cm^{-1} in the range from 650 to 4000 cm^{-1} . The diamond crystal was used to record the ATR-FTIR spectra, and 64 scans were signal-averaged.

The surface of wool fabrics treated with various concentrations of ANSA was examined by a scanning electron microscope (SEM) using a Hitachi SEM (Model: TM3030Plus, Hitachi Corporation, Japan) at an acceleration voltage of 15 kV without any conductive coating. The elemental analysis of C, H, S, and O was carried out by an energy dispersive X-ray (EDX) using the same model of SEM equipped with Quantax75 energy dispersive X-ray attachment (Bruker Nano GmbH, Germany).

3. Results and discussion

3.1. Characterization of various ANSA polymers

The synthesized polymers of ANSA were characterized by FTIR, UV-vis, and mass spectrometry and also by gel permeation chromatography.

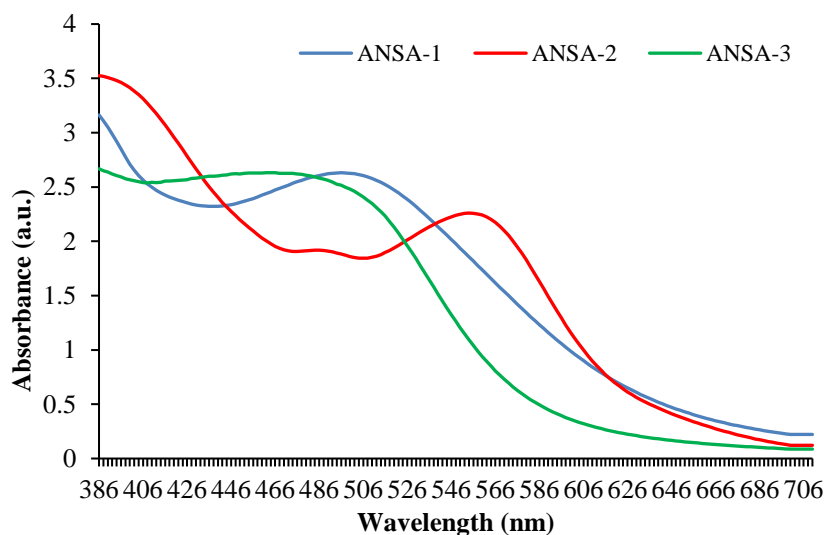


Fig. 1. UV-vis spectra of polymerized ANSAs (concentration = 1000 mg/L).

3.1.1. UV-vis spectra

Fig. 1 shows the UV-vis spectra of an aqueous solution of various ANSA dimers/polymers. The UV-vis spectrum of ANSA-1 shows an absorption peak at 496 nm, while ANSA-3 exhibited an absorption peak at 466 nm. On the other hand, ANSA-2 shows two major peaks at 554 and 386 nm and a minor peak at 496 nm. The color strength of ANSA dimers/polymers is related to the absorbance of the ANSA solution, i.e., the higher the absorbance the stronger is the color. The absorption peaks at 466, 496, and 554 nm exhibited by ANSA-1, ANSA-3, and ANSA-2 respectively are associated with characteristics π - π^* transition of benzenoid type rings and n - π^* transition of the quinoid type rings present in polymerized ANSAs (Ho et al., 2011). The ANSA-1 and ANSA-3 showed almost similar absorbance, but the wavelength of maximum absorption was different, while ANSA-2 produced a lower absorbance compared to the other two ANSAs. In terms of chemical structure, all the ANSAs are very similar except ANSA-1 which has disulfonate groups, but all of them have similar substituent sulfonic acid and amino groups. It is evident that the position of the substituent groups in the naphthalene affects the intensity and shade of the produced color and thus the wavelength for maximum absorption. The mechanism of formation of poly(ANSAs) is presented in Fig. 2.

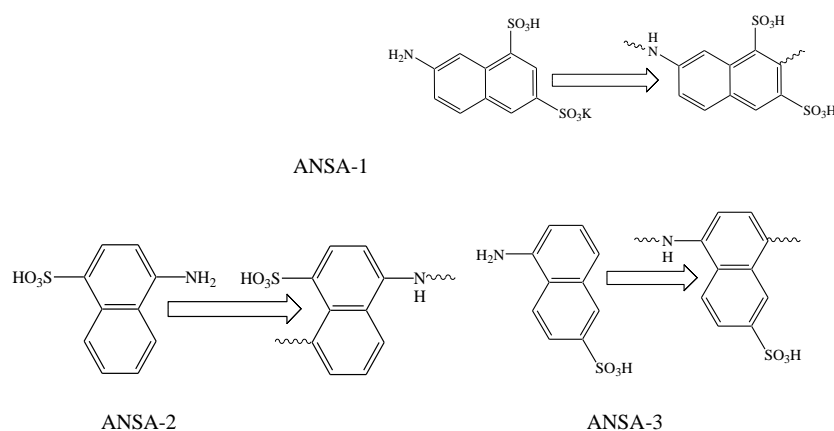


Fig. 2. Mechanism of formation of dimers/polymers from various ANSAs by the oxidative polymerization method.

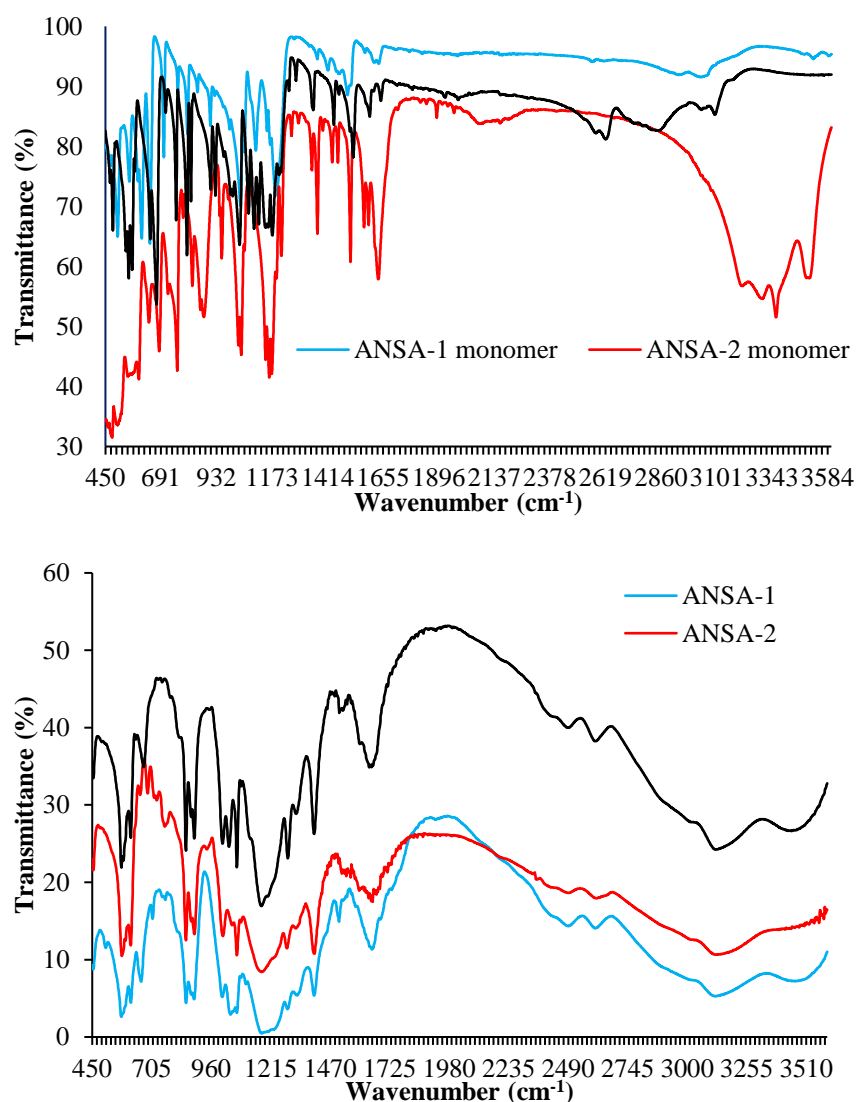


Fig. 3. ATR-FTIR spectra of ANSA-1, ANSA-2, and ANSA-3 monomers (top) and polymers synthesized by oxidative polymerization (bottom).

3.1.2. FTIR

Fig. 3 shows the FTIR spectra of various ANSA monomers and oxidative polymerized ANSAs before dialysis. The monomers show the characteristic IR bands of sulfonated amino naphthalene with sulfonate-related IR bands at 1041 cm⁻¹ and primary amino-related IR bands at around 1633 to 1650 cm⁻¹. On the other hand, their polymers exhibited strong IR

bands at 574, 1009, 1180, 1289, 1401, 1509, 1650, 3124, and 3460 cm^{-1} . The IR bands at 574 and 1009 cm^{-1} are associated with the benzene ring of naphthalene and sulfonate moieties respectively (Hassan and McLaughlin, 2015). The band at 1289 cm^{-1} is related to the C-N stretching of aromatic amine, and the band 1648 cm^{-1} is associated with vibrations of N-H groups formed due to polymerization of the amino naphthalene. The bands at 1400 and 1500 cm^{-1} are related to the naphthoquinonoid and benzenoid groups of the polymerized ANSAs (Ho et al., 2011). The band at 3124 cm^{-1} is related to hydroxyl groups due to the absorbed moisture but the spectra of ANSA-1 and ANSA-3 exhibited a strong IR band at 3460 cm^{-1} (very weak in the spectra of ANSA-2) associated with the stretching vibrations of N-H, which suggests successful polymerization of the ANSAs. The Low-intensity IR band observed at 3008 cm^{-1} is due to the characteristic C-H vibrations of the naphthalene ring. The absorption band observed at 1402 cm^{-1} corresponds to C=C skeletal vibrations of the aromatic ring. Ciric-Marjanovic et al. investigated the aqueous oxidative polymerization of 4-amino-3-hydroxynaphthalene-1-sulfonic acid using ammonium peroxydisulfate as an oxidant (Ciric-Marjanovic et al., 2006). The substitution patterns shown by IR spectroscopic analysis combined with MNDO-PM3 semi-empirical quantum mechanical calculations revealed that N-C coupling reactions were dominant in forming polymer, where C belongs to unsubstituted amino-naphthalene ring.

3.1.3. MALDI-TOF Spectra

The MALDI-TOF spectra are shown in Fig. S1 (Supplementary Materials) which demonstrate that the oxidation polymerization of ANSAs produced low molecular weight oligomers with just a couple of monomeric units. The mechanism for ANSA-1 shows the joining at the amine group with the possibility of only dimers. This was supported in the mass

spectrum. The isotope patterns revealed a difference of one Dalton and therefore all the ion charges were 1+. The lower part of the spectrum ($< 1000m/z$) showed the presence of a polymer with a difference of 22 Da (addition of Na and minus H) and may indicate the occurrence of sodium substitution with hydrogen on the benzene rings.

The addition of sodium ions occurred 1-10 times on the ANSA-1 dimer mass spectrum whereas it only occurred four and three with ANSA-2 and ANSA-3 respectively. When the number of sodium and the molecular weight of the dimer (665.736) was subtracted from the m/z of the ANSA-1 spectrum, there was a weight of 75.2 m/z for up to 3 substituted sodium and 63.34 m/z for the dimer with five to nine sodium substitutions. As fragmentation was not done, the molecular formula explaining the remaining weight of the ANSA-1 xNa dimers could not be determined as there are many chemical formula options for these masses. The spectra for ANSA-2 showed a trimer with one, two, or three sodium substitutions and a remaining m/z of 120.4 which again could not be determined. The spectrum also showed one and two additional monomers + sodium additions to the trimer with two additional sodium equating to the presence of a tetramer and pentamer of the ANSA-2 with sodium being added for each additional monomer.

ANSA-3 showed larger polymers compared to the other two dyes with the largest molecular weight of 1546.405 Da. The larger ions also differed by 22 Da showing that these larger polymers are present with different amounts of sodium substitutions. Like ANSA-2, most of the dye was present as a trimer with either none, one, or two substituted sodium. The tetramer, pentamer, and hexamer were also present by further additions of the single sodium substituted ANSA-3 monomer. The mass spectral analysis suggests that the oxidation polymerization of ANSA-1 produced dimers, but ANSA-2 and ANSA-3 produced polymers. The molecular weight of oligomers produced by oxidation polymerization of the ANSAs was further characterized by gel permeation chromatography (GPC).

3.1.4. GPC

Fig. S2 (Supplementary Materials) shows the GPC chromatograms of the oxidation polymerized ANSAs and the corresponding molecular weight data are shown in Table 1. The absence of a low molecular weight peak (Peak 2) for ANSA-2 and ANSA-3 is evidence that dialysis with 2k MWCO dialysis membrane removed the unreacted ANSA monomers. However, in the case of ANSA-1, some unreacted monomer remained in the dialyzed sample due to the presence of two sulfonic acid groups in the ANSA-1 allowing ionic bonding between amino groups of ANSA-1 monomer and the sulfonic acid groups of ANSA-1 dimers. All three ANSAs studied were successfully polymerized to relatively similar molecular weights (Table 1). The molecular weight (M_w) of the ANSA-1, ANSA-2, and ANSA-3 polymers was low, 2574, 2601, and 2635 g/mol respectively, compared to the molecular weight achieved by others (Amare and Admassie, 2020; Hassan and Leighs, 2017), as we used a quite low concentration of monomers. The low molecular weight of the polymer is beneficial for textile coloration as they can be exhausted into the interior of the fibers providing higher durability to washing. It is known that in the case of oxidation polymerization of aniline, the oxidation proceeded non-monotonically forming oligomers, which is followed by a rapid exo-thermic step of the polymer chain propagation (Tzou and Gregory, 1992; Sapurina and Stejskal, 2008). We believe that the polymerization of ANSA also followed the same route.

3.2. CIE $L^*a^*b^*$ values, and color strength

Wool fabrics treated with different ANSAs by in situ oxidative polymerization produced a range of colors on wool fabric samples. The treatment parameters, monomer concentration, treatment pH, temperature, and time affected the shade produced, shade depth, and colorfastness to washing. The intensity and depth of color increased with an increase in the concentrations of ANSA and the treatment temperature. The increase in pH also affected the color of the fabric turning from darker to lighter with an increase in the treatment pH. The effect of various treatment parameters on the color of the fabrics is discussed below:

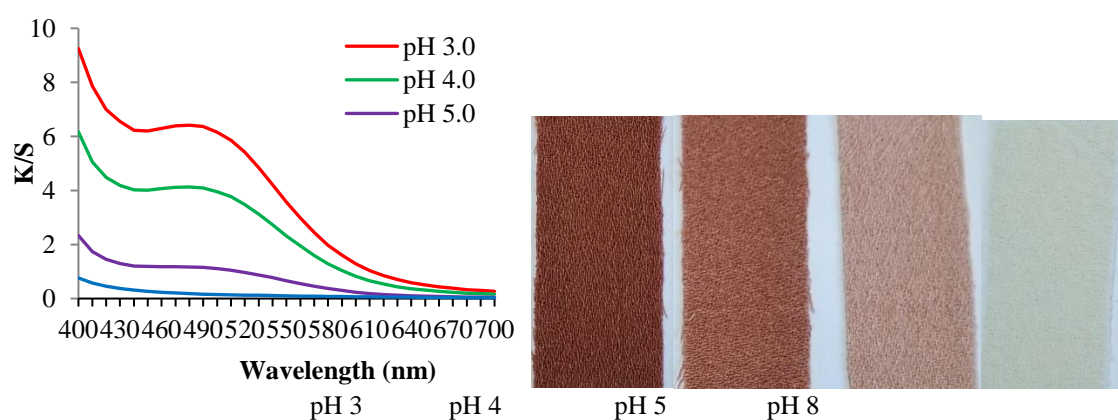


Fig. 4. Effect of pH on the color strength of fabrics treated with 4% owf ANSA-1 for 120 min at 30 °C.

3.2.1. Effect of pH

It is very important to evaluate the effect of pH on the color of the fabric as the absorption of ionic dyes is dependent on the treatment pH and the ionic property of the fiber. As the ANSAs used in this study were anionic, it can be assumed that the effect of pH on the resulting color will be similar. Therefore, the effect of pH on the shade produced was assessed only for ANSA-1 (Fig. 4). The depth of shade decreased with an increase in the treatment pH. The shade produced at pH 3 was deep maroon which turned to light maroon and light brown when the treatment was carried out at pH 5 and 7 respectively. The fabric

treated at pH 8.0 produced hardly any color on the fabric. The fabric treated at pH 3 showed the highest color strength of 9.25 observed at a wavelength of 400 nm. The color strength decreased with an increase in pH. At pH 8 barely produced any color with a color strength of 0.76.

The effect of pH on the *CIE L*a*b** values of the wool fabrics treated with ANSA-1 polymer is presented in Table 2. The lightness value (L^*) of wool fabric increased with an increase in pH, i.e., the color became lighter with an increase in the treatment pH. The value of L^* increased from 42.1 for the fabric treated at pH 3 to 82.2 for the fabric treated at pH 8.0. The reddish and yellowish tone of the color decreased with an increase in pH evident from decreased a^* and b^* values. The pH had a little effect on the color fastness of washing as all fabrics treated showed very good colorfastness to washing with grades consistently between 4 and 4-5.

The absorption of anionic dyes by wool fiber is electrostatically governed and therefore the pH of the treatment plays a great role in the absorption of anionic dyes. The isoelectric or chargeless point of wool in an aqueous medium is pH 4.5 to 5.0, below which the fiber surface is cationic and above is anionic, i.e., anionic compounds are attracted to the fiber surface at pH below 4.5 but with an increase in pH, the repulsion of anionic compounds by wool fiber increases (Capablanca and Watt, 1986). At pH 3, wool fiber is cationic and therefore attracts anionic ANSA. Conversely, above pH 5 both ANSA and wool fiber are anionic and therefore the adsorption of ANSA is not controlled by electrostatic bonding but is rather governed by the hydrogen bonding or van der Waals' force, which is weaker than electrostatic attraction. For the oxidative polymerization of aniline, it was reported that the coupling of the monomer units occurs through electrophilic substitution mechanism. The oxidized terminal imino structure is substituted with a proton in the benzene ring and the

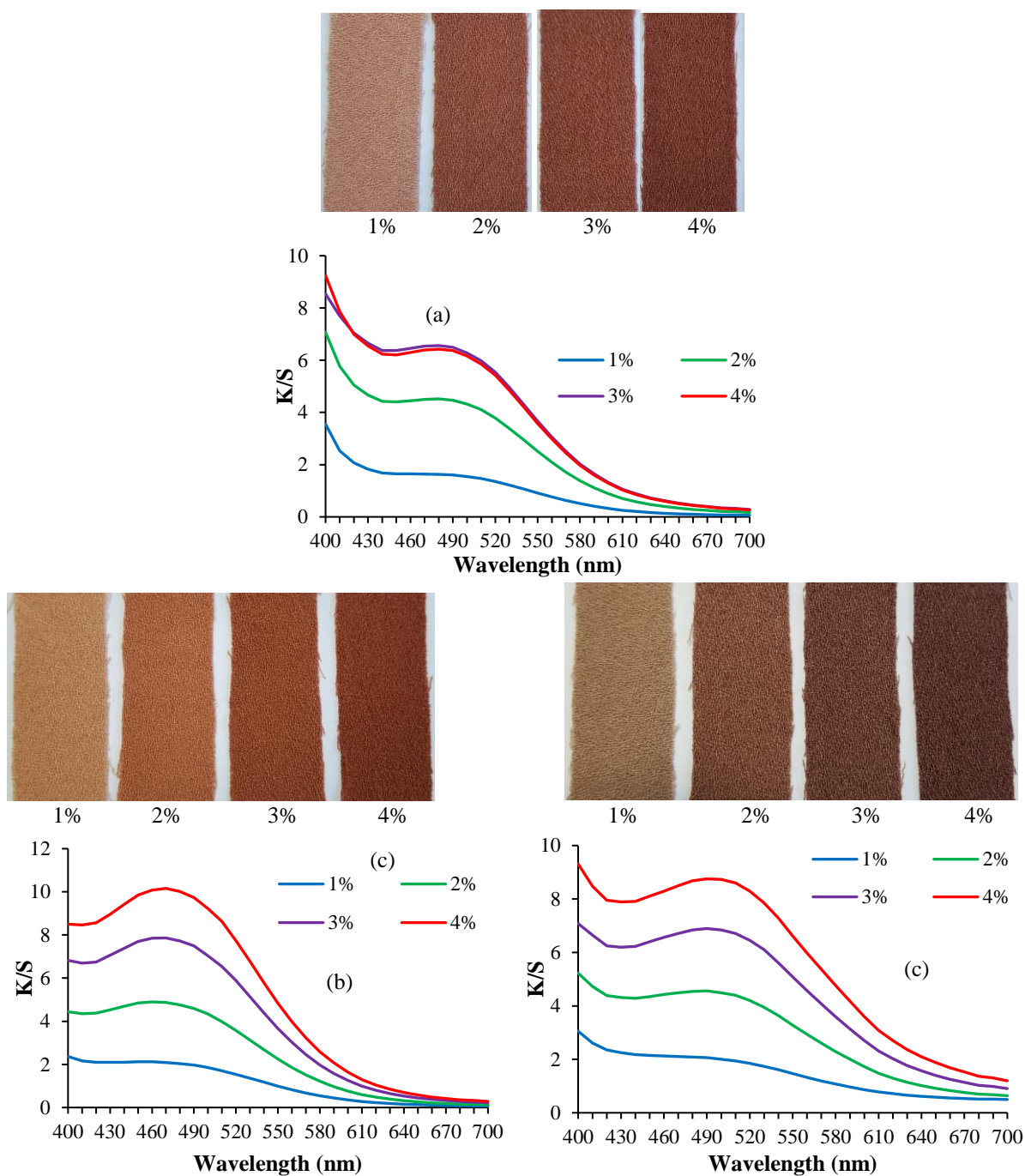


Fig. 5. Effect of ANSA concentration on the color strength of the fabrics treated with ANSA-1 (a), ANSA-2 (b), and ANSA-3 (c).

liberation of the proton increases the acidity of the polymer solution (Sapurino and Stejskal, 2008). This is a normal phenomenon for all oxidative polymerization processes that proceed

by the electrophilic substitution mechanism. Oxidation polymerization mostly takes place in mild to strong acidic conditions. For oxidative polymerization of dopamine, it was observed that the redox potential decreases with an increase in pH (Salomäki et al., 2018). Therefore, the fabric treated at pH above 5.0 produced barely any color.

3.2.2. Effect of ANSA concentration

Fig. 5 shows the shade produced and the color strength (K/S) of wool fabrics treated with various ANSAs over the visible wavelength of light and detailed results are presented in Table 2. The color strength of wool fabric over visible wavelengths range increased with an increase in ANSA concentration. At a dosage of 1% owf ANSA-1, the fabric treated with ANSA-1 produced a reddish-brown color, while ANSA-3 produced a yellowish-brown color.

The color produced by ANSA-2 was in between ANSA-1 and ANSA-3. Fabric samples treated with 4.0% owf produced the highest color strength and the lowest by the wool fabric treated with 1.0% ANSAs. Of them, ANSA-2 produced the highest color strength (10.35), and the fabric sample treated with ANSA-1 and ANSA-3 produced similar but slightly lower strength. The color strength of ANSA-1 treated wool fabric increased from 3.55 to 9.25 when the applied dosage of ANSA-1 was increased from 1% owf to 4% owf as with an increase in the concentration of ANSA, the absorption slowly reach saturation. Similarly, for the ANSA-2 and ANSA-3, the color strength increased from 2.12 to 10.15 and 3.05 to 9.31 respectively when the ANSA concentration was increased from 1% owf to 4% owf.

The influence of ANSA concentration on the *CIE L*a*b** values is presented in Table 2. Generally, the increase in the concentration of ANSAs decreased the lightness value (L^*), i.e., the color of the fabric became darker with an increase in the concentration of ANSAs. In

the case of ANSA-1, the value of L^* decreased from 66.1 to 42.1 when the applied dosage of ANSA-1 increased from 1% owf to 4% owf. The redness of the fabric increased with an increase in the ANSA concentration, but the yellowness of the fabric increased from 1 to 3% owf and decreased when the concentration of ANSA-1 was further increased. In the case of ANSA-2, the L^* value decreased from 65.2 to 42.7 when the concentration of ANSA was increased from 1% owf to 4% owf. The redness of the fabric also increased with the increase in pH but the yellowness increased for 1 to 2% owf and then started decreasing with the further increase in the concentration of ANSA. The increase in the concentration of ANSA-3 exhibited a similar effect on the L^* value but the redness increased when the concentration was increased from 1 to 2% owf but a further increase decreased the redness of the fabric. However, the yellowness of the fabric decreased with an increase in the concentration of ANSA-3.

The increase in ANSA concentration increased the saturation of ANSA molecules inside the fibers and led to some ANSA polymer molecules residing near the surface. They were possibly removed during the washing test resulting in a slight decrease in colorfastness. Of the ANSAs studied in this work, ANSA-1 has two sulfonic acid groups which did not affect the adsorption of ANSA-1 into wool fiber as the treated fabric showed almost similar color strength to the fabric samples treated with the other two ANSAs. On the other hand, the wool fabric treated with ANSA-2 showed the highest color strength, but the aqueous solution of this ANSA polymer showed considerably lower absorbance than the other two polymeric dyes. The chemical structure of ANSA-3 is quite similar to ANSA-2 but produced a different color due to the change of position of the substituent sulfonate group in its structure.

Therefore, it can be concluded that different colors produced by ANSA-2 and ANSA-3 illustrate that the position of substituent sulfonate groups affects their color, which is consistent with their UV-vis spectra shown in Fig. 2. The effect of monomer concentration on

the color strength produced by the ANSAs is consistent with the oxidative polymerization of sulfonated aniline reported in our previous work (Hassan, 2021).

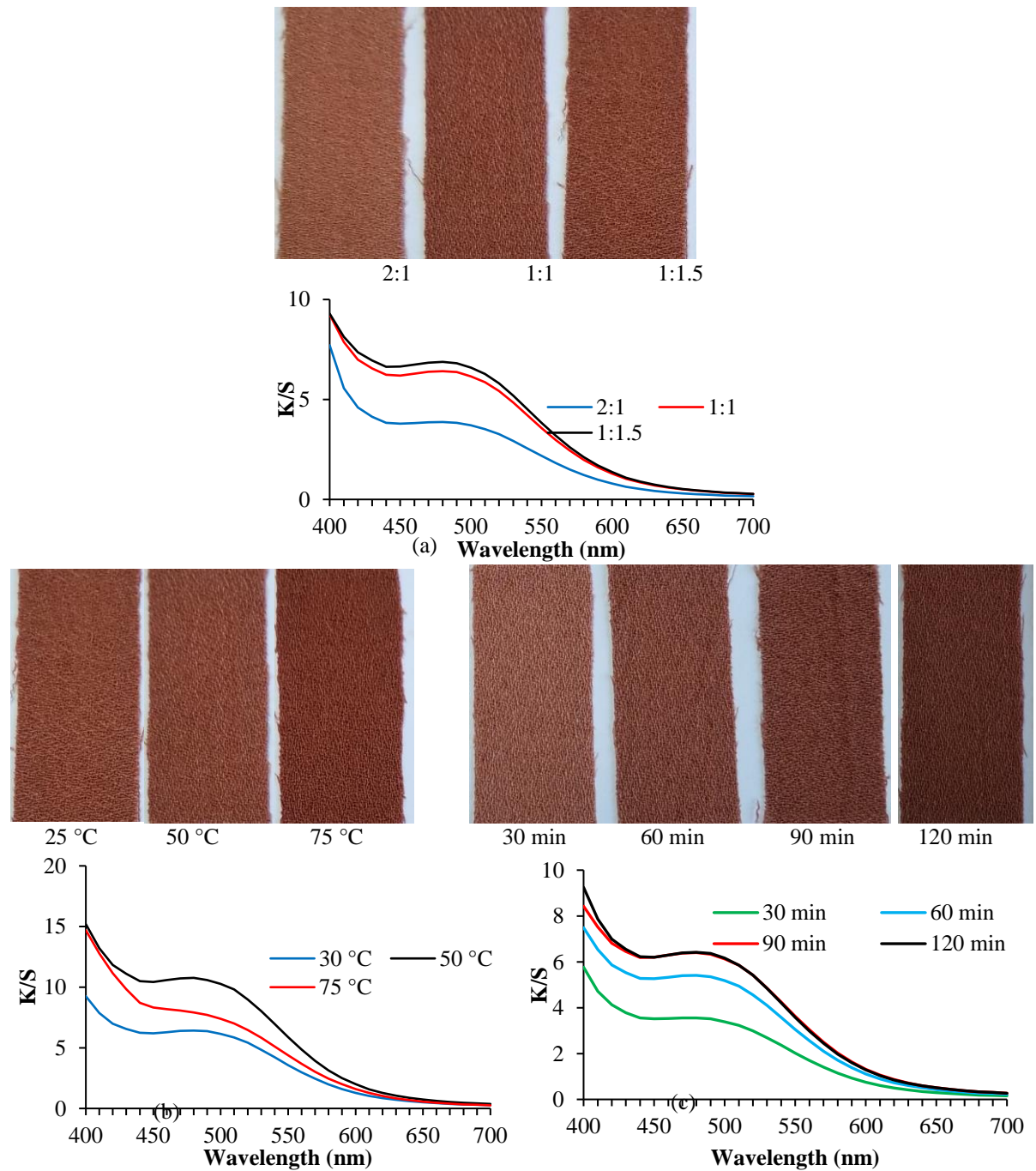


Fig. 6. Effect of ANSA to SPS ratio, treatment temperature, and time on the color strength of wool fabric treated with 4% owf ANSA-1 at pH 3.0.

3.2.3. *Effect of concentration of SPS, treatment time, and temperature*

Fig. 6 shows the effect of SPS concentration on the shade and color strength of the wool fabric treated with ANSA-1. The change in the ratio of SPS to ANSA had a positive effect on the color strength of wool fabrics, but a negative effect on their colorfastness of washing. The color strength of fabric treated with 4% owf ANSA-1 increased from 7.71 to 9.25 when the ANSA to SPS ratio was increased from 2:1 to 1:1. Similarly, the value of L^* decreased from 49.9 to 42.1 along with an increase in redness and a decrease in yellowness. Further increasing the ANSA to SPS ratio to 1:1.5 only marginally increased the color strength and decreased the lightness of the treated fabric. Similarly, the colorfastness to washing decreased with a possible increase in the oxidation rate of ANSA. This may have reduced the diffusion of ANSA molecules into wool fiber causing some pASA molecules to only be adsorbed to the surface of the fiber and removed during the washing test.

Increasing the treatment temperature had a positive effect on color strength and colorfastness to washing of wool fabrics treated with 4% owf of ANSA at pH 3.0. The color strength of the treated fabric increased from 9.25 for the fabric treated at 25 °C to 15.30 for the fabric treated at 50 °C. The fabric also became darker with the value of L^* decreasing from 42.1 to 35.9. However, a further increase of temperature to 75 °C slightly reduced the color strength and increased the lightness of the fabric. Raising the treatment temperature to 50 °C also increased the colorfastness to washing due to an increase in the diffusion of ANSA molecules. However, at 75 °C, the affinity of the ANSA to wool fiber increased, which caused clogging of wool fiber pores affecting the diffusion of the ANSA molecules. The decrease in dyeing temperature will hugely save energy costs for dyeing as traditionally wool fibers are dyed at the boil with anionic acid dyes.

Treatment time also had a great effect on color strength and colorfastness to washing when wool fabrics were treated with 4% owf of ANSA at pH 3.0. Color strength increased from 4.72 for the fabric treated for 30 min to 9.25 for the fabric treated for 120 min. The fabric also became darker with the value of L^* decreasing from 49.3 to 42.1. The increase in treatment time also increased the colorfastness to washing due to an increase in the diffusion of ANSA molecules. It can be summarized that the optimum conditions for the dyeing of wool with ANSAs are a 1:1 ANSA to SPS ratio, 50 °C, and 120 min treatment time.

3.3. Colorfastness, durability to washing, and energy savings

For becoming a useful industrial textile dye, the color produced by the oxidation polymerized ANSAs will need to be durable to wash, which is assessed by the colorfastness to washing test. Table 2 shows the colorfastness to washing data of the fabrics treated with dimers/oligomers of various ANSAs. All of them showed very good colorfastness to washing with fastness grades from 4 to 4-5. The colorfastness to washing grades decreased with an increase in the ANSA concentration, as the fibers become saturated with ANSA molecules. This leads to ANSA molecules staying near the surface of the fibers and post-dyeing washing caused their loss decreasing the color intensity and fastness grade. The deposition of ANSA-3 polymer on the surface of fibers was further characterized by scanning electron microscopy.

Energy consumption of dyeing with ANSAs was carried out to evaluate the sustainability of the developed method. As mentioned early, wool fibers are dyed at the boil using materials to liquor ratio of 1:30, and depending on the depth of the shade the dyeing time is varied from 60 to 120 min as deeper shades require longer dyeing time. We assume that the dyeing time

for wool fabric at 4% owf using synthetic acid dyes and ANSAs are equal. Usually, for the traditional dyeing at the boil, the energy consumption of a jet dyeing machine is 4.4 kWh/kg with heating but even without heating, the energy consumption is 1.0 kWh/kg (Palamutcu, 2010). If the dyeing is carried out at 50 °C, the energy consumption is 2.3 kWh/kg. Therefore, for each kilogram of fabric, the energy savings is $4.4 - 2.3 = 2.1$ kWh, which is almost a 48% reduction of the energy cost compared to the dyeing with acid dyes. ANSAs have low toxicity compared to many dyes and therefore there will be huge environmental benefits over using synthetic dyes.

3.4. Surface morphologies

The SEM image of the control wool fabric shows the characteristic scaly structure of wool fiber and also some debris of wool fiber scales (Fig. 7a). The surface of wool fibers treated with ANSA-1 is relatively clean, but some level of scale damage occurred, and debris of wool fiber scales is visible on the fiber surface (Fig. 7b). No deposition of polymer is visible suggesting that ANSA-1 formed dimers that were readily absorbed into the wool fiber. On the other hand, the surface of wool fibers treated with ANSA-2 shows some fiber surface deposition of polymer suggesting the formation of a polymer by oxidative polymerization of ANSA-2 (Fig. 7c). In the case of wool fabric treated with ANSA-3, deposition of ANSA-3 polymers is clearly visible on the treated fiber surface suggesting polymerized ANSA-3 molecules did not exhaust into fibers and stayed on the fiber surface indicating successful polymerization of ANSA-3 (Fig. 7d). The surface morphologies of wool fabric surface treated with various ANSAs suggest that ANSA-1 did not form any polymer but the other two ANSAs were successfully polymerized.

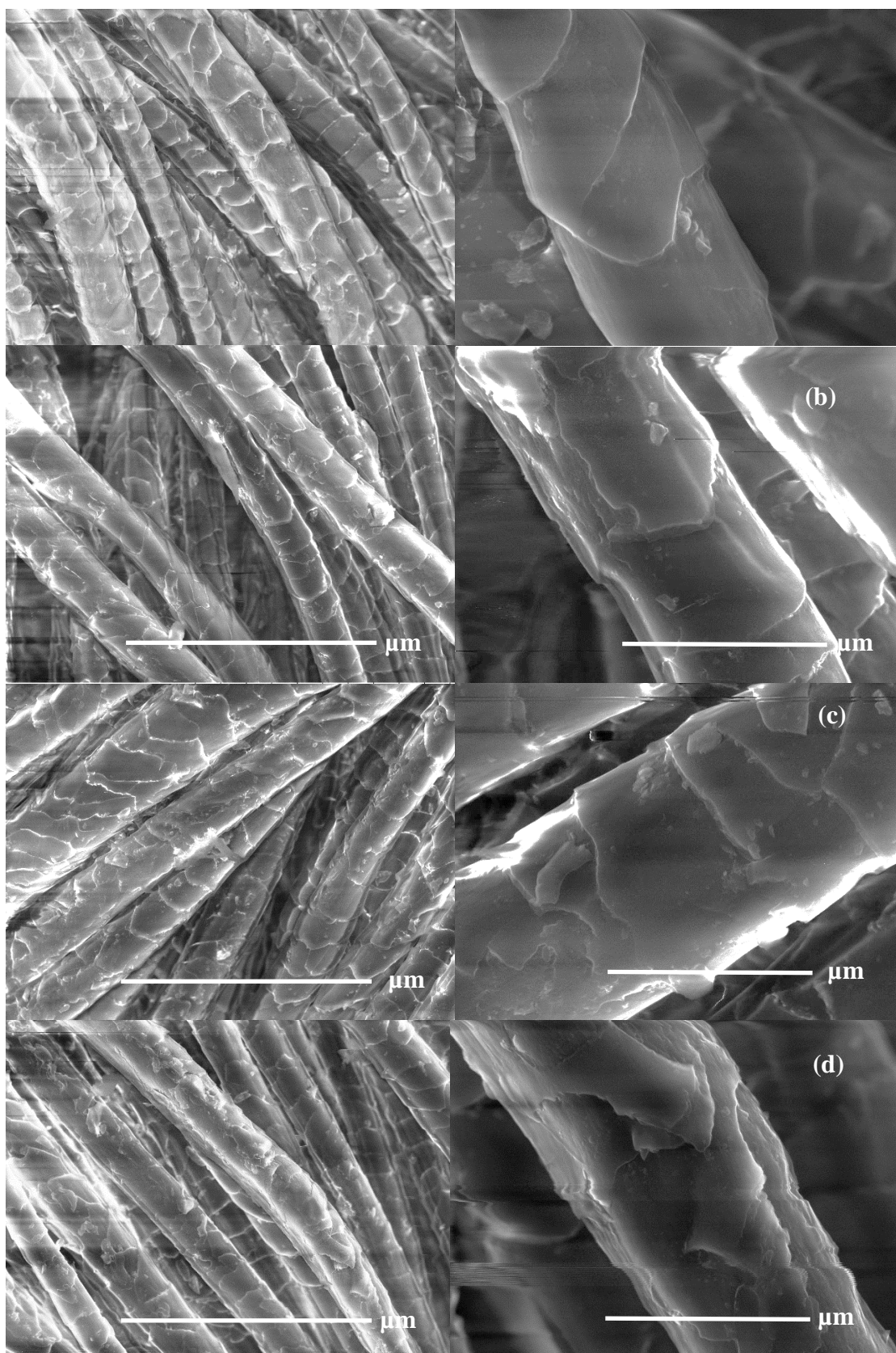


Fig. 7. SEM micrographs of the surfaces of control wool fabric (a) and also wool fabrics treated with 4% owf ANSA-1 (b), ANSA-2 (c), and ANSA-3 (d) at pH 3.0 for 120 min.

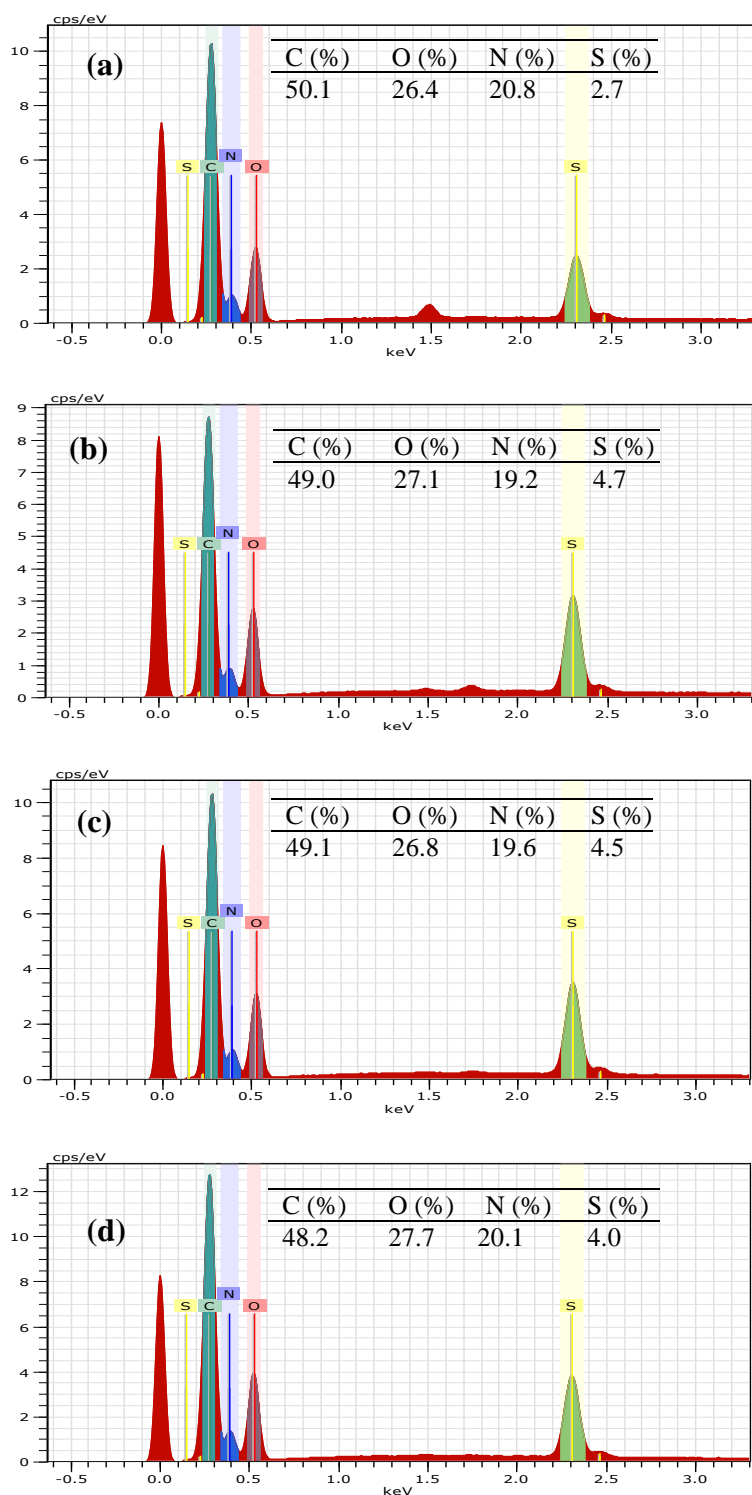


Fig. 8. EDX spectra of untreated (a) and wool fabrics treated with 5% owf ANSA-1 (b), ANSA-2 (c), and ANSA-3 (d).

3.5. Elemental analysis by EDX

The EDX spectra and elemental composition of C, N, O, and S of wool fabric treated with ANSAs are shown in Fig. 8. The elemental composition of C, N, O, and S of untreated wool fiber is 50.07, 20.77, 26.41, and 2.74% respectively, which is consistent with our previous works (Hassan, 2019). The S content compared to the untreated fabric as ANSAs contain sulfonic acid groups. The wool fabric treated with ANSA-1 showed the highest increase in S content as it has two sulfonic acid groups compared to the one sulfonic acid group of ANSA-2 and ANSA-3. A considerably higher S content for wool fabric dyed with ANSA-2 suggests that it was better absorbed into wool fabric compared to ANSA-3. The fabric treated with ANSA-2 showed slightly higher color strength than ANSA-3 suggesting that the higher molecular weight of ANSA-3 affected its absorption into wool fabric affecting the color strength of the treated fabrics.

The elemental distribution of C, O, N, and S on the surface of wool fabrics treated with various ANSAs are presented in Fig. S3 (Supplementary Materials). The elemental mapping shows that the elements (especially S) are evenly distributed on the surface suggesting very uniform treatments of fabrics.

3.6. ATR-FTIR

The spectrum of untreated wool fabric shows typical wool fiber keratin-associated IR bands, such as amide III, amide II, and amide I peak at 1227, 1540, and 1635 cm^{-1} , respectively (Fig. S4 in Supplementary Materials). The IR band at 1506 cm^{-1} could be attributed to the C–N stretching and also to the N–H in-plane bending vibrations (amide II).

The IR spectrum of the control fabric also shows a broad IR band at 3250 cm^{-1} , which could be attributed to the hydroxyl groups of wool fiber. The band at 1040 cm^{-1} could be attributed to the Bunte-salt groups of wool fiber (Millington and Church, 1997; Hassan and Leighs, 2017). The wool fabrics treated with ANSAs show new bands near 1030 cm^{-1} , which could be attributed to the sulphonate groups of ANSAs. The intensity of hydroxyl bands at 3250 did not change as ANSAs do not have hydroxyl groups in their chemical structure. The intensity of these peaks slightly increased with an increase in the concentration of ANSAs.

4. Conclusions

This work has demonstrated that multicolored dyes can be produced by oxidative polymerizations of ANSAs, and multicolored wool fabrics can be produced by treating them with ANSA dyes. The shade produced and the color strength can be varied by changing treatment parameters, such as ANSA concentration, ANSA to oxidant ratio, and also treatment pH, time, and temperature. Of the ANSAs studied, ANSA-2 produced a slightly higher color strength compared to other ANSAs. Dyeing is only possible in acidic conditions, which is ideal for wool fibers as ANSAs can be exhausted into wool fibers at these conditions without causing the degradation of the wool fibers. The treated fabrics showed excellent colorfastness to washing. The dyeing technique can be used as a sustainable coloration method for producing multicolored wool fibers in the textile industry with excellent colorfastness to washing.

Author contributions

The conceptualization, methodology development, investigation, collation of data, and article writing, have been carried out by Dr. Mohammad Mahbubul Hassan. Jessica Gathercole and Armin Thumm carried out GPC and MALDI-TOF MS scanning and also contributed to writing and editing the article.

Declaration of conflict of interest

The authors declare no conflict of interest.

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