

Measurement of aluminum ions across the mordanting process of wool substrates with potassium
aluminum sulfate and effluent characterization

by

Kowshik Saha

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Approved by:

Major Professor
Sherry Haar

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Abstract

The purpose of this research was to determine the distribution of aluminum (Al) ions across mordanting procedures and characterize the effluent of wool challis fabric and wool yarn premordanted with potassium aluminum sulfate (PAS) at three concentrations (7%, 12%, 17%) by weight of fiber. ATSM D5673-16 Standard Test Method for Elements in Water by ICP-MS (American Society for Testing and Materials, 2016) measured the Al ions in the liquors and substrates. The effluent was characterized by measuring chemical oxygen demand (COD) and total organic carbon (TOC) by utilizing TNTplus®—Method 8000 and Shimadzu TOC-L Series.

The Al percentage in the treated liquors for both substrates ranged from 26% to 68%. The findings met the Environmental Protection Agency Al in freshwater limits. The wool yarn absorbed a significantly lower percentage of Al than the wool challis. With the increase of the PAS mordant concentration, the percentage of Al ions detected in the substrates decreased significantly and the Al ions percentage significantly increased in the treated liquors. Thus, the 7% PAS concentration was significantly more efficient compared to the recommended 12% concentration. The TOC and COD values of the effluents met the Code of Federal Regulations for textile mill effluent discharge and Global Organic Textile Standard limits as output; however, dilution and neutralization are required before disposing of the effluents.

This research confirmed the safe usage of PAS as a mordant for the selected wool substrates in terms of Al input, disposal with pH neutralization, and discharge standards. Further studies could investigate lower concentrations of PAS, the feasibility of reusing the treated liquors, and the impact of PAS amount to dye color parameters.

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Chapter 1 - Introduction

The growing tension surrounding the textile wet processing industry is due to the industry's high-water consumption, high wastewater discharge, and pollution potential (Gomes, Sanches, & Duran, 2000). As a water-intensive industry, the textile wet process industry strains the global water resource (Hussain & Wahab, 2018; Saxena & Raja, 2017). Water is the lifeline of a textile mill, especially the wet processing section, where every process requires a large volume of water. A typical textile factory with a capacity of about 8000 kg of fabric per day consumes around 1.6 million liters of water daily (Hussain & Wahab, 2018; Ravi, Parthasarathy, Vijayabharathi, & Suresh, 2014). The dyeing and printing processes consume about 16% and 8% of an average sized textile mill's water consumption, respectively (Kant, 2012). The textile industry is possibly the third most significant contributor to water pollution after tanneries and the pulp and paper industries (Nimkar, 2018). In 2003, China's textile waste discharge accounted for 1.6 billion cubic meters per year among the total industrial wastewater discharge that is 21.2 billion cubic meters per year (Lu, Liu, Liu, & Chen, 2010). Further, these textile facilities discharge over 80% textile wastewater (Lu et al., 2010). Such industrial waste is from the 5 billion kg of dyes, pigments, and finishing chemicals used worldwide, including over 8000 chemicals and 3600 different dyes (Hussain & Wahab, 2018; Nimkar, 2018). Thus, the textile wet-processing creates a tremendous amount of pollutants that are disturbing the eco-balance of nature (Ghorpade, Darvekar, & Vankar, 2000).

Textile effluents from dyeing and finishing consist of both organic and inorganic compounds at high concentrations that contribute to environmental degradation and human illness (Hassaan & El Nemr, 2017; Kant, 2012). Apart from water pollution, effluents cause detrimental impacts on soil and marine animals (Hassaan & El Nemr, 2017). Further, high

exposure to dyes and chemicals contribute to various human health issues such as respiratory and immune system problems, itching, watery eyes, sneezing and symptoms of asthma such as coughing and wheezing (Hassaan & El Nemr, 2017).

The growing awareness of environmental harm from the textile dyeing industry has created an interest in natural dyes as a sustainable option for niche markets and capsule collections (DuFault, 2017; Laughlin, 2017; Schneider-Levy, 2018). Natural colorants from flora and insects are considered safe as they are non-toxic, non-carcinogenic, and biodegradable (Mirjalili, 2011). Natural dyes are less toxic, less allergenic, and highly compatible with the environment due to their biodegradability (Deo & Desai, 1999; Feng, Zhang, Chen, & Zhang, 2007), while synthetic dyes are associated with toxicity and allergic reactions (Deo & Desai, 1999; Feng et al., 2007). Bechtold, Turcanua, Ganglbergerb, and Geissler (2003) considered the use of natural dyes as progress for the sustainability of textile dyeing and finishing process that consume water, chemicals, and energy. However, there are challenges of using natural dyes including poor color fastness and strength, reproducibility of the shade, scalability, and the lengthy extraction of dyes increase the cost of production (Bechtold et al., 2003).

Further, concern has been expressed questioning the toxicity of metal mordants and biodegradability of large amounts of organic dyestuffs. Generally, this concern is associated with the wastewater containing residual metal ions from metal salt mordants, which can harm the environment and public health (Burkinshaw & Kumar, 2009; Zheng et al., 2011). The metal salt mordant, most often an aluminum compound, is applied to the fiber before, during, or after dyeing to increase the affinity of dyes towards the fiber which improves the color fastness properties. However, considerable amounts of mordant chemical remain in the residual dye bath and if improperly released as effluents may contaminate land and water resources (Shahid, Islam,

& Mohammad, 2013). When evaluating the amount of aluminum remaining in aluminum acetate mordant baths of cotton print cloth, over 90% of the aluminum remained (Saha, Patwary, & Haar, 2018).

Aluminum mordants are common for treating natural fibers and considered safe compared to historically used mordants of chromium, copper, and tin. However, the toxicity of aluminum can limit plant growth in acidic soil (Bojórquez-Quintal, Escalante-Magaña, Echevarria-Machado, & Martinez-Estévez, 2017). Under certain conditions, as in high concentrations, and in low acidic or high alkaline conditions, aluminum can be harmful to aquatic life and its food sources (Goudie, 2013). High aluminum exposure to humans may contribute to diseases like Alzheimer's, Parkinson's, and kidney disease (AlKindy, Al-Hinai, Al-Rasbi, Suliman, & Al-Lawati, 2015; ATSDR, 2008). Despite concern over mordant effluent amounts, limited information is available on the measurement and amount of metal ions in residual mordant dye baths. This study investigated the distribution of aluminum (Al) ions across the mordanting process on wool substrates with potassium aluminum sulfate (PAS) as the mordant.

Purpose of the Study

The purpose of the study was to determine the amount of Al ions from the mordant, potassium aluminum sulfate, that remains in the effluent water following the mordanting of two substrates, wool challis fabric and wool yarn. This was accomplished by measuring Al ions across the mordanting process with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Thus, Al was measured in the aqueous solutions (water, scour bath, mordant control, treatment bath, and rinse water) and substrate conditions (untreated, scoured, and mordant treated). Three concentrations, 7%, 12%, and 17% by the weight of fiber (owf) were examined. In addition, the

effluent characteristics of chemical oxygen demand (COD) and total organic carbon (TOC) were measured to determine the safety of the effluent as compared to disposal, discharge, and output standards and regulations.

Research Questions and Hypotheses

Some researchers measured and some estimated the Al ions in the natural dye effluents. However, minimal research was found that measured the Al as a result of premordanting. As premordanting is a typical step in the natural dye process and does have an effluent it was important to establish Al absorption prior to dyeing. The prior research for premordanting wool indicated most (94%) of the Al was in the effluent (Smith & Wagner, 1991). Similarly, 90% - 91% Al remained in the effluent for premordanting cotton (Saha et al., 2018; Smith & Wagner, 1991). As wool has improved ion bonding compared to cotton (Patel, 2011), for this research it was predicted that 80% of the Al ions would remain in the mordant bath. Measuring the Al distribution across the premordanting process will indicate Al amounts in all liquor and substrate conditions and overall loss. Thus, the first research question and hypothesis were:

1. What is the distribution of Al ions across the mordanting process for selected wool substrates pre-mordanted with potassium aluminum sulfate at three concentrations?

H1: At least 80% of Al ions will remain in the mordant bath, and the substrates will absorb 10% or less.

The second research question focused on the substrates. It was assumed that yarn would absorb more Al than fabric due to the better dye absorption ability of skeins compared to woven fabric (“Wet Processing Engineering”, n.d.). In addition, the compact structure of the fabric compared to the yarn led to the assumption that yarn would have better absorption than the fabric (“Terminology: What’s the difference between worsted”, 2014).

2. How does substrate structure, woven wool fabric compared to wool yarn, influence mordant absorption?

H1: Wool yarn will have a significantly higher percentage of Al ions absorbed compared to wool challis.

The commonly used 12% PAS concentration along with 5% lower and higher concentrations were investigated to find the impact of concentration on mordant absorption and amount remaining in the treated liquor. Even though mordant concentration was not often varied in prior studies, knowing impact from concentration may advise dyers on mordant amounts and guide future work on optimal mordant concentration. Thus, the third research question and hypothesis were:

3. a) How will mordant concentration influence absorption of Al ions on the woven and yarn wool substrates?

H1: The percentage of Al ion absorption in wool substrates will significantly increase with an increase in the PAS concentration.

3. b) How will mordant concentration influence the percentage of Al ions remaining in the treated bath of the woven and yarn wool substrates?

H1: The percentage of Aluminum ions remaining in the treated bath will significantly increase with an increase in PAS concentration.

The biodegradability of matter in the effluent was measured from COD and TOC. Prior research reported biodegradability of natural dye effluents as COD/BOD₅ and BOD; and as meeting discharge standards (Chan et al, 2002; Saxena & Raja, 2014). As this study measured the organic matters in the mordant effluent, COD and TOC test were appropriate. As prior studies were within the discharge standards for biodegradability it was assumed that the COD

and TOC values would be within the existing standards and limits. Based on the prior study findings, the following research question and hypothesis were established.

4. What is the mordant treated liquor characterization in terms of chemical oxygen demand (COD), total organic carbon (TOC), and pH?

H1: Mordant effluents will meet the disposal and discharge regulations by the Code of Federal Regulations (CFR) and the Global Organic Textiles Standard (GOTS).

Justification

Though synthetic dyes are used widely for coloring textiles, natural dyes are becoming more popular for small scale production. Synthetic dyeing processes, especially in developing countries, release highly polluted effluents in nearby waterbodies or land with little to no further treatment. As a result, surface and ground water become contaminated. While natural dyes are biodegradable under certain conditions, many assume that natural dyes, their processes, and effluents are safe. Yet, few studies have examined the pretreatment mordant chemicals, such as Al, that enhance dye to fiber bond and resulting colorfastness. At high exposure and high or low pH, aluminum can be harmful to humans, plants, fish and aquatic invertebrates. Thus, there is a need to know the amount of chemical mordant being disposed and what those amounts mean to human and environmental safety.

Currently, limited information is available on actual amounts of Al mordant remaining in the effluent bath and minimal information has been presented on how amounts were determined. By presenting a valid method to measure the distribution of Al mordant ions across the premordanting process, other scientists may be guided to conduct related studies to build the knowledge of mordant distribution. In addition to measuring the Al ion distribution, this research tested the effluent for COD and TOC to quantify its biodegradability. Knowing the

biodegradability allowed the findings to be contextualized against waste water disposal, discharge, and output regulations. Thus, the findings and recommendations from this research can inform individual, small scale, and volume dyers on safe disposal methods.

Definitions

Table 1.1 Terms and definitions

Terms	Definitions
Mordant	An auxiliary chemical that can itself be fixed on the fiber and form a chemical bond with the natural dyes (Prabhu & Bhute, 2012). It assists in the absorption and fixation of natural dyes.
Effluent	The wastewater generated from various chemical treatment processes like dyeing and washing. In this study, effluent is the mordant treated liquor and rinse water.
Input	An input is a raw material used for production processes. It is also a “general term for all substances and preparations directly applied as textile auxiliary agents, dyes or pigments” (GOTS, 2017, p. 37).
Discharge	The discharge is the aqueous effluent released directly to freshwaters or municipal sewage.
Processed output	The processed output is the treated water from a wastewater treatment facility.
Chemical Oxygen Demand (COD)	COD measures the amount of oxygen required to oxidize both organic and inorganic matter.
Biological Oxygen Demand (BOD)	BOD determines the oxygen consumed in the biological processes that break down biodegradable organic matters in the water or wastewater samples through the biochemical process (Chan, Yuen, and Yeung, 2002).
COD/BOD ₅ ratio	The COD / BOD helps to qualify the biodegradability of effluent. Here 5 means five day analysis time for BOD.
Total Organic Carbon (TOC)	It is the measure of total organic carbon present in a sample. However, the measure excludes the inorganic compounds.
ppm ppb	Parts Per Million Parts Per Billion

Chapter 2 - Review of Literature

Natural dyeing is a coloring process with dyes extracted from various plants and insects (Boutrup & Ellis, 2018). There is a great interest of natural dyeing in both research fields as well as textile industries because of the growing concerns regarding water pollution, sustainability of raw materials and processed products, biodegradability and environment-friendly characteristics (Bechtold, Mahmud, & Komboonchoo, 2009). As natural dyes are less toxic and more biodegradable compared to synthetic dyestuffs, the use of natural dyes can be good start for the continuous development of textile wet processes regarding water, chemical and energy consumption (Bechtold, Turcanu, Ganglberger, & Geissler, 2003).

Mordanting is an important process for dyeing natural fibers with natural dye extracts as affinity of these dyes are not good towards them. Mordants create a chemical bridge from dye to fiber that helps to bind the dyes with fabrics, eventually increasing the staining ability of a dye as well as improve the fastness properties (Vankar, 2000). Among different mordanting methods, pre-mordanting is a commonly used method and provides good outcomes (Böhmer, 2002), as several fabrics can be prepared in advance and the main bath is not changed chemically as with everything in one bath (Cardon, 2007). In natural dyeing, a major proportion of the mordants remain in the process bath (Chavan, 1995). The purpose of this research was to measure the mordant not only in the process bath, but across the mordanting procedure. To understand the environmental impact, COD and TOC were measured and contextualized against standards and regulations.

The review of literature included the raw materials, chemicals and processes used in this study. Further, this section justified the selection of materials and methods as well as the overall rationale of this study providing prior study findings regarding the natural dye effluents, residual

metals in the effluents and finally, presenting the standards and regulations in terms of input, discharge and processed output.

Wool Fiber

Wool fiber is one of the most commonly used natural protein fibers in textile manufacturing after silk fiber (Cook, 2005). The primary source of wool fiber is sheep, and these fibers are widely used for dyeing purposes as they have excellent absorbency properties (Cook, 2005). Wool is a protein fiber and composed of a protein substance called keratin. Wool fibers are composed of amino acids, which have high moisture regain capacity, good elasticity, and resiliency (Cook, 2005). The fibers can range in a variety of staple lengths (1 to 15 in.) and fiber diameters or micron counts from fine (15 micrometers) to coarse fibers (around 34+ micrometers) (The Code of Federal Regulations of the United States of America, 1976). Wool fibers need carbonizing to remove the cellulosic matters. Carbonizing is a process of removing burrs, twigs, and other vegetable matters by steeping wool in dilute sulphuric acid and heating them at high temperature (Cook, 2005). Further, these fibers require scouring before textile processing to remove lanolin and dirt through several washing in a warm, soapy, and alkaline solution (Cardon, 2007). As a result, this process breaks down the cellulosic material and finally, removal of matter from the wool. Dyeing can occur at the fiber, yarn, skein, knitted, or woven stages. Patel (2011) reported that wool is receptive to mordants and natural dyes more than cotton as the fiber absorbs both acids and bases effectively due to its amphoteric nature. According to Chemicool dictionary, an amphoteric compound is one that can react with both acids and bases. Therefore, being amphoteric, wool can react to both the acid and base part of a dyestuff and, depending on the medium, these fibers can act either an acid or base (“What does amphoteric...”, n.d). Several researchers found that wool substrates mordanted with PAS gave

good colorfastness to laundering and light (Doty & Haar, 2013; Shams-Nateri, Hajipour, Dehnavi, & Ekrami, 2014).

Prior research established a method for measuring Al ions across the mordanting process for cotton, with the recommendation to do the same for a protein fiber (Saha, Patwary, & Haar, 2018). Thus, this research established a foundation for measuring Al ions in the mordanting of a wool yarn and fabric.

Potassium Aluminum Sulfate

Mordants are usually metallic salts used to fix the color to the fibers (Cardon, 2007; Richards & Tyrl, 2005). Most of the plant and insect colorants require mordants to affix color to the fibers (Cardon, 2007). Mordants react with the dye molecules that help the fabric to retain more natural dyes (Broadbent, 2001). The metal atom of the mordant molecule form both covalent and coordination bonds to create a large complex and provide a bridge between the dye and fiber ("How to mordant," n.d). Traditionally used mordants included aluminum salts (potassium aluminum sulfate, aluminum sulfate), iron (ferrous sulfate) or copperas (green hydrated ferrous sulfate), chrome (potassium dichromate), copper (cupric sulfate), and tin (stannous chloride) (Richards & Tyrl, 2005). Due to awareness of toxicity, copper, chrome, and tin are not commonly used today (Cardon, 2007). According to the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) (n.d.), aluminum does not have any input limits, however, the input limits for copper, chromium, and tin are 250 mg/kg, 100 mg/kg, and 250 mg/kg respectively. Metals are present in the human body as trace elements; however, concentrated metallic salts are toxic (Richards & Tyrl, 2005).

Aluminum is the most commonly found metal in the earth's crust (8.3 % by weight), followed by iron (6.2 %) (Cardon, 2007). Potassium aluminum sulfate (PAS) and aluminum

sulfate are the most commonly used aluminum mordants, with aluminum acetate seeing increased use for mordanting cellulose fibers (Haar, Schrader, & Gatewood, 2013). Aluminum mordants show a good affinity for both protein and cellulosic fiber (Doty, 2013). Aluminum compound or alum has been an essential commodity for textile production both as craft and industrial scale for several thousand years (Cardon, 2007). "The word 'alum' and its variants in different modern European languages are derived from the Latin alumen, but the ultimate source of the term is unknown" (Cardon, 2007, p. 21). Aluminum is derived from deserts, volcanic areas, and plant sources. Aluminum is obtained from alunite and alum shale; however, nowadays, it is typically mined from bauxite (Cardon, 2007). According to Wipplinger (2004), sulfuric acid is used to remove most of the impurities, such as iron and silica. This form is aluminum sulfate. Purification with potassium removes even more impurities, such as iron which can alter the color, and thus potassium aluminum sulfate is most often used for mordanting textiles. Potassium aluminum sulfate (PAS), $KAl(SO_4) \cdot 12H_2O$, is a chemical compound with a molar mass of 474.3884 g/mol with mass percentages of aluminum at 5.68%, Sulphur 13.52%, hydrogen 5.09%, potassium 8.24%, and oxygen 67.45%.

PAS is presently one of the most commonly used mordants for animal fibers as it does not change the dye color and is relatively non-toxic (Cardon, 2007; Dean, 2010; Samanta & Konar, 2011). According to the Safety Data Sheet (SDS), PAS is not classified as a physical or health hazard under the Globally Harmonized System (GHS) (Safety Data Sheet, 2015). It may have some acute health effects like an irritation to skin and eyes upon contact, or upon ingestion and inhalation, however, no harmful impacts data are available regarding potential chronic health effects caused by PAS. However, the SDS provides a remark for humans based on animal data concerning chronic health effects (effects on embryo or fetus). For safety purposes, the SDS

recommends wearing impermeable material and resistant gloves, and eyeglasses with side shields while handling this substance. They also recommend having dust control equipment and oxygen deficient environment; eye wash fountains and safety showers facilities near the workplace. No data on ecotoxicity and toxicity to animals were provided. Regarding waste disposal, SDS recommends that the wastewater is diluted and flushed before releasing to the sewer. Besides, the wastewater should be disposed of according to local, state, and federal environmental control regulations ("Safety Data Sheet," 2015).

Fürstenhagen and Appleyardthe (1888) reported that the amount of sulfate in the fiber remains constant after mordanting wool with concentrations from 10% to 20% of the PAS on the weight of the wool. However, no information was provided whether the sulphuric acid is adsorbed by or combined chemically with the alumina. According to Havrez (1872) and von Georgievics (1895), the baths containing above 24% of potash alum (i.e., PAS) on the weight of the wool, the adsorption of alumina and sulphuric acid are relatively the same and sulphuric acid absorbed by the wool increases as the concentration rises. Yusuf, Islam, Khan, and Mohammad (2016) investigated the effects of PAS concentration (1% to 5% owf) on the color strength and dye uptake percentages of pre-mordanted wool yarns. They reported that the color strength and the dye uptake of wool yarns increased with the increase of PAS concentrations.

Due to its relative purity and frequent use as a textile mordant for wool fiber, potassium aluminum sulfate was the pre-mordant used in the study. A commonly used concentration by weight of fiber (owf) is 12% (Wipplinger, 2005). Three concentrations of PAS, 7%, 12%, and 17% owf, were evaluated for Al distribution across the mordanting process.

Aluminum Exposure

Aluminum is abundant in the earth (e.g., rocks, water, air), and it may not cause harm from little exposure. However, high levels of exposure can have detrimental impacts on humans and as noted prior to aquatic life. Workers in the aluminum industry can suffer from lung problems like coughing because of inhaling large amounts of aluminum. Some studies found high exposure to aluminum may develop Alzheimer's disease (AlKindy, Al-Hinai, Al-Rasbi, Suliman, & Al-Lawati, 2015); however, other studies have not found this to be true (ASTDR, 2008). Further, high levels of aluminum in the body may cause kidney, brain, and bone disease in children (ASTDR, 2008).

Potassium

Potassium is originated from the English word potash. It is found in the earth mostly as minerals and it can be found in vegetables, fruits, milk, and nuts. Potassium is an essential element for humans as it helps with the fluid and nervous systems (Lentech, n.d). However, inhalation of potassium dust can irritate the eyes, throat, and nose, causing sneezing and with high exposure can cause death because of fluid accumulation in the lungs (Lentech, n.d).

Potassium is necessary for soil health, plant growth, and animal nutrition. Conversely, potassium with high water solubility can damage germinating seedlings, inhibit the uptake of other minerals, and reduce the quality of the crop (Lentech, n.d). According to the US EPA, potassium does not have any recommended or mandatory limits in drinking water like aluminum (Water Quality Parameters, EPA, 2001). Further, ETAD and GOTS do not have an input limit or discharge standard for potassium. Potassium is not listed in the recommended analytical mass and estimated instrument detection limit by the ICP-MC method, ASTM D5673 -16. Therefore, the potassium (K) ions were not measured in this study.

Other Minor Substances in PAS

PAS contains two primary metals, aluminum and potassium; however, there are some other negligible but lethal metals like Pb (lead), As (arsenic), Fe (iron) and water-insoluble substances present in PAS (Technical Data Sheet, Brenntag, n.d). The maximum limit available for Pb and As in PAS is 20 and 2 ppm respectively (Technical Data Sheet, Brenntag, n.d). According to GOTS and ETAD, the input limits are 100 mg/kg and 50 mg/kg for Pb and As respectively. The Resource Recovery and Conservation Act (RCRA) listed lead and arsenic in the eight heavy metals group, which is also known as RCRA8. They monitor the heavy metals as they are lethal even in small concentration. The US EPA allowable limits in solid waste for Pb and As is 5 mg/L or ppm.

Scouring Agent

During the production of yarn commercially, wool is scoured to remove lanolin, potassium carbonate and dirt from the fiber, which requires several washings in a warm, soapy, and alkaline solution (Cardon, 2007). However, the term scouring also refers to the cleaning or washing of fiber to remove dirt and oil from spinning, weaving, and shipping. In this study, scouring agents or reagents were used to clean the impurities, dirt, dust from the substrates. Orvus paste is a common scouring agent used in the wool scouring process. Orvus paste is a synthetic detergent, which is mixture of water and sodium lauryl sulfate (SLS). GHS Classification in accordance with 29 CFR 1910 (OSHA HCS) notes the SLS or its mixture are flammable solids, harmful if swallowed or inhaled, cause skin irritation, serious eye damage, and may cause respiratory irritation (“Safety Data Sheet”, Sigma-Aldrich, 2018). It is recommended to use protective equipment during handling the substance. SDS does not provide any COD, BOD₅ value limits for sodium lauryl sulfate. However, they mentioned BOD/ThBOD ratio,

which is 95.9% that is the substance effluent is 95% biodegradable. Our study used Orvus paste as a scouring agent for scouring wool substrates before mordanting at 2% owf. SLS does not have ETAD input or discharge limits, however, it is classified with one of the specific hazard statements related to health hazard by the Global Harmonized System (GHS). SLS is classified as GHS, H411: 'toxic to aquatic life with long lasting effects' (GOTS, 2017, p.11). Thus, use of SLS does not meet the standards for organic certification. While the scientific data sheets for SLS identify its hazards to aquatic life, the Proctor and Gamble SDS for Orvus® WA Paste Surfactant Cleaner do not (P&G Professional, 2015). Bondi, Marks, Wroblewski, Raatikainen, Lenox, & Gebhardt (2015), confirmed SLS as an acceptable surfactant for household cleaning purposes considering the toxicological and sustainability views. They also concluded that SLS is not a threat to humans and the environment if the quality and formulation was properly maintained.

Textile Processing Effluents

Effluents from the textile industry are a significant concern for the natural environment. Wet processing mills discharge 5 billion kg of dyes, pigments, and finishing chemicals (Hussain & Wahab, 2018; Nimkar, 2018). There are about 40 million organic compounds present in the environment, which is usually determined with combination of parameters such as Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Suspended Solids (TSS), Total Dissolved Solids (TDS) and heavy metals. Textile effluents comprise considerable pollution masses in terms of COD, BOD, TDS, and TSS (Aslam, Hassan, Qazi, Malik, & Saeed, 2004). Chemical Oxygen Demand (COD) is a measure of the water capacity to consume oxygen for decomposing the organic matters and oxidation of inorganic chemicals ("COD or Chemical Oxygen Demand...", n.d.). In other words, COD measures the amount of oxygen required to

decompose both organic and inorganic matters. BOD is defined as the oxygen needed to oxidize the biodegradable organic matters in the wastewater through biochemical process (Chan et al., 2002). COD is expressed in mg/L representing the mass of oxygen consumed per liter of solution to decompose both organic and inorganic matters in water. BOD₅ is also expressed as mg/L, which means the mass of oxygen consumed per liter of water to decompose biodegradable matters during 5 days of incubation. Aslam et al., (2004) studied the characterization of textile process effluents and concluded that textile effluents from processes like desizing, mercerizing, bleaching, dyeing, and finishing are highly toxic for human beings and the environment as well as a significant threat to ground and surface water resources. The wastewater they analyzed was alkaline and had high BOD that ranged from 700 to 2,000 mg/L, and the COD was about 2 to 5 times the BOD values. The high BOD value means the wastewater contains high amount of organic matters that need to be decomposed through biochemical process. Therefore, the mass of the oxygen required is higher to break down the matters.

Total organic carbon (TOC) is a measure of the total organic carbon present in the wastewater, which determines the organic contamination of water (“BOD, COD, TOC and TOD – sum parameters...”, n.d.). TOC is also expressed in mg/L that measures the amount of organic carbon in mg per liter in the solution of wastewater. TOC is an effective method to measure wastewater effluent (“TOC monitoring of effluent...”, HACH, n.d). This process can detect some pollutants more precisely than BOD or COD tests and can do so faster and in real-time. According to Shimadzu TOC analyzer brochure, the typical TOC values for polluted surface water ranges between 50->100 mg/L. Asano, Burton, Leverenz, Tsuchihashi, and Tchobanoglous (2007) reported the typical TOC values in the untreated domestic effluents ranged from 80 to 260 mg/L.

The textile industry often measures the COD and BOD₅ values separately, however, the COD/BOD₅ ratio is necessary to know whether the wastewater is treatable biologically (Chan, Yuen, & Yeung, 2002). According to Chan et al., (2002), the perceived COD/ BOD₅ ratio for natural dye effluents was around 2.0 and within the aspired ratio of most of the treatment plants. However, the COD/BOD₅ ratio for textile operations was found between 1.6 and 6.0, and the average of synthetic dye house effluent was approximately 3.0 (Chan et al., 2002)

Further, dyes considered non-polluting could stain a large amount of water (Hussain & Wahab, 2018). These colorants decrease light penetration, and as a result, various algae species find it difficult to produce food and oxygen (Tüfekci, Sivri1, & Toroz, 2007). Recycling wastewater is a way to resolve this problem; however, higher COD and BOD values and varying pH make the recycle work a challenge (Priya & Selvan, 2017).

This study measured the COD and TOC of the PAS mordant treated solutions. However, the BOD₅ was not measured in this study as the measured COD value was very low, which is discussed in the discussion chapters in detail. Knowing the COD and TOC allows for determining if the mordant treated effluent meets discharge to municipal sewage and processed output standards.

Aluminum and Effluent Disposal

Small-scale dyers and artisans are mostly the users of natural dyes. However, there is increasing inclusion of naturally dyed product by retailers in capsule collections (DuFault, 2017; Laughlin, 2017; Schneider-Levy, 2018). Thus, it is essential to understand how aluminum compounds may impact humans and the environment from different disposal methods. There are a few ways how the natural dye effluents can end up in the environment as wastewater. After

pre-mordanting or dyeing, the effluent may be released directly to the natural environment such as onto the ground or into standing or flowing fresh waters. The effluent may also be discharged by disposal through a drainage system, which then may flow into a municipal sewage system or fresh waters. Finally, the metals could be discharged to the environment following wastewater treatment as processed output.

According to the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) (n.d.), aluminum does not have any input limits and restrictions for discharge. However, aluminum, dyes, and auxiliaries have regulations as processed output and discharge by other regulatory institutions like the US Environmental Protection Agency (EPA) and Global Organic Textile Standard (GOTS).

Freshwater Disposal

Aluminum effluents may cause harm to aquatic life and the environment. According to the EPA Draft Aquatic Life Ambient Water Quality Criteria for Aluminum in Freshwaters (2017a), aluminum enters the freshwater from mining and industrial processes through the usage of aluminum compounds.

Rosseland, Eldhuset, and Staurnes (1990) reported that high concentrations of aluminum are a toxic agent to aquatic freshwater organisms and as a toxic agent on fish and invertebrates. Under circumstances of high acidity, certain metals like aluminum are readily mobilized, which increase the concentration in freshwaters (Goudie, 2013). At “critical” pH levels (i.e., pH 5.0 or lower, classified by the EPA), fish growth is reduced, and it has also been reported that fish gills are damaged at even lower concentrations. The aluminum undesirably affects the fish gills operation resulting in mucus collecting in large quantities, which eventually hinders the fish from taking essential oxygen and salts (Goudie, 2013). Apart from harming fish, aluminum can reduce

phosphates, which decreases the availability of phytoplankton and other aquatic plant foods. Similarly, Comber, Gardner, and Churchley (2005) reported that aluminum under certain pH conditions could be toxic to fish because of precipitation at the gill surface.

On the other hand, aluminum on plants has both positive and negative impacts. The aquatic plants are less delicate than fish and other aquatic life (Comber et al., 2005). Some tree leaves like tea, symplocos and lycopodium contains a considerable amount of aluminum (ATSDR, 2008), which can be used as bio mordants in natural dyeing (Cunningham, Maduarta, Howe, Ingram, & Jansen, 2011). Conversely, Rosseland et al. (1990) reported that the mycorrhiza and the delicate root systems of terrestrial plants are harmfully affected by high levels of inorganic monomeric aluminum.

The Environmental Quality Standard (EQS) limit for aluminum concentration in wastewaters is 0.01 mg/L and 0.025 mg/L for waters of a pH value below 6.5 and above 6.5, respectively. The more bioavailable the aluminum, the more toxic it is, and the water quality parameters like pH, Dissolved Organic Carbon (DOC) and hardness greatly impact aluminum bioavailability. Bioavailability is defined as a measure of availability of a compound that can enter organisms like fish (EPA, 2017). The EPA (2017) recommended level of aluminum in fresh water for acute (1-day, total aluminum) and chronic (4-day, total aluminum) criterion are 1400 $\mu\text{g/L}$ (i.e. 1.4 ppm) and 390 $\mu\text{g/L}$ (0.39 ppm) respectively under neutral pH condition with 1 mg/L DOC and 100 mg/L hardness value. Therefore, aluminum in high amounts and higher or lower pH level than neutral has the potential to harm aquatic life, especially to the fish population.

Discharge to the Sewage System

Bechtold, Turcanu, Ganglberger, and Geissler (2003) calculated the chemical load of natural dye effluents and compared against conventional dyeing effluent standards. They used Austria's wastewater limits for textile effluents and diluted the effluents before comparison. Bechtold et al., (2003) estimated aluminum metal for naturally dyed linen and wool and compared with legal limits for textile effluent. The initial aluminum estimation was 5000 mg/L in the dye bath; however, the final estimated concentration after dilution was 70 mg/L aluminum, which was below Austria's 100 mg/L limit for textile effluents released to communal wastewater treatment plants.

Chan, Yuen, and Yeung (2002) investigated heavy metal contents in natural dye effluents comprising various types of mordants. They dyed wool fiber with tea and flower petals using aluminum mordants and found that aluminum metals remaining in the effluent ranged from 3 to 57 mg/L. Further, they calculated the COD/BOD₅ ratio and found 2, which is an acceptable value for biodegradable effluent treatments.

However, some researchers estimated metal amounts that did not meet standards. Glover (1995) estimated 340 mg/L of aluminum in the effluent bath which did not meet the acceptable level, 0.5 to 10 mg/L, or other heavy metal discharge to U.K. public sewers. Further, Smith and Wagner (1991) reported high concentrations of metal ions remaining in the mordant liquor while dyeing wool with aluminum and cream of tartar. Compared to the original liquor of 340 g/l Al, the spent amount of liquor was 320 mg/L Al that accounts for 94%, which eventually went to the wastewater stream.

Textile Mill Discharge Limits

The Code of Federal Regulations (CFR) is the organization of both the general and permanent rules and regulations published in the Federal Register by the executive departments and agencies of the United States federal government ("About the Code of Federal Regulations," n.d). The kkg is a unit of volume of wool items by weight. According to 40 CFR part 403, the discharged pollutants from wool pretreatment should not exceed the BOD₅ limit 3.6 kg/kkg (for any one day) and 1.9 kg/kkg (for 30 consecutive days) of wool. Further, COD limit should not be over 52.2 kg/kkg (for any one day) and 33.7 kg/kkg (for 30 consecutive days) of wool. The pH should be between 6 and 9. For woven wool fabric finishing, the BOD₅ values are 6.6 kg/kkg (for one day) and 3.3 kg/kkg (for 30 consecutive days) respectively. Similarly, COD limit should not be over 60 kg/kkg (for any one day) and 30 kg/kkg (for 30 consecutive days) respectively for woven wool fabric finishing.

Treated Wastewater

Global Organic Textile Standards (GOTS) is a standard that ensures the organic status of the textile product through environmentally and socially responsible manufacturing (GOTS, 2017). It covers raw material processing, textile wet-processing to trading and distribution. Textile wet processing generates a tremendous amount of effluents and effluent treatment plants treat the wastewater before releasing to the environment. GOTS has certain limits regarding treated wastewater that are released to the environment. The limit values depend on the fulfillment of specific parameters like pH, temperature, TOC (Total organic carbon), BOD (Biological oxygen demand), COD (Chemical Oxygen demand). According to GOTS (2017), the processed textile wastewater output from any wet processing treatments should not have a value

of over 20 g COD/kg. Further, the wastewater that is released to the surface water should be within the pH range (6-9), and the temperature of the wastewater should not exceed 35 °C.

Drinking Water

The United States EPA has no regulations of acceptable limits for aluminum in drinking water; however, they have a Secondary Maximum Contaminant Level (SMCL) that is 0.05 - 2 mg/L. The aluminum at or above this level does not pose health problems from drinking, but it has issues with the aesthetics (e.g., color and cloudiness) of water (“Aluminum fact sheet,” n.d). Similarly, the World Health Organization (WHO) has a limit for acceptable aluminum in drinking water supplies that is within 0.2 ppm or 0.2 mg/L.

Metal Detection Method

Various methods have been developed to determine the aluminum metal as it is abundant in the earth. The widely used methods for determining the amount of aluminum are inductively coupled plasma atomic emission spectrometry (ICP-AES), ICP-mass spectrometry (ICP-MS), graphite furnace atomic absorption spectrometry (GF-AAS), and spectrophotometry (Al-Kindy et al., 2105). Among them, inductively coupled plasma mass spectrometry (ICP-MS) is a technique which is strong enough to measure ultra-trace metals in a wide range of sample types (Pranaitytė, Padaruskas, & Naujalis, 2008). The American Society of Textile and Testing (ASTM) D5673-16 covers the ICP-MS test method. This method can detect trace metal in groundwater, surface, and wastewater. Further, this method can measure several metals in the periodic table, including aluminum. It covers the analysis of mine dewatering groundwater and wastewater effluent from 2 to 120 µg/L dissolved antimony and 3–200 µg/L dissolved arsenic. According to ASTM D5673-16, for aluminum with recommended atomic mass 27, this

instrument has detection limit up to 0.05 $\mu\text{g/L}$. However, this instrument does not have any detection limit for potassium.

Potassium aluminum sulfate is considered safe as a mordant for treating wool fiber. However, aluminum at high exposure can pose detrimental effects on aquatic life, plants, animals, and humans. Besides, aluminum has standards and regulations for EPA ambient freshwater discharge, GOTS treated output, and textile mill discharge. Thus, it was necessary to determine the metal amount across the mordanting process before disposing the effluents into freshwater or sewer. ICP-MS, due to the ability to detect trace amounts of Al in liquids and solids, was the metal detection method selected.

Chapter 3 - Methods

The purpose of this research was to determine Al ions across the mordanting procedure following the treatment of wool substrates with potassium aluminum sulfate (PAS). Further, this study characterized the effluents through the Chemical Oxygen Demand (COD) and Total Organic Compound (TOC) tests. Prior measuring the Al ions, the pretreatment processes such as scouring, mordanting were done following the standard laboratory procedures. ASTM D5673-16 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to measure the Al ions both in the treated liquors and in the substrates. The rationale of choosing the ICP-MS method was because of its precise measuring capability of trace metals with very low detection limit (Pranaitytė et al., 2008). Chemical Oxygen Demand (COD) and Total Organic Compound (TOC) were measured by using COD method from HACH and Shimadzu TOC analyzer respectively. The COD and TOC was measured to compare our findings against the existing standards. Several researchers measured COD and TOC to characterize natural dye effluents. Finally, the pH was measured using a digital pH meter. This chapter presented the experimental materials, procedures, and analysis to compare Al ions percentage remaining in the treated liquors and the percentage detected in the substrates.

Materials

Experimental Substrates

This study used two substrates, wool fabric and wool yarn (see Table 1). The fabric was 100% worsted wool challis, 109 g/m², style #452 from Testfabrics Inc. The samples weighing 8 g +/- 0.01 were cut randomly from the challis yardage. The yarn was Kona sport yarn, 100% superwash merino wool, from Dharma Trading Co. Skeins weighing 8 g +/- 0.01 were wound from the full skein with the use of a skein winder and selected randomly for processes.

Table 3.1 Wool substrate information

Structure	Fiber	Weight	Width (cm)	Source
Worsted wool challis	100% Wool	109 g/m ²	139	Testfabrics Inc., West Pittston, PA
Kona sport yarn	100% Merino Superwash Wool	227 g/m ²	n/a	Dharma Trading Co., San Rafael, CA

Scouring Agent

The fabric and skein samples were scoured with Orvus paste obtained from Dover Saddlery (www.doversaddlery.com). Orvus paste is a pH neutral synthetic surfactant paste, made mainly of water and sodium lauryl sulfate, with excellent detergency, emulsifying, and dispersing properties (www.doversaddlery.com).

Mordanting Agent

Potassium aluminum sulfate dodecahydrate (Brenntag) $KAl(SO_4)_2 \cdot 12H_2O$, in crystal form, was the mordant. The Technical Data Sheet (Brenntag, 2011) for potassium aluminum sulfate dodecahydrate (PAS) indicated a minimum .99% concentration, pH 3.0-3.5, and solubility in 20 °C water. Chemical properties included Fe (iron) at maximum 0.02% and heavy metals Pb (lead) and As (arsenic) at a maximum 20 ppm and 2 ppm respectively.

Sample Conditions

The liquor and substrate samples were collected across the scouring and mordant processes to account for possible metal ion distribution. Additionally, the untreated substrates

and deionized water samples were collected to calculate the precise measurement of the metals.

Each condition was collected at three replications, with a total of 78 samples (see Table 3.2).

Table 3.2 Sample conditions across the scour and mordanting procedures

Label	Condition	Substrate	PAS Concentration % owf	Rep.	<i>n</i>
DI	Deionized water	n/a	n/a	3	3
CL	Control mordant solution liquor	n/a	7.0, 12.0, 17.0	3	9
TL	Mordant treatment liquor, upon removal of substrate	Fabric	7.0, 12.0, 17.0	3	9
		Yarn	7.0, 12.0, 17.0	3	9
RW	Rinse water of mordant treated substrate	Fabric	7.0, 12.0, 17.0	3	9
		Yarn	7.0, 12.0, 17.0	3	9
US	Untreated substrate	Fabric	n/a	3	3
		Yarn		3	3
SS	Scoured substrate	Fabric	n/a	3	3
		Yarn		3	3
TS	Scoured and mordant treated substrate	Fabric	7.0, 12.0, 17.0	3	9
		Yarn	7.0, 12.0, 17.0	3	9

Note. owf = on weight of fiber; Rep. = replication; *n* = number of samples

Sample Preparation

Twenty-seven wool fabric samples were randomly cut from the challis yardage and at least six inches from each selvage edge. Fabric sample dimensions were 7.5 x 11.0 inch with the 11.0 inch length parallel to the fabric selvage edge. Samples weighed 8 +/- 0.01 gram, with adjustments to size made as needed to meet the weight requirement. The fabric sample edges were overlock stitched with polyester thread to prevent fraying and loss of fiber. However, the weight of the overlock thread was not counted towards the total weight of the fabric.

Yarn samples were cut in approximately 15 cm lengths to maintain the same weight with the fabric samples. The yarn lengths were then wound with the use of a skein winder to prevent tangling during wet processing. For yarn samples, this study used 27 skeins each weighing approximately 8 +/- 0.01 gram.

Scour Procedure

In this study, scouring refers to cleaning of dirt and dust from spinning and handling the substrates. The wool fabric and yarn samples were scoured in solutions of Orvus paste and deionized water (DI). Before scouring, samples were wetted-out at 25 °C (77 °F) in DI water for 30 minutes. The purpose of wetting-out was to saturate the fiber with water to assist in even uptake by the surfactant. The scour solution was 2% Orvus paste to owf (by the weight of fiber), and the process temperature was 40 °C +/- 3 (100 °F). Water to the material ratio of 80:1 was maintained throughout the scour procedure.

Three scour baths were prepared, and nine fabric samples were added to each scour bath. The samples were stirred gently with a glass stirring rod every 5 min for 20 min and then rinsed in 25 °C (77 °F) DI water and laid flat for drying on a clean white towel. Skein scouring followed the same procedures, except individual beakers were used for each yarn skein in place of three scour baths. The purpose of individual scour baths was to prevent yarn tangling during the scour process.

Three scoured samples of each substrate were labeled under the scoured substrate (SS) identification and reserved for testing. The remaining 18 samples (9 for fabric, 9 for yarn) moved onto the mordanting procedure.

Mordant Procedure

The mordanting process used in this study was established by Doty and Haar (2013). The scoured fabric and yarn samples were mordanted in a PAS and DI water solution at three replications per PAS concentration (7.0%, 12.0%, 17.0% owf). Each substrate sample was mordanted individually in a 900 ml beaker on a hot plate. Samples were wetted-out in DI water at 25 °C (77 °F) for 30 min before the mordant treatment. The PAS was dissolved in 100 ml of

hot DI water by stirring with a glass rod inside a laboratory fume hood. Approximately 300 ml of additional water was added until the substrate to water ratio of 50:1 was achieved. Substrate samples were then added to the mordant baths. The temperature of the bath was raised from 25 °C (77 °F) to 90 °C (194 °F) over 30 min and was held at 90 °C (194 °F) for 60 min. The temperature fluctuated during the procedure due to the use of hot plates. Thus, the temperature setting was adjusted to maintain a temperature between 85 °C and 93 °C throughout the process. Each mordant solution was stirred continuously for the first minute and then 30 rotations every 10 minutes throughout the process. The solutions cooled to room temperature (25 °C (77 °F)) by sitting for 60 min inside a fume hood. The cooled solution was stirred for 30 rotations, and the substrate sample was then removed for rinsing. The solution was again stirred for 30 rotations, and a 15 ml of solution was retained for testing by pouring into a 15 ml polypropylene conical tube with the screw-on lid. These solutions were labeled as mordant treated liquors (TL), with designations for fabric or yarn and replication.

In addition to preserving the mordant treated liquors, mordant control liquor (CL) solutions were also prepared. The control solution followed the mordanting procedure except without any substrate. The control solution established the initial amount of mordant applied in the process to compare to the amount remaining in the substrate treated bath. For each of the nine solutions (3 concentrations x 3 replications), a 15 ml solution was preserved and labeled with the mordant control solution liquor (CL) identification.

Rinse Procedure

Mordant treated substrate samples were individually rinsed in 400 ml DI water (25 °C (77 °F)) in an 800 ml beaker for 60 sec., with continuous stirring. To remove excess rinse water, the wool samples were removed from the beaker, squeezed by hand and then laid flat on a clean

white towel to dry. The rinse solutions were stirred, and 15 ml were collected in a conical tube and labeled with the rinse water (RW) identifier, as well as by substrate, concentration, and replication.

Substrate Specimens

Three replications of each substrate test specimen were randomly cut from the fabric substrate samples (untreated, scoured, and mordant treated). Specimen dimensions were 2 cm x 2 cm and weighed approx. 0.050 gram. The yarn specimens were randomly cut to 15 cm lengths from the yarn samples (untreated, scoured, and mordant treated). The 15 cm length correlated with fabric specimen weight of approx. 0.050 gram. The 45 fabric and 45 yarn specimens were placed in individual funnel tubes and labeled.

Test Methods

ICP-MS Test Method

ICP-MS is one of the best methods that can measure trace metals with a very low detection limit (Smith & Nordberg, 2015). It can detect low limits with a wide linear dynamic range, multi-element capability, and high sample quantity (Vanhaecke & Köllensperger, 2003). ATSM D5673-16 Standard Test Method for Elements in Water by ICP-MS (American Society for Testing and Materials, 2016) was used to determine the Al metal across the mordanting procedure. This ICP-MS method comprised three steps i.e. digestion, dilution and testing.

Digestion. Digestion of the liquor and the substrate specimens were done by using a 70% concentrated HNO₃ (Nitric acid, trace metal grade). For digestion, ten micro liters (μL) of each liquor (deionized water, control liquor, mordant treated liquor, rinse water) was poured into an ICP funnel tube and 2 ml of 70% conc. HNO₃ was added with mixing using a vortex mixer.

This mixed solution was kept 8 hours at 90 °C in a heating block for proper digestion and cooled overnight.

Wool fabric (2 cm x 2 cm) and wool yarn (15 cm in length) specimens both weighing approx. 0.05 gram were transferred into the ICP funnel tubes and 2 ml of 70% conc. HNO₃ was added for the digestion with vortex mixing. For proper digestion, these solutions were also kept in the heating block for 8 hours at 90 °C and left outside of the block overnight to cool down.

Dilution. The dilution factor was calculated from the molecular weight of the PAS mordant and the initial concentration of the mordant used during mordanting. A dilution factor of 10000 was used for the dilution of all the liquors (DI, CL, TL, RW) to achieve the precise Al within the ICP-MS detection limit. A stock solution was prepared with 10µL of the solution from all of the liquors and DI water was added to reach 10000 µL (10 ml). Finally, 500 µL of solution was taken from the stock, and DI water was added to make a final 5000 µL (5 ml) solution to complete the dilution of all the liquors.

For wool substrates, the stock solution was prepared by adding DI water to 2 ml of digested substrate solution to get a 10000 µL (10 ml). Then, from that stock solution, 100 µL solution was taken, and 4900 µL DI water was added. The specimens were further diluted by transferring 500 µL of the last diluted solution and 2% HNO₃ was added to make a 5 ml solution to complete the dilution. Therefore, the dilution factor for the substrate specimens were 5000. However, for the highest concentration (17%), treated specimens were showing a higher amount of Al than expected. So, the specimens were diluted to detect the Al ions within the ICP-MS detection limit. Specimens treated with 17% PAS concentration owf were diluted one more time by taking 2000 µL of solution from the previous solution and 3000 µL of 2% HNO₃ was added

to make a final 5000 μL (5 ml) solution. The dilution factor for the 17% concentration was 12500.

Potential Hydrogen (pH) Measurement

The pH was measured to see whether the effluents are acidic or basic using a digital pH meter from Markson. The pH was measured in the control liquors, treated liquors, rinse water and the deionized water with three replications.

Chemical Oxygen Demand Test Method

The TNT 821 Chemical Oxygen Demand method from HACH (HACH Company, 2019) was used to measure the COD values of the control liquors (CL) and mordant treated liquors (TL). This apparatus has a detection range from 3-150 mg/L. The mg/L COD results are defined as the mg of O_2 consumed per liter of a sample under the conditions of the procedure. In this procedure, the sample is heated for 2 hours with a 2 TNT 821 Chemical Oxygen Demand strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion to green chromic ion.

First, the reactor was preheated to 150 $^{\circ}\text{C}$ (302 $^{\circ}\text{F}$) inside a fume hood. The COD vial used for the test was inverted a few times to bring the sediment into suspension. The vials were opened, and 2 ml of CL and TL were added carefully using a pipet. The vials were closed and inverted 2-3 times over a sink. The lid of the vials was held by hand to shake them as the vials got hot during mixing. Then the vials were placed in the preheated reactor for 2 hours. Initial cooling was done for 20 minutes and inverted several times while the vials were still hot. The vials were placed into a rack and cooled down to room temperature. Finally, the outside of vials was cleaned thoroughly and inserted into the cell holder of a DR 1900 VIS spectrophotometer

for HACH and HACH LANGE water analysis methods. The COD reading in mg/L was collected from the display of the spectrophotometer.

Total Organic Carbon Test Method

Total Organic Carbon Analyzer TOC-L Series from Shimadzu was used to measure the TOC of the liquors (CL and TL). The Shimadzu TOC-L uses a unique combustion catalytic oxidation and Nondispersive Infrared (NDIR) method that permits measurements of all samples from ultrapure water to highly contaminated water. Range of measurement is 4 µg/L to 25000 mg/L. Digestion of the liquors were done by injecting a 50 µL of the liquors with three injections conforming to SD +/- 0.1 and dilution was completed by using 1.5% HCl (hydrochloric acid).

Analysis

Aluminum Ions

The ICP-MS provided values for Al were in ppb for approximately 0.050 g substrate specimens. The dilution factors were 5000 and 12500 for the substrate specimens. For the calculation of the Al ions in the wool substrate specimens, the Al amounts found in ppb were multiplied by the dilution factor during specimen preparation for the ICP-MS testing and converted to µg. Finally, the Al amounts in µg were converted in terms of 8 g weight substrates. The amounts reported from nine specimens were averaged as three specimens were cut from each experimental substrate sample.

Aluminum Distribution

To determine the amount and distribution of Aluminum (Al) ions in total liquor (400 ml) across the pre-mordanting process, the following equation was used:

$$CL = TL + TS + RW + EL$$

Where CL = control liquor detected Al amount; TL = treated liquor detected Al amount; TS = Al detected in mordant treated substrate; RW = Al available in rinse water; EL = Loss of Al to the environment or operational loss of Al from the procedures.

From the above equation, the actual loss of Al from mordanting processes was measured as:

$$\text{Actual Loss} = \text{TL} + \text{RW} + \text{EL}$$

Al Ions Percentage Calculation

The Al absorption percentage in substrates and treated liquors were determined by comparing the Al amount in the control solution with the Al detected in the substrates and treated liquors at their respective concentrations. The calculation was completed by dividing the Al amount measured in the substrates and treated liquors by the Al amount detected in the control solution and multiplied the result by 100 for each of the concentrations for each replication. The replications were then averaged to obtain the mean percentage. See the equations below.

For the Treated Liquors

$$\frac{TL}{CL} \times 100$$

Here, CL = control liquor detected Al amount; TL = treated liquor detected Al amount

For the Treated Substrates

$$\frac{TS}{CL} \times 100$$

Here, CL = control liquor detected Al amount; TS = treated substrate detected Al amount

Statistical Analysis

Statistical analysis was performed using Minitab®, version 17.1.0. Descriptive statistics (mean and standard deviation) were used to outline means and standard deviations for Al distribution across the mordanting process. Two-sample t-test was utilized to examine if there

was a significant effect of the substrate type (i.e., yarn or fabric) on mordant absorption. One way analysis of variance (ANOVA) was conducted to observe the effects of the independent variable concentration (i.e., three mordant concentrations of 7%, 12% and 17% owf) on the Al ions absorption of woven and yarn wool substrates at the 95% confidence level. Additionally, one way ANOVA was used to observe the effects three mordant concentrations of 7%, 12% and 17% owf on the Al ion available in the treated liquors at the 95% confidence level. This statistical procedure showed if there was any significant effect from the three PAS mordant concentrations on Al ion absorption on substrates and on the Al remaining in the treated solutions.

Chapter 4 - Results and Analysis

The purpose of this research was to measure aluminum (Al) amounts in the effluent solution and the substrates following the mordanting of wool challis woven fabric and Kona Sport wool yarn with a potassium aluminum sulfate (PAS) mordant. This research was important as it can inform natural dyers about the Al ion amounts in the fiber and effluent, as well as the COD and TOC values of effluents. This information yields recommendation for safe disposal of the mordant effluent. ATSM D5673-16 Standard Test Method for Elements in Water by ICP-MS (American Society for Testing and Materials, 2016) was used to measure the Al metal across the mordanting procedure. The characterization of wastewater was determined through tests of chemical oxygen demand (COD) and total organic carbon (TOC). TNTplus®—Method 8000 was used for COD tests and Shimadzu TOC-L Series was used for TOC measurement. This chapter presents the results and the data analysis for the research questions.

Research Question One

Question 1. What is the distribution of Al ions across the mordanting process for selected wool substrates pre-mordanted with potassium aluminum sulfate at three concentrations? Wool substrate samples (weighing 8 g) were treated with PAS mordant at three concentrations (7%, 12%, and 17%) by the weight of fiber (owf). According to the ASTM D5673-16 test method (American Society for Testing and Materials, 2016), ICP-MS measured Al across the mordant treatment process. As mentioned in the method section, the substrate specimens were digested and diluted to obtain the proper concentration and to detect the Al within the detection limits. According to the Al concentrations (7%, 12% and 17% owf) and the Al available in PAS, the appropriate dilution factor was established to set the Al detection limits to determine the results within that limit. Detection limits were set from 0.1 ppb (parts per billion) to 80 ppb. The ICP-

MS provided values for Al were in ppb for approximately 0.050 gram substrate specimens. For the calculation of the Al ions in the wool substrate specimens, the Al amounts found in ppb were multiplied by the dilution factor during specimen preparation for the ICP-MS testing and converted to μg . Finally, the Al amounts in μg were converted in terms of 8 g weight substrates and reported amounts from specimens were averaged. Two wool substrates, wool challis fabric and wool yarn (Kona sport), were evaluated; results for wool challis are presented first.

Wool Challis Fabric Results

The amount of Al in the control solutions were 32.14 mg, 73.35 mg, and 100.02 mg at their respective concentrations of 7%, 12%, and 17% owf. See Table 4.1 Following the mordant treatment, the amount of Al in the fabric was 19.93 mg, 28.5 mg, and 29.95 mg, while the amount remaining in the treated solution following removal of the substrate was 11.52 mg, 33.45 mg, and 65.32 mg. No Al was detected in the rinse water following rinsing of the substrate. Environmental loss, such as operational loss during procedures, accounted for 2.07 mg, 4.98 mg, and 2.76 mg. Thus, at the 7% mordant concentration, 62.01% of the available Al was detected in the fiber and 35.84% in the effluent. At 12% concentration, 38.88% was in the fiber and 54.33% in the effluent. The distribution of Al at the 17% concentration was 29.94% in the fiber and 65.30% in the effluent. See Table 4.1.

Table 4.1 Aluminum distribution across the mordanting procedure for wool challis

Concentration owf %	Control liquor mg*	Fabric treated liquor mg** (%)	Fabric mordant treated mg (%)	Fabric rinse water mg***	Environmental loss mg
7	32.14	11.52 (35.84)	19.93 (62.01)	0.00	2.07
12	73.35	39.85 (54.33)	28.52 (38.88)	0.00	4.98
17	100.02	65.32 (65.30)	29.95 (29.94)	0.00	2.76

Note- Al present in the scoured wool fabric was subtracted from the Al found in the mordanted fabric. However, no amount was deducted from the control liquor (CL), fabric treated liquor (FTL) and fabric rinse water (FRW) as no Al amount was detected in the deionized water (DI).

**All the Al ion detected in the control liquors are in mg/315 ml*

***All the Al ion detected in treated liquors are in mg/310 ml*

****Al ion detected in rinse water are in mg/400 ml.*

At 12%, one of the replications had an outlier for FTL, so, for consistency in the calculation, the outlier value has been removed.

Wool Kona Sport Yarn Results

The Al available in the control solutions were 32.14 mg, 73.35 mg, and 100.02 mg at their respective concentrations of 7%, 12%, and 17% owf. See Table 4.2. After the mordanting procedure, the amount of Al in the yarn was 13.90 mg, 14.53 mg, and 16.99 mg, while the amount remaining in the treated solution was 8.52 mg, 42.65 mg, and 68.44 mg. The Al detected in the rinse water were 4.08 mg, 8.0 mg, and 8.08 mg at their respective concentrations of 7%, 12%, and 17% owf following the rinsing of wool yarn. Environmental loss accounted for 5.71 mg, 8.17 mg, and 6.52 mg. The combined Al percentage from the rinse solution and environmental loss accounted for 30.46%, 22.04%, and 14.60% at their respective 7%, 12%, and 17% concentration owf. Therefore, 43.25% of the Al was detected in the wool yarn and 26.51% in the effluent at the 7% concentration. At 12% concentration, 19.91% Al was in the fiber and

58.15% in the effluent. Finally, the distribution of Al at the 17% concentration was 16.99% in the wool yarn and 68.43% in the effluent. See Table 4.2.

Table 4.2 Aluminum distribution across the mordanting procedure for kona sport yarn

Concentration owf %	Control liquor mg*	Yarn treated liquor mg **(%)	Yarn mordant treated mg (%)	Yarn rinse water mg***	Environmental loss mg
7	32.14	8.52 (26.51)	13.90 (43.25)	4.08	5.71
12	73.35	42.65 (58.15)	14.53 (19.91)	8.0	8.17
17	100.02	68.44 (68.43)	16.99 (16.99)	8.08	6.52

Note- Al present in the scoured wool yarn was subtracted from the Al found in the mordanted yarn. However, no amount was deducted from the control liquor (CL), yarn treated liquor (YTL), and yarn rinse water (YRW) as no Al amount was detected in the deionized water (DI).

** All the Al ion detected in the control liquors are in mg/315 ml*

*** All the Al ion detected in treated liquors are in mg/310 ml and*

**** Al ion detected in rinse water are in mg/400 ml.*

Research Question Two

Question 2. How does substrate structure, woven wool fabric compared to wool yarn, influence mordant absorption? The Al absorbed in the wool challis fabric and Kona sport yarn was compared to find out the influence of substrate structure in the absorption. Following the mordant treatment, the amount of Al in the fabric was 19.93 mg, 28.5 mg, and 29.95 mg, while the amount of Al absorbed in the yarn was 13.90 mg, 14.53 mg, and 16.99 mg at their respective concentrations of 7%, 12%, and 17% owf. See Table 4.1 and 4.2. Hence, at the 7% concentration, 62.01% of the available Al was detected in the wool fabric and 43.25% in the wool yarn. At 12% concentration, 19.91% was in the yarn and 38.88 % in the fabric. The Al

available at the 17% concentration was 16.99% in the yarn and 29.94% in the fabric. See Table 4.3.

Statistical analysis. Two sample t-tests were performed on the Al absorption percentage of the substrates at their respective concentrations (7%, 12%, and 17% owf) to determine whether the yarn structure absorbed significantly more Al than the challis fabric. The wool fabric substrate had a higher Al ion percentage than wool yarn. Two-sample t-tests did not show significance at the $p < 0.05$ confidence level between the wool yarn and fabric; t value (-7.94, -10.04, and -9.82) and p-value (0.998, 0.995, and 0.995), which rejected the hypothesis that wool yarn absorbed a significantly higher percentage of Al ions than fabric. See Table 4.3.

Table 4.3 Two sample t-test to compare the effects of substrate type in Al absorption

Concentrations owf (%)	Wool Yarn		Wool fabric		t-value	p-value ($p < 0.05$)
	Mean Al (%)	SD	Mean Al (%)	SD		
7	43.25	3.12	62.01	0.80	-7.94	0.998
12	19.91	1.45	38.88	2.83	-10.04	0.995
17	16.99	1.05	29.94	2.03	-9.82	0.995

Research Question Three

Question 3a. How will mordant concentration influence the absorption of Al ions on the woven and yarn wool substrates? This research question examined the influences of three PAS mordant concentrations on the absorption of Al by the wool substrates (challis woven fabric and Kona sport yarn). As discussed in the analysis section, the Al absorption percentage in substrates was determined by using the equation that divided the Al amount detected in the control solution by the Al amount measured in the substrates and multiplied the outcome by 100 for each of the

concentrations for each replication. The replications were then averaged to obtain the mean percentage.

The amount of Al in the treated fabric was 19.93 mg, 28.5 mg, and 29.95 mg at their respective concentrations of 7%, 12%, and 17% owf, while the Al in the control solutions were 32.14 mg, 73.35 mg, and 100.02 mg. See Table 4.1. Therefore, at 7% concentration, the Al measured in the fabric was 62.01%. For 12 % and 17% concentration, the Al detected was 38.88% and 29.94% respectively. The Al amount (mg) in wool fabric increased with the increase of the PAS mordant concentrations. However, the Al absorption percentage decreased as the concentration increased. The Al percentage available in fabric was the highest with 7% concentration owf. The Al percentage in fabric was the lowest with 17% concentration owf.

On the other hand, at 7% concentration, the Al percentage in yarn was 43.25%. For 12% and 17% concentrations, the Al measured were 19.91% and 16.99% respectively. The highest percentage of Al measured in yarn was with 7% concentration and the lowest amount with the 17% concentration owf.

Statistical analysis. One way ANOVA analysis was done to observe the effects of the three PAS mordant concentrations on aluminum absorption percentage of wool fabric. For this test, 95% confidence interval was used. Wool challis had highly significant differences in terms of Al absorption percentage among the concentrations. At the 95% confidence interval ($p < .05$), the wool fabric absorption was significantly different ($p = 0.00$) among the three concentrations (7%, 12%, and 17% owf). See Table 4.4.

Table 4.4 ANOVA to compare the effects of PAS mordant concentrations (7%, 12%, and 17% owf) in wool fabric Al absorption

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Al Concentrations % (owf)	2	1671.01	835.505	196.11	0.000
Error	6	25.56	4.260		
Total	8	1696.57			

One way ANOVA analysis was performed to analyze the effects of three PAS mordant concentrations (owf) on aluminum absorption percentage of wool yarn. Wool Kona sport yarn also had highly significant differences regarding Al absorption percentage among the three concentrations. Similarly, 95% confidence interval was used and at 95% confidence interval ($p < .05$), the wool yarn absorption was significantly different ($p = 0.00$) among the three concentrations (7%, 12%, and 17% owf). See Table 4.5.

Table 4.5 ANOVA to compare the effects of PAS mordant concentrations (7%, 12%, and 17% owf) in wool yarn Al absorption

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Al Concentrations % owf	2	1264.56	632.279	146.56	0.000
Error	6	25.88	4.314		
Total	8	1290.44			

Question 3b. How will mordant concentration influence the amount of Al ions remaining in the treated bath for the woven and yarn wool substrates? This research question examined the influences of the three PAS mordant concentrations on the percentage of Al remaining in the effluent following the mordant treatment of two wool substrates (challis fabric and sport weight yarn). The Al percentage was determined the same as Question 3a, that is by considering the

control solutions as standard, dividing by the detected Al in the treated liquor, and multiplying the quotient by 100. Results were averaged across replications.

The measured Al in the fabric treated liquors were 11.52 mg, 39.85 mg, and 65.32 mg at their respective concentrations of 7%, 12%, and 17% owf, while the Al in the control solutions were 32.14 mg, 73.35 mg, and 100.02 mg. See Table 4.1. Therefore, at 7% concentration, the Al available in the fabric treated liquor was 35.84%. At 12% and 17% concentration, the Al remained was 54.33% and 65.30% respectively. The Al percentage remaining in the effluent increased with the increase of the PAS mordant concentrations. The percentage of Al detected in the fabric treated liquor was the highest at 17% concentration and lowest in the 7% concentration.

At 7% concentration, the Al percentage in yarn treated liquor was 26.51%. At 12% and 17% concentrations, the Al available in the effluent was 58.15% and 68.43% respectively. The highest percentage of Al measured in the yarn treated effluent was at the 17% concentration and the lowest percentage at the 7% concentration.

Statistical analysis. One way ANOVA was performed to determine whether the percentage of Al remaining in the treated bath was significantly different across the concentrations for wool fabric. For the Al percentage remaining in the fabric treated bath, one way ANOVA found a significant effect at the $p < 0.05$ level for Al concentrations (7%, 12%, and 17%) $F = 14.42$. At the 95% confidence interval, the p-value ($p = 0.008$) showed significant difference. See Table 4.6.

Table 4.6 ANOVA to compare the differences in Al remaining in the fabric treated effluent across PAS mordant concentrations (7%, 12%, and 17%) owf

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Al Concentrations % (owf)	2	1300.2	650.12	14.42	0.008
Error	5	225.5	45.10		
Total	7	1525.7			

One way ANOVA was conducted to find out whether the percentage of Al remaining in the treated bath was significantly different across the concentrations for wool yarn treated effluent. The Al percentage in yarn treated effluent showed significant differences among the concentrations. One way ANOVA indicated a highly significant effect at the $p < .05$ level for Al concentrations (7%, 12%, and 17%), $F = 14.42$. The p-value ($p = 0.000$) showed highly significant difference at a 95% confidence interval. See Table 7. However, with the increase in concentration, the difference becomes less significant, especially between 12% and 17% owf. See Table 4.7.

Table 4.7 ANOVA to compare the differences in Al remaining in the yarn treated effluent across PAS mordant concentrations (7%, 12%, and 17%) owf

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Al Concentrations % (owf)	2	2804.1	1402.03	43.92	0.000
Error	6	191.5	31.92		
Total	8	2995.6			

The scatter plot (Figure 4.1) showed the effects of the three concentrations (7%, 12%, and 17% owf) on Al ion distribution percentage in wool fabric and its treated liquor (FTL). This scatterplot (blue regression line) showed a strong, negative, linear association between concentration percent and Al ion absorption percentage in wool fabric. As this plot had groups,

the red regression line in the scatter plot showed a strong, positive, linear association between concentration percent and Al ion percentage remaining in the treated liquor. However, this grouped scatter plot did not have any outlier value. See Figure 4.1.

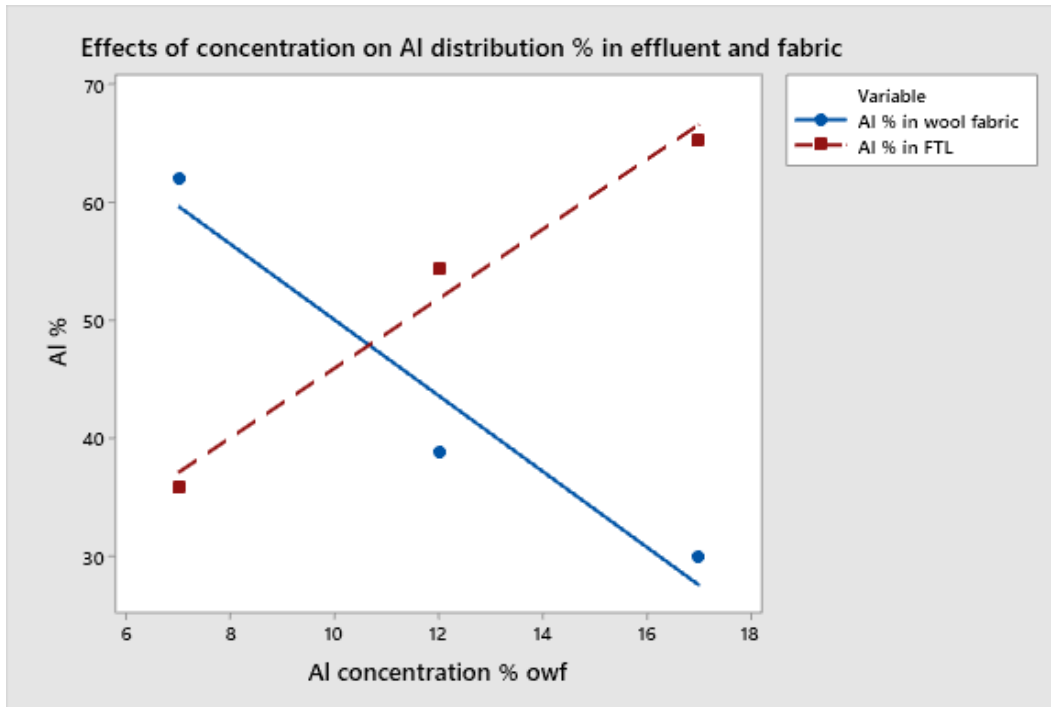


Figure 4.1 Al distribution percentage in fabric treated liquor (FTL) and wool fabric at the 7%, 12%, and 17% concentration (owf)

Figure 4.2 scatter plot showed the effects of three concentration (7%, 12%, and 17% owf) on Al ion distribution percentage in wool yarn and its treated liquor (YTL). The blue regression line in the plot showed a strong, negative, linear association between concentration percent and Al ion absorption percentage in wool yarn. On the other hand, the red regression line in the scatter plot showed a strong, positive, linear association between concentration percent and Al ion percentage remaining in the yarn treated liquor. Similarly, this grouped scatter plot did not have any outlier value. See Figure 4.2.

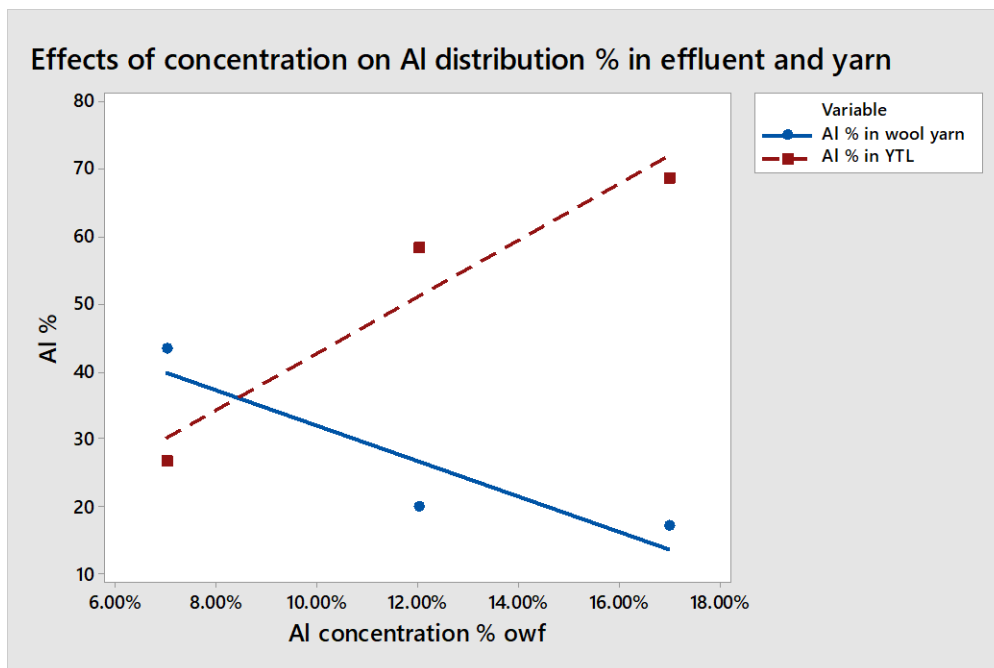


Figure 4.2 Al distribution percentage in yarn treated liquor (YTL) and wool yarn at the 7%, 12%, and 17% concentration (owf)

Research Question Four

Question 4. What is the mordant treated liquor characterization in terms of chemical oxygen demand (COD), total organic compound (TOC), and pH? The COD, TOC, and pH values of the PAS mordant treated liquors were measured to determine if the effluent meets disposal and discharge regulations. The TNTplus®—Method 8000 and Shimadzu TOC L series analyzer were used to collect COD and TOC values, respectively. Three replications of treated liquors for each concentration and substrate type were analyzed. Finally, the values were averaged across the replications.

Chemical Oxygen Demand (COD) Results

The COD values were collected utilizing the TNTplus®—Method 8000 instrument and the DR 1900 VIS spectrophotometer displayed the results directly in mg/L in the display monitor. The COD value in the control solution was 2.04 mg/L at 17% concentration owf.

However, no COD values were found in the control solution at 7% and 12% concentrations owf respectively as the values were lower than the detection limit of this COD measuring instrument. See Table 4.8. The COD values in the fabric treated solutions were 53 mg/L, 70.37 mg/L, and 66.67 mg/L, while the COD in the yarn treated solutions were 95.13 mg/L, 94.63 mg/L, and 80.8 mg/L at their respective concentrations of 7%, 12%, and 17% owf. See Table 4.8.

Table 4.8 COD values in control and PAS mordant treated solutions for yarn and fabric

PAS concentration owf	COD values (mg/L)		
	Control solution	Fabric treated liquor	Yarn treated liquor
7%	ND*	53	95.13
12%	ND*	70.37	94.63
17%	2.04 mg/L	66.67	80.8

*ND= Not detected

The study characterized the PAS mordant treated liquors of wool yarn and fabric substrates at three concentrations owf. Fabric treated liquors showed COD values ranged from 53 mg/L to 70.37 mg/L, while the yarn treated liquors showed higher COD values (80.8 mg/L to 95.13 mg/L) than the fabric specimens despite having the same PAS mordant concentrations owf. The COD values decreased with the increase of the PAS mordant concentrations for both substrates. The highest COD value found was 95.13 mg/L in yarn treated liquor with 7% owf PAS mordant. See Figure 4.3.

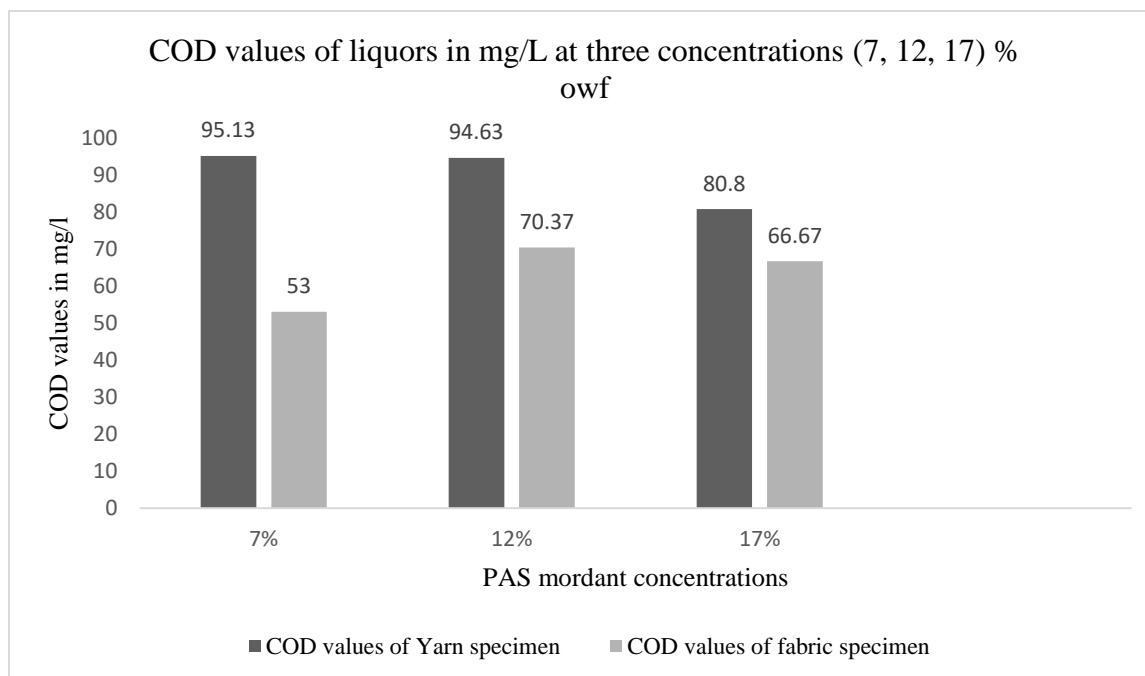


Figure 4.3 COD values of liquors in mg/L at three concentrations (7, 12, 17) % owf

Total Organic Compound (TOC) Results

The TOC value of the liquors was measured using a Shimadzu TOC L series analyzer. This analyzer was PC controlled with the use of TOC control software to calculate the results. The proper protocol mentioned in the method section was maintained, and the results were collected directly from the PC monitor. The TOC values of the control solution were 2.64 mg/L, 2.71 mg/L, and 2.47 mg/L at their respective 7%, 12%, and 17% concentrations owf. At 7% concentration owf, the TOC value for fabric treated liquor was 26.01 mg/L, while this value for yarn treated liquor was 41.78 mg/L. The TOC values both for fabric and yarn treated liquor were 30.92 mg/L and 36.17 mg/L, respectively at 12% concentration owf. Finally, at 17% concentration owf, the TOC for fabric treated liquor was 38.83 mg/L and for yarn treated liquor the value was 35.12 mg/L. See Table 4.9.

Table 4.9 TOC values in control and PAS mordant treated solutions for yarn and fabric

Concentrations % owf	TOC values (mg/L)		
	Control solutions	Fabric treated liquors	Yarn treated liquors
7	2.64	26.01	41.78
12	2.71	30.92	36.17
17	2.47	38.83	35.12

Potential Hydrogen (pH) of the Liquors

The average pH of the DI and scour effluent were 6.75 and 4.5. The average pH of the mordant solution before and after the treatment with substrates were 3.70 and 3.50 respectively.

Further, the pH values were consistent across the three concentrations (7%, 12%, 17%) owf.

Chapter 5 - Discussion and Conclusion

The overall purpose of this study was to measure Al ions across the mordanting procedure and characterize the treated liquors in terms of COD and TOC. The reasoning for this study was to increase the knowledge of Al ion determination in PAS mordant effluents to inform natural dyers about the Al remaining in the effluent as most of the dyers use aluminum mordants for mordanting protein and cellulosic fibers. By measuring the biodegradability and pH of the effluent dyers can be informed of safe disposal of the mordant effluent. The ICP-MS method from ASTM was used to measure Al ions in the wool substrates and treated liquors. For the treated liquors characterization, the Shimadzu COD and TOC L series analyzer were utilized.

In this chapter, the research questions and hypotheses are discussed regarding the percentage of Al ion detected in the substrates and treated liquors, the effects of various PAS mordant concentration on Al ion absorption percentage on wool substrates and Al ions remaining in the treated liquors. Finally, the effluents characterization is discussed. The chapter concludes with limitations, recommendations for further study, and conclusions.

Discussion of the findings

Question 1: What is the distribution of Al ions across the mordanting process for selected wool substrates pre-mordanted with potassium aluminum sulfate at three concentrations?

Hypothesis 1: At least 80% of Al ions will remain in the mordant bath, and the substrates will absorb 10% or less.

The first hypothesis was not supported that at least 80% of the Al ions will remain in the treated bath following the PAS mordanting of two substrates, wool challis, and wool yarn. The Al percentage in the treated liquors for both fabric and yarn was less than 80%. The findings indicate that the substrates absorbed a higher percentage of Al than expected. For the wool

fabric, the percentage of Al in the fiber was 62%, 39%, and 30% respective of the PAS concentration owf at 7%, 12%, and 17%. Even though the Al percentage in the wool fabric decreased with an increase in PAS, all contained more Al than the expected 10%. The wool yarn had a similar trend but also had more Al distribution in the treated liquor, rinse water, and environmental loss. Thus, the percentage of Al in the yarn was 43%, 20%, and 17% respective of the 5%, 12%, and 17% PAS concentrations owf.

The finding, while positive, is not consistent with prior research. To make a comparison, the results presented as mg/310 ml from Tables 4.2 and 4.3 have been converted to mg/L (see Table 5.1). Several researchers reported higher amounts of Al in the effluent compared to the study at hand. Smith & Wagner (1991), reported 320 mg/L (94%), of Al in the effluent following mordanting wool with alum. Glover and Pierce (1993) estimated 340 mg/L Al ions in the effluent at a concentration of 15% owf. Similarly, Koestler, Sheryll, and Indictor (1985), measured various metal ions (Al, Cr, Fe, Zn, etc.) on fabrics such as cotton, wool, and silk using Energy Dispersive X-Ray Spectrometry (ESD). They concluded that 10% of the metal ions were incorporated with the fiber after the mordanting procedure, though it was not clear about the initial concentration of the mordant.

Table 5.1 Al ions available in the treated liquors and substrates in mg/L

Concentration owf %	Control liquor mg/L	Fabric treated liquor mg/L	Yarn treated liquor mg/L	Fabric mordant treated mg/L	Yarn mordant treated mg/L
7	80.35	23.04	21.30	49.83	34.75
12	183.38	99.63	106.63	71.25	36.33
17	250.10	163.30	171.10	74.88	42.48

Chan, Yuen, and Yeung (2002) measured Al ions in the effluents following the dyeing of wool fiber with natural dyes that ranged from 3-57 mg/L. The findings of the current research were consistent with Chan et al., (2002) amounts for both fabric and yarn treated liquors at 7% concentration owf. However, the Al ions measured in this study was higher at 12% concentration owf. At 17% concentrations, the detected amount of Al in the effluents was almost thrice the amount detected in the Chan et al. (2002) study. Chan et al. (2002) measured the Al amount that detached from the wool fiber during the dyeing process. Therefore, they did not consider the amount lost during the mordanting process. The finding from our study can be interpreted in a way that after the dyeing process, the wool fiber may lose more Al ions. On the other hand, the amount of Al detected by Chan et al. (2002) could be more if they would have considered the Al remaining in the premordanted effluents.

In addition to the prior studies that estimated or measured large amounts of Al in the effluents following wool dyeing, the hypothesis writing was influenced by the Saha et al. (2018) investigation of mordanting cotton with aluminum acetate. Findings from the cotton study indicated over 90% of the Al ions were in the treated liquor while only 2-5% of Al was in the cotton print cloth. In addition to wool having an increased affinity over cotton to bond with Al, there may have been influences from the procedures that impacted the higher percentage of Al in the wool substrates. The concentration in terms of material to liquor ratio was lower in this study as the ratio was 50:1 instead of 70:1 used in the cotton study. Further, the temperature differences impacted the overall volume. This study maintained a temperature of 85-93 °C throughout the mordanting process, while the cotton study using aluminum acetate does not use heat. Due to evaporation, the final volume of the treated liquors was reduced to 310 ml from the

400 ml initial volume. Thus, the decreased material to liquor ratio from evaporation may have had some impact of Al distribution between liquors and substrates.

The findings in terms of Al amount in freshwater met the EPA Al in freshwater limits. The amounts of Al ions to be disposed from fabric and yarn treated liquors at three concentrations ranged from 21 mg/L to 171 mg/L. See Table 5.1. Without any further dilution, these amounts in the fresh water are below the EPA 2017 Aquatic Life Ambient Water Quality Criteria for Aluminum in Freshwater's acute limit of 1,400 mg/L and chronic limit of 390 mg/L.

This study measured the distribution of Al ions across the mordanting procedure for wool challis and Kona sport wool yarn. Results indicated there were more Al ions absorbed in the substrates than expected. Absorption was impacted by both substrate type and PAS concentration. Both variables are discussed below.

Question 2: *How does substrate structure, woven wool fabric compared to wool yarn, influence mordant absorption?*

Hypothesis 2: *Wool yarn will have a significantly higher percentage of Al ions absorbed compared to wool challis.*

This research hypothesis was not supported that wool yarn will have a significantly higher percentage of Al ions absorbed compared to wool fabric. It was found that fabric absorbed a significantly higher percentage of Al than the wool yarn. At the 7% concentration, the Al ions in the fabric (62.01%) was higher than the Al percentage detected in yarn (43.25%). The trend was similar at the 12% and 17% concentrations. At 12% concentration, the fabric absorbed twice the Al ions percentage (38.88%) than the Al ions percentage (19.91%) detected in the yarn. The Al percentage (29.94%) detected in the fabric at the 17% concentration also doubled the percentage (16.99%) in the yarn.

The assumption was that yarn would absorb more Al than fabric as skein dyeing has good dye penetration compared to woven fabric (“Wet Processing Engineering”, n.d.). In addition, the fabric was woven from worsted yarn. Worsted wools are made of long fibers from sheep that lie parallel and when spun produce a compact yarn leaving less space between the fibers (“Terminology: What’s the difference between worsted”, 2014). Space between the fibers is further compacted when woven into a fabric structure. However, even though challis is a plain weave fabric structure, the yarns are crimped which can increase absorbency to the fiber and through the looser interlacement of the warp and weft yarns (Islam, Chowdhury, & Akter, 2018). Therefore, the waviness of challis structure may have influenced its ability to absorb Al ion.

The Kona Sport yarn used in this study was made of four single spun yarns twisted in opposing directions. Twisted plied yarns have high pile density (Islam, Chowdhury, & Akter, 2018). So, the yarns are less open in structure (i.e., more compact), which can lead to less water absorption (Cruz, Leitão, Silveira, Pichandi, Pinto, & Fangueiro, 2017). Therefore, the yarn’s twist and density may have impacted its ability to absorb Al ions.

The surface area of the substrates can affect Al ion absorption of yarn and fabric. The wool fabric had a greater surface area than yarn. In addition, during the wet processes, there was noticeable fiber loss from the stirring. It may be that there were Al ions in the fiber that detached from the yarn strand. This could explain the 4 to 8 mg of Al in the rinse water and the 5 to 8 mg of Al attributed to environmental loss (see Table 4.2). Further, wool yarn weighing approximately 0.050 gm was cut for ICP-MS testing, which is a small amount of loose fiber. Therefore, the absorption may be different if a larger amount of yarn was used.

Question 3a: *How will mordant concentration influence the percentage of Al ions absorbed on the woven and yarn wool substrates?*

***Hypothesis 3a:** The percentage of Al ion absorption in wool substrates will significantly increase with an increase in PAS concentration.*

The hypothesis was partially supported that PAS mordant concentration had a significant influence on the percentage of Al ion incorporated with both substrates. However, it was not supported that the increase in PAS concentration percentage will increase the percentage of Al ions detected in the substrates. The percentage of Al ions detected in the substrates decreased significantly with the increase of the PAS mordant concentration % owf.

The 62.01% of Al ions detected in the treated fabric at 7% concentration was approximately two times higher than the Al ions (29.94%) available at 17% concentration and approximately 1.5 times more than Al ions (38.88%) measured at 12% concentration. See Table 4.1. On the other hand, the 43.25% of Al ions measured in the yarn at 7% concentration was 2.5 times higher than the Al ions (16.99%) detected at 17% concentration. However, at 12% concentration for yarn, the percentage of Al ions (19.91%) was a little higher than the percentage detected at 17% owf. See Table 4.2.

Saha et al. (2018), reported a low percentage (2-5%) of Al ions detected on cotton print cloth that was not significantly different across five concentrations. However, this study found significant differences in Al ions detected for both wool fabric and yarn at three concentrations. Instead of an increase in the percentage of Al ions absorbed with an increase of PAS, the reverse was found. Natural dyers typically apply 12% PAS concentration owf. This study utilized +/-5% owf from the 12% owf to examine any differences in Al absorption percentage. However, the Al ion absorption percentage for wool fabric at 7% owf was significantly higher than the Al ion absorption percentage than at the 12% owf, that is 62% compared to 39%. See Table 4.1. While the percent absorbed is greater at 7%, the amount of PAS absorbed by the fabric is lower, that is

20 mg at 7% compared to 29 mg at 12%. These differences may impact the color performance of natural dyes. Thus, further investigations are needed to examine the impact of PAS concentration on the color performance of naturally dyed wool fabrics. The findings do indicate to focus future research on PAS concentrations at 12% and lower on wool yarn.

Question 3b: *How will mordant concentration influence the percentage of Al ions remaining in the treated bath of the woven and yarn wool substrates?*

Hypothesis 3b: *The percentage of Aluminum ions remaining in the treated bath will significantly increase with an increase in PAS concentration.*

This hypothesis was supported that wool challis and Kona sport yarn pre-mordanted with a PAS mordant were significantly influenced by three (7%, 12%, and 17% owf) concentrations in terms of Al ions remaining in the treated liquors. The Al percentage in the treated liquors increased as the PAS concentration increased. The percent of Al ions (65.30%) available in fabric treated liquor (FTL) at 17% concentration for the wool fabric was almost two times higher than the Al ions (29.94%) remaining at 7% concentration and approximately 1.5 times higher than Al ions (54.33%) detected at 12% concentration. See Table 5.2. In yarn treated liquor (YTL), the Al ions (68.43%) in the 17% concentration was 2.5 times higher than the Al ions (26.51%) detected at 7% concentration. However, the difference between the Al ions in YTL at 12% and 17% concentrations was not as high with 58.15% and 68.43%. See Table 5.2.

Table 5.2 Al ion distribution in control and treated liquors

PAS mordant Concentrations owf (%)	Mean Al in control liquor (mg)	Mean Al in Fabric treated liquor mg (%)	Mean Al in Yarn treated liquor mg (%)
7	32.14	11.52 (35.84)	8.52 (26.51)
12	73.35	39.85 (54.33)	42.65 (58.15)
17	100.02	65.32 (65.30)	68.44 (68.43)

Most of the natural dyers use the 12% PAS mordant concentrations while mordanting wool fiber and sometimes go up to 20% owf. This research indicated that with the increase of the PAS concentration, the percentage of Al absorption in the fabric decreased while the percentage in the treated liquor increased. So, the wool fiber could have a limit to absorb Al from the PAS mordant solution, and after increasing certain concentrations, it could reach its saturation point. By examining the interrelationship between the Al remaining in the treated liquor and the substrates (Figures 4.1 and 4.2), for wool challis around 11% concentration and for yarn around 9% concentration appear to be efficient concentrations. Future research is recommended to determine optimization for concentration of PAS absorption on substrates.

A prior cotton study used five mordant concentrations % owf, and the percentage available in the treated liquors was not significantly different (Saha et al., 2018). The prior study by Chan et al. (2002) used 10 g/L alum concentration for mordanting wool fabric. However, our study took alum concentration by the weight of fiber (owf), which were 7%, 12%, and 17%. The liquor to material ratio was 50:1 for this research, and as the material (wool substrates) weighed approximately 8 gm, the total liquor used for this study was 400 ml. Therefore, the concentration of PAS was 1.4 g/L, 2.4 g/L, and 3.4 g/L respectively in terms of the total liquor used in the study. So, the mordant concentration in the Chan et al. (2002) study was higher than this

research. Also, their study measured Al that detached from the mordanted fabric during the dyeing process. Therefore, it's difficult to compare the results of this study with research by Chan et al. (2002).

This study examined the commonly used 12% PAS concentration along with 5% lower and higher concentrations to determine the impact of concentration on mordant absorption and amount remaining in the treated liquor. The 7% concentration of PAS had a higher percentage of Al ions in the substrates and a lower percentage in the treated liquors. Thus, natural dyers may be able to use less than 12% PAS concentration for premordanting wool fibers. As a result, there would be less Al chemical as input and less to be disposed of as output. However, as noted prior, the impact on color properties would need to be examined from using a lower amount of PAS.

4. What is the mordant treated liquor characterization in terms of chemical oxygen demand (COD)?

Hypothesis 4: *Mordant effluents will meet the disposal and discharge regulations by the Code of Federal Regulations (CFR) and the Global Organic Textiles Standard (GOTS).*

This hypothesis was supported that the PAS mordant treated liquors will meet the CFR textile mill discharge limit and the GOTS standard for COD. The COD values of the control liquors were low (2.04 mg/L). On the other hand, the COD values for treated liquors ranged from 53-70 mg/L for fabric and 80-95.13 mg/L for yarn (see Table 4.8). According to the CFR textile mill discharge limit for wool pretreatment and finishing, the COD limit is 30 kg/kkg daily average over 30 consecutive days and 60.0 kg/kkg COD maximum for one day (Code of Federal Regulations, 2014). The COD values measured in our study was in terms of volume of the liquor in mg/L. So, the COD values were converted from mg/L to kg/kkg (in terms of the volume of the substrate) to compare results with CFR textile mill discharge limit. The COD values after

conversion ranged from 6.63 to 11.90 kg/kg, which were lower than the limits provided by CFR standard limit. According to GOTS (2017), the wastewater generated from any wet processing treatments as the output should not have a value of over 20 g COD/kg. Thus, the values in this study of, 6.63-11.90 g COD/kg, are below the GOTS limits.

However, the waste effluents should have a 6-9 pH with 35 °C liquor temperature before releasing to the surface water (Code of Federal Regulations, 2014; GOTS, 2017). In this study, the pH of the treated liquors was 3.50, indicating the need to be neutralized prior disposal to sewage systems or through waste treatments prior to release to surface waters. The reasons behind the acidity of the effluents was the acidic nature of the PAS mordant. Without further dilution and neutralization, the pH of the effluents in the fresh water does not seem to meet the EPA 2017 Aquatic Life Ambient Water Quality Criteria for Aluminum in Freshwater. The effluent temperature was 89-93 °C after the mordanting process, however, the effluents were cooled down for an hour to the room temperature before disposing. Though the effluents met the discharge limit by CFR, SDS recommends diluting the PAS effluents before releasing to the environment (“Safety Data Sheet,” 2015). Apart from that, according to SDS, the effluents should be disposed of by the local, state, federal, and environmental control regulations. As the mordant treated liquors met the CFR discharge limits and GOTS standard as output, small scale natural dyers may drain the PAS mordant effluent into municipal sewage systems (through the sink), as long as the pH is neutralized, and the effluent cooled to room temperature.

The higher COD values in the mordant treated liquors (53-95 mg/L) compared to the mordant control liquor (2 mg/L) was most likely due to surfactant from scouring remaining in the substrates. The wool substrates were treated with 2% sodium lauryl sulfate o/w for scouring before mordanting. Sodium lauryl sulfate is a synthetic organic compound used as an anionic

surfactant (Bondi, Marks, Wroblewski, Raatikainen, Lenox, & Gebhardt, 2015). According to the Safety Data Sheet (SDS), this chemical is toxic to aquatic life and harmful to aquatic life with long lasting effects (Safety Data Sheet, Sigma-Aldrich, 2018). The SDS does not have any COD value limits. However, they provided BOD/ThBOD ratio which is 95.9%. According to SDS, this is 95% biodegradable. We did not measure BOD in this study as the COD values were low compared to prior studies and existing standards. ThBOD is theoretical oxygen demand, which is also lower than COD values. Therefore, the effluents containing sodium lauryl sulfate should not be a concern in terms of treatability. Further, the yarn treated liquors had higher COD values than the fabric treated liquors. The Kona Sport yarn used in this study was a superwash merino wool yarn (Dharma Trading Co.). The superwash procedure uses an acid bath or a polymer coating to remove the scales from the fiber to make the yarn machine washable (“Superwash merino yarn,” n.d.), which may contribute to the COD values. So, while the mordant had little effect on COD values, the scouring agent and yarn finishes appeared to influence the COD. This may indicate that less surfactant is required, or increased rinsing be implemented.

BOD₅ was not tested for this study as the COD values were low in the treated liquors. The typical values of BOD₅ in domestic wastewater ranges from 100 to 300 mg/L (Abdalla & Hammam, 2014). The COD values were below the range mentioned above, irrespective of concentration or substrate type. BOD₅ was expected to be lower than COD values. BOD₅ values are always lower than the COD values for natural dye effluents (Chan et al., 2002). They measured COD values of tea dye and flower petal dye effluents with alum pre-mordanted wool fiber. Chan et al. (2002) reported COD values ranging from 1758 mg/L to 4790 mg/L for tea dye and 2895 mg/L to 3787 mg/L for a flower petal dye effluent. In our study, COD values of the mordant effluent (i.e., treated liquor) were measured, and the values were exceptionally low,

ranging from 53 mg/L to 95.13 mg/L. According to Chan et al. (2002), the organic matter of the natural dyes are the main contributors to the higher COD values. Hence, the lower COD values obtained in this study of measuring mordant effluent.

COD/BOD₅ ratio is an indicator of whether the effluent waste is biodegradable or not (Abdalla & Hammam, 2014). It provides a cutoff point to biodegradable treatability. Chan et al. (2002) reported that the ratio of 2 was highly biodegradable by most wastewater treatment facilities. Since the COD values were low, BOD₅ was not determined. However, it was expected that with the low values of COD, the treatability of the mordanted effluents would be biodegradable. This inference is important as it informs natural dyers that the pre-mordant effluents examined in this study are treatable through municipal sewage systems.

TOC is a measure of total organic carbon present in a solution. Like COD, TOC measures organic matters in effluents. The TOC values for our study ranged from 26 to 41 mg/L for both wool substrates treated liquors. TOC values are always lower than the COD values. The findings of our study support that statement. Dubber & Gray (2010) established that TOC has a highly significant linear relationship with COD and TOC can be used as an alternative of COD. They concluded that TOC can measure precisely without generating analytical waste like COD. TOC is faster than COD and the estimation of COD and BOD₅ is possible from TOC values (“Understanding Laboratory Wastewater Tests...”, n.d.). The TOC values were within the typical TOC values for polluted surface water, which ranged between 50->100 mg/L (Shimadzu TOC-L brochure, n.d.). The values were also lower than the typical values of 80-260 mg/L in the untreated domestic water (Metcalf and Eddy, Inc, Asano, Burton, Leverenz, Tsuchihashi, & Tchobanoglous, 2007). Therefore, this study informs the natural dyers that the PAS premordanted effluents contains lower organic matters than the untreated domestic water.

Limitations

This study measured Al ions by using the ICP-MS method, which was not able to detect other major metal ions such as potassium (K) in the PAS mordant. Sulfate percentage and the effects of sulfate in the treated liquors were not investigated. Apart from the ICP-MS method, no other method was utilized to compare the results. The treated liquors characterization was done after mordanting the wool fibers. However, some of the previous research and standards measured COD, BOD₅, and TOC after the dyeing process. Bioavailability of Al was not calculated as the Dissolved Organic Carbon (DOC), and hardness of the treated liquors was not determined. This study did not do any fabric and yarn structure analysis, such as scanning electron microscopic images, to see the distribution of Al ions in both substrates, and the structural change in them. This study used three concentrations (7%, 12%, and 17% owf), which showed a trend. However, it did not provide enough information to recommend an optimized concentration for mordanting wool fibers. This research evaluated one fabric and one yarn structure. Thus, generalizations cannot be made regarding absorption of Al ions across fabric and yarn structures.

Recommendations for Further Research

The general purpose of this study was to measure Al ions across the mordanting procedure at three PAS concentrations, present a method to measure Al ions, and characterize the treated liquors to see whether the values were within the existing input and discharge standards and limits. The ICP-MS method was selected to detect Al ions once it was established that ultra violet spectrophotometry did not provide an accurate wavelength range of the control mordant liquor. While proper procedures and protocol were followed, and ICP-MS provided results for small amounts of Al ion detection, use of other methods to further validate results is

recommended. While the ICP-MS method may be available at a research institute, is not a viable option for most natural dyers. There are aluminum test kits available to consumers. It would have been beneficial to examine if such kits could detect the low amounts of Al found in this study.

Because of inadequate knowledge of wool fabric and yarn structure and their orientation after the mordant treatment, future research could add scanning electron microscopic image technology to analyze the wool fiber structural differences after the process. Further, this research evaluated one wool fabric and one wool yarn. To understand the absorption of wool fabrics compared to yarn, other structures and weights should be evaluated in the future.

The results of the study indicate that the typical 12% owf concentration of PAS may not be necessary. Thus, future work is recommended to determine optimal amounts of PAS. Besides, it is recommended to investigate the impact of PAS amount to dye color parameters. Further, there is likely mordant chemical loss from the dyeing procedures. Thus, future work should examine the natural dye effluent for metal ions and biodegradability of the dyestuff.

Though PAS was found safe to use as a mordant for wool fibers in terms of Al input, disposal (with pH neutralization) and discharge, the PAS solid waste can contain minor but lethal substances like Pb and As. PAS can contain up to 20 ppm of lead (Pb) in the composition, which does not meet the US EPA allowable limit in solid waste for Pb (5 ppm). Thus, future work can determine the initial Pb concentrations in PAS.

Future study can investigate the effluents of scouring as the SLS (sodium lauryl sulfate) may contribute to the increase of COD values. Though the Proctor and Gamble SDS for Orvus® WA Paste and other researchers do not consider SLS as a hazardous chemical, GOTS does not certify SLS as an organic good. Thus, its recommended to characterize the scouring effluents in future study.

The results of this study indicated the amounts of Al remaining in the mordant bath; further studies could be conducted to investigate the viability of reusing the treated liquors. Such a practice would save resources and reduce the amount of chemicals disposed.

Conclusions

In conclusion, this research measured Al ions using the ICP-MS method in PAS treated liquors and wool substrates at three concentrations. The findings contribute to the knowledge of pre-mordanted treated liquors before natural dyeing and the liquor's water quality characteristics. Pre-mordanting was conducted as many natural dyers separate the mordanting and dyeing processes. The findings are important as it may inform natural dyers to the expected amounts of Al ions being disposed to the environment or sewage system. These findings will provide the dyers estimation about the Al ions percentage in their dye effluents based on the concentration used in our study. Therefore, the natural dyers may able to determine whether their bath is safe to dispose into the system or have enough Al for reuse. In addition, knowing the amount of Al ions remaining in the treated liquor can influence concentration selection based on the intent to dispose of or reuse the mordant bath.

For both wool challis fabric and Kona sport yarn at 7% concentration of PAS mordant, more Al ions were detected in the fiber compared to the effluent. While at 12% and 17% concentrations, more Al was found in the effluent. Therefore, this finding suggests that a lower PAS mordant concentration than the commonly used 12% owf be used for mordanting wool fibers. As recommended prior, lower PAS concentrations would need to be evaluated on naturally dyed fibers for impact to color parameters. The findings also indicate that there is available Al remaining in the mordant bath and bath reuse is recommended. Reuse of the

mordant bath would reduce overall chemical input and discharge amounts, as well as conserve water.

The crimped and interlaced structure of the challis fabric appeared to influence the higher absorption of Al ions compared to the 4-ply superwash yarn. While it cannot be stated that all fabrics will absorb more Al ions than yarn, it can be said that this particular wool challis absorbed more than half (62%) at the 7% PAS concentration.

The COD values were low as well as the TOC values, which confirm that the effluents of pre-mordanting with PAS are not harmful as discharge and output effluent if the effluents are neutralized and cooled down before releasing to the fresh water or sewage system. COD values met the CFR textile mill effluent discharge and GOTS limits as output. Further, TOC values meet the typical polluted surface water value. Thus, natural dyers can drain the PAS mordant effluent into the municipal sewage system, however, neutralization of the effluents is required before disposal.

The pH of the treated liquors was around 3.50, which was very acidic. The pH did not meet the US EPA 2017 Aquatic Life Ambient Water Quality Criteria for Aluminum in Freshwater. Thus, natural dyers should not to dump the effluents into the environment without neutralizing the liquors. Further, SDS reports that PAS mordant exposure can be an irritant to human and animals. Thus, is not recommended to dispose of the effluent to the ground or in standing water. However, the effluents can be drained through the sink after neutralizing them as the effluents are below the COD discharge limit to the sewage system.

The ICP-MS method was used as it can measure trace metals precisely. The method utilized in this study is widely known for detecting metals of low detection limits. Another advantage of this method is that it requires a small of amount of sample to run the test. However,

the ICP-MS method used to determine the Al ions across the mordanting process is expensive and not available for small scale natural dyers to evaluate the effluents. In addition to that, the test requires specific lab facilities and expertise. Though this test method provides the precise results in terms of trace metal detection a challenge is it's unavailability outside of the research institute. There are several Aluminum test kits (Aluminum test kit Quantofix®, range 5-500 mg/L) available in the market, which measure Al ions at predetermined ranges (Sigma Aldrich, n.d.). Such kits may provide a general range of Al in the effluent. However, the effectiveness of those test kits is yet to be checked with the ICP-MS results.

This research increased the knowledge of pre-mordanted wool substrates and the treated liquors characteristics. This study not only measured the Al ions but also presented a method to measure Al ions in substrates and liquors. Further, this research confirmed the safe usage of PAS as a mordant for select wool substrates in terms of Al input, disposal with pH neutralization, and discharge. Finally, this study can be a good starting point to measure other metals from various mordants used in natural dyeing.

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