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Mitigating the Formation of Hexavalent Chromium in Leather by Using *Aloe Barbadensis* Miller Mixed with Carrageenan

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ABSTRACT

Aloe barbadensis miller (Abm) mixed with carrageenan has been investigated as an alternative eco benign ingredient in mitigating hexavalent chromium Cr (VI) formation in thermally and photoaged wet blue and leather crust. The effect of post-tanning operations on the formation of Cr (VI) in wet blue and leather crusts due to spontaneous and accelerated ageing caused by exposure to the temperature of 80 °C and UV radiations for 132 hours is also presented. The Cr (VI) content was analysed according to ISO 17075 standard procedure of Diphenyl carbazide and UV-VIS spectrophotometer at 540 nm. The levels of Cr (VI) in retanned wet blue leather were detectably high, while for tanned, dyed and fatliquored crusts, the levels were below detection limit of 0.2247 mg/kg. After ageing, the Cr (VI) content increased to a detectable level, the highest recorded in retanned wet blue, followed by fatliquored crust and with the lowest levels recorded in dyed wet blue leather. In all the aged samples, the levels were remarkably higher than the recommended 3 mg/kg. The levels of Cr (VI) in wet blue leathers processed with Abm/carrageenan were below detection limit of 3.587 mg/kg, even after exposing the samples to accelerated ageing conditions. Abm/carrageenan completely inhibits formation of Cr (VI) in wet blue and leather crusts. Abm/carrageenan will contribute to the eco benign and sustainable production of leather under the superior chrome-tanning technology.

KEYWORDS

Cr (VI), carrageenan, aloe barbadensis miller, leather

INTRODUCTION

Conventional leather processing employs chemicals and mechanical operations that are aimed at modifying the structural, chemical and physical state of a highly putrescible organic material into a stabilized collagen matrix [1-4]. Although many tanning agents are available, Cr (III) compounds account for more than 90% of tanning done globally due to the superior quality of leather produced and their unmatched efficiency [2,5-8]. The downside of this chromium tanning, however, is that the

Cr (III) compounds get oxidized to Cr (VI), a carcinogenic and environmentally hazardous compound, which has considerable impact on the environment, public health and general human health [2,8-9]. Agents that accelerate the oxidation include atmospheric oxygen, UV rays (photo ageing), extremely high or low pH (such as during neutralization and dyeing), extreme high or low humidity, temperatures higher than 80 °C (thermal ageing), fatliquoring (especially those with double bond, vegetable oils, animal oils) and natural waxes and resins used during dry finishing [8-17]. Oxidation mechanisms involve radical formation and hydro peroxides necessitated by energy provided by the aforementioned agents. As regulated by REACH Annex 17 and national/regional legislation in countries where leather and its products are exported, normative eco-certification draft imposes limits on Cr (VI) content in accordance with ISO 17075. According to Eco-label Dec. 2002/231/CE, Cr (VI) should be less than 3 ppm (non-detectable). Considering chromium tanning and retanning technology, this is hard to achieve and, consequently, this has caused leather tanning industry to be at loggerheads with policy makers and environmentalists. Due to the superiority of this technology, the industry requires a sustainable technology that will facilitate the solution to its critical environmental and public health problems.

Vegetable tanning agents, both condensed and hydrolysable, such as quebracho, mimosa, tara, chestnut, valonia and sumac, have shown significant efficacy in minimizing the formation of Cr (VI) and formaldehyde in leathers [17]. Studies have recommended incorporation of plant products that have antioxidative power or radical scavenging characteristics to minimize or inhibit the formation of Cr (VI) [18-21]. Antioxidant power of natural plants, such as valonia, henna, *Coridothymus capitatus* (thyme), *Olea europaea* (olive shoots), *Corylus avellana* (hazelnuts) and *Juglans regia* (walnut leaves) have been examined and their efficacy in preventing formation of Cr (VI) and free formaldehyde in leathers has been reported [17-19]. So far, the best reduction of up to 89.24 % has been reported for *Coridothymus capitatus* extract under the ageing conditions of 80 ^{0}C for 24 hours. Tannic acids used for the re-tanning process have been shown to curtail the formation of Cr (VI) to levels lower than 3 ppm in artificially aged leathers [20]. The offer of 3 wt % tannic acid reduced Cr (VI) formation up to 98 %.

Phytochemical results have shown that Abm has glutathione peroxidase, superoxide dismutase enzymes and phenolic compounds (aloin and aloe emodin) that possess scavenging and antioxidant characteristics (reducing power) as well as anti-allergic property [22-26]. Incorporation of Abm into the leather matrix has shown to improve its softness, cooling effect, and effects such as antimicrobial, antibacterial, antiviral and antifungal properties [26-27]. A study by Litke and Widdemer used carrageenan, a seaweed hydrocolloid polysaccharide, to enhance the penetration of Abm gel in the leather [26]. Carrageenan molecules have negative charge which enables them to react with positive ions or protein in the collagens [28]. The molecules also have the ability to suspend particles to maintain relatively better distribution of Abm particles within the leather matrix [26,29]. It has been

found that Abm can be used as a natural mordant for optimizing natural dye from the Hambo Hambo (*Cassia singueana*) [30].

Although Abm has been appreciated for application in leather, no study has determined the effect of this product on the prevention of Cr (VI) formation in leathers. This study focused on the effect of the Abm gel, mixed with carrageenan powder in the same ratio, on the inhibition of Cr (VI) in post-tanned leather crusts, using UV-VIS spectrophotometer in accordance with ISO 17075. Leather samples treated with the Abm gel were exposed to both photoaging and thermal ageing conditions prior to Cr (VI) determination. The aim of this study was to examine Cr (VI) formation on post-tanned leathers exposed to accelerated ageing conditions such as a temperature of 80 °C and UV at different durations and how the mixture of Abm and carrageenan affected the Cr (VI) formation in leather under these conditions compared with the control samples (without the mixture).

MATERIALS AND METHODS

Materials

Leather preparation

Bovine wet blue leathers at tanned (T), retanned (R), dyed (D) and fatliquored (F) stages of processing were cut along the backline as shown in figure 1.

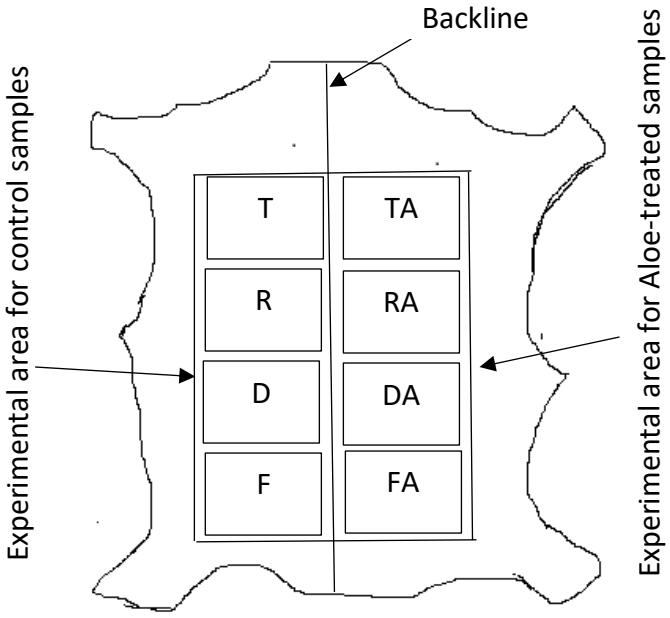

Figure 1. Representation of sample preparation for control and samples treated with additives

Aloe barbadensis miller (Abm) and carrageenan preparation and incorporation

Abm leaves, harvested from the Egerton University Botanic garden Njoro at the age of approximately one year, were washed thoroughly with running water to remove soils and dirt and air dried. The leaves were peeled and the fillet washed using clean running water and soaked in the citric acid solution for half an hour before soaking in ascorbic acid for 20 minutes. After rinsing under running water, the fillets were gelled with a blender and a mixer at the speed of 120 revolutions per second for half an hour in order to refine the gel. The gel solution was then sprayed into the drying chamber of a spray drier to coincide with the direction of heating air, with the inlet temperature of 140 ^{0}C and the outlet of 80 ^{0}C. After evaporation, the dried powder particles were sifted to approximate the size of 150 microns.

The 6% of both Abm powder and carrageenan powder by weight of the wet blue leathers were reconstituted with 100 parts of water at 37 ^{0}C to form an acidic solution of pH 5.5. The wet blue leather parts labelled TA, RA, DA and FA in figure 1, one at a time, were run in a drum with pure water at 37 ^{0}C. The prepared gel of Abm and carrageenan solution was introduced into the drum via the axle and the drum ran at a speed of 20 rpm for one hour. The penetration of the solution was checked against control samples. Samples with complete penetration assumed yellow-brown colour.

Sampling, sampling location and sample conditioning

The specimens were kept in a standard atmosphere at the temperature of 25±2 °C and relative humidity of 65 % ± 2 % for at least 48 hours in accordance with ISO 2419: 2012. Sampling was done in accordance with the standard ISO 2418: 2005 procedure. In this procedure, the samples were cut within the butt and around the backline to avoid the rapidly changing composition areas.

Ageing Process

Suitably cut specimens were aged in a heat-adjustable chamber at 80 °C for 24 hours and a UV cabinet (UV light with wavelength of 254 nm) for 132 hours mimicking most application fields of leather.

Grinding and Cr (VI) Extraction

The samples were milled using Thomas-Wiley laboratory mill in quadruplets of 2.00 ± 0.01 g and placed into a 250-ml flask, and 100 ml of degassed dipotassium hydrogen phosphate (K_2HPO_4) solution was pipetted into it. The reagent solution was prepared by dissolving 22.8 g of salt in 1,000 ml of distilled water and adjusting the pH value to 8.0±0.1. The flask was tightly sealed and the leather powder suspension was mixed in an automatic mechanical shaker for 3 hours at room temperature. After mixing, the pH value of the solution obtained was checked again to maintain it at 8.0. The contents of

the conical flask were then filtered through a membrane filter into a glass bottle. The filtrates were analysed for Cr (VI) concentration. Blank solutions were prepared in the same way but without leather samples.

Methods

UV-VIS Spectrophotometry

The Cr (VI) analysis of leather samples was conducted at 540 nm using a JENWAY 7315 UV-VIS spectrophotometer model in accordance with the ISO 17075 standard method. The analysis was replicated four times using chemical reagents of analytical grade purity. Ten microlitres of the filtered solution were placed in a 25-ml flask, and 0.5 ml of the 1, 5-diphenyl-carbazide solution was added. The reagent solution was prepared by dissolving 1.0 g of reagent in 100 ml of acetone and acidifying with glacial acetic acid; 0.5 ml of phosphoric acid solution in distilled water (7:10 parts per volume) was added. After filling up to volume, the solution was left for 15 min. to form a stable coloured metal complex. The absorption was then measured by UV–VIS spectrophotometry at 540 nm.

Standard Calibration

Calibration was performed using a stock standard Cr (VI) solution prepared by dissolving 2.829 g of potassium dichromate ($K_2Cr_2O_7$) dried for 16.5 h at 102 °C in 1,000 ml of distilled water. One microliter of this stock solution was diluted in up to 1,000 ml, and the resulting solution was used for preparing the calibration standards. Calibrating solutions were made using standard solutions from 1 ml to 150 ml. The solutions were pipetted into 25 ml, 50 ml, 100 and 250 ml volumetric flasks, 0.5 ml of phosphoric acid and 0.5 ml of diphenylcarbazide solution were added into each volumetric flask. The volumes in each flask were made to full capacity using degassed dipotassium hydrogen phosphate solution, mixed well and left for 15 minutes. The absorbance of the solutions was measured in the same photometric cell as the samples at 540 nm against the distilled water as blank solution. Calibration curve of the absorbance of the six standard solutions against Cr (VI) concentrations in micrograms per ml was plotted.

Calculation of Cr (VI) content

Cr (VI) was calculated as shown in equation (1):

$$W_{Cr(VI)} = \frac{(A_1 - A_2) \times V_0 \times V_2 \times V_4}{V_1 \times V_3 \times m \times F} \quad (1)$$

Where $W_{Cr(VI)}$ is the mass fraction (mg/kg) of soluble Cr (VI) in leather, F is the gradient of calibration curve (ml/µg), A_1 is the absorbance of sample solution with DPC, A_2 is the absorbance of sample solution without DPC, *m* is the mass (g) of leather sample taken, V_0 is the extract volume of the initial sample in ml, V_1 is the aliquot taken from the extract volume of the initial sample; V_2 is the total eluate (S_1) volume after passage through the SPE column, to which the aliquot V_1 was made up; V_3 is the aliquot taken from S_1; V_4 is the final make-up volume of the aliquot from S_1.

2.2.4 Determination of recovery rate

To determine the effect of matrix on the results, recovery rate was calculated. The result was based on dry matter as shown in equation (2):

$$W_{Cr(VI)-dry} = W_{Cr(VI)} \times D \quad (2)$$

Where *D* is the factor for conversion to dry matter $D = \frac{100}{100-w}$

W is the mass fraction of the volatile matter determined using ISO 4684, expressed as a percentage.

Recovery rate (η) was calculated as shown in equation (3):

$$\eta = \frac{[(A_{1s}-A_{2s})-(A_1-A_2)]}{\rho \times F} \times 100\ \% \quad (3)$$

where η is the recovery rate in percent (%); ρ is the mass concentration of Cr (VI) spiked in µg/ml; F is the gradient of calibration curve (ml/µg); A_{1s} is the absorbance of solution after adding chromium (VI) and DPC; A_{2s} is the absorbance of solution after adding Cr (VI), but without adding DPC; A_1 is the absorbance of the sample solution with DPC, and A_2 is the absorbance of the sample solution without DPC.

The limits of quantification and detection were calculated using equations (4) and (5), respectively.

$$Quantification\ Limit\ (QL) = \frac{10\sigma}{slope\ of\ the\ calibration\ curve} \quad (4)$$

$$Limit\ of\ Detection\ (LOD) = \frac{3.3\sigma}{slope\ of\ the\ calibration\ curve} \quad (5)$$

where σ is the standard deviation of the y-intercepts of regression lines.

RESULTS AND DISCUSSION

Effect of post-tanning operations on the Cr (VI) concentrations

The absorbance of different concentrations of Cr (VI) is tabulated in Table 1 and the corresponding curve plotted in Figure 2.

Table 1. Standard calibration data

Conc. of std sol (µg/ml)	blank	1	3	6	9	12	15	30	60	90	120
Absorbance	0.000	0.016	0.046	0.090	0.134	0.179	0.225	0.445	0.889	1.333	1.778

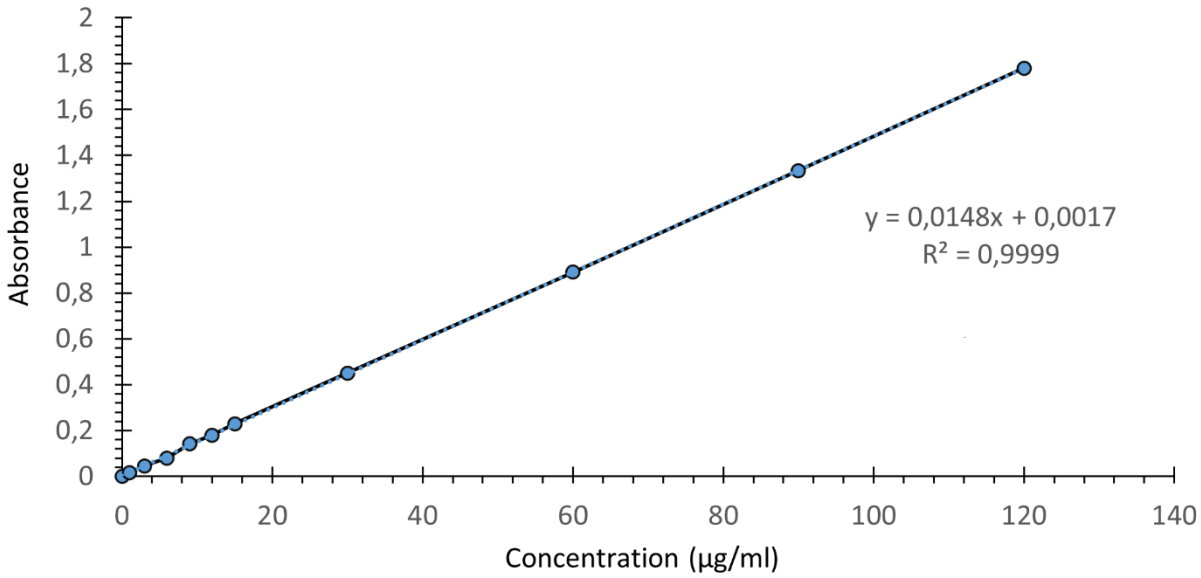

Figure 2. Calibration curve 1

The linearity of the calibration curve ($R^2 = 0.9999$) shows close agreement with the Beer-Lambert's law. Using the slope from Figure 2, the limits of detection and quantification were determined to be 0.2247 and 0.681 mg/kg, respectively. The absorbance of the tanned, retanned, dyed wet blue leathers and fatliquored crusts and their corresponding aged samples were significantly different ($p < 0.05$).

Table 2. Absorbance of post-tanned leathers (132 hours UV+ 24 hours at 80 °C)

		Tanned	Retanned	Dyed	Fatliquored	Recovery rate (%)
Control samples	With DPC (A_1)	0.046	0.033	0.058	0.036	98.6
	Without DPC (A_2)	0.046	0.023	0.058	0.036	
Aged samples	With DPC (A_1)	0.033	0.048	0.078	0.022	98.72
	Without DPC (A_2)	0.017	0.047	0.067	0.017	

The determined value of recovery rate of 98.6 % indicates that the influence of the matrix on the results was negligible and hence the procedure conforms to ISO 17075. The values of Cr (VI) were calculated and tabulated in Table 3.

Table 3: Calculated values of Cr (VI) in both control and aged post-tanned leathers

	Tanned	Retanned	Dyed	Fatliquored
Non-aged samples	n.d.*	183	n.d.*	n.d.*
Aged samples	18.2	292.7	91.45	201.23

n.d.*-not detectable

For non-aged post-tanned leathers, only the retanned crusts recorded a detectable Cr (VI) concentration of 183 mg/kg while the levels in tanned, dyed and fatliquored leathers were below the detection limit. This observation highlights a considerable effect of retanning process using chromium compounds on the levels of Cr (VI) due to autoxidation. Although autoxidation occurs in all the samples to form reactive oxygen species (radicals) of hydro peroxides, the complex bonds of Cr (III) with the carboxylic groups of collagen in the leather are too strong to be dismantled by autoxidation [9,30]. Hence only the unbound Cr (III) are culpable to react with the reactive species to form Cr (VI) [16,31]. Retanning process in this case, using chromium compounds that are not chemically cross-linked with collagen but suspended within the fibres, increases the free, soluble (unbound), extractible and total chromium concentration that correlates with the Cr (VI) formed, since its absorption rate is not as strong as during the initial tanning process [10,16,21,31-32]. After ageing, significant levels of Cr (VI) were detected in all the samples, attributed to thermal and photo ageing that induce formation of Cr (VI) through radical formation [33]. An average level of 18.3 mg/kg Cr (VI) was detected in tanned wet blue leathers. These results are comparable to those published by Bayramoglu and colleagues; 9.39-24.02 mg/kg on chrome-tanned leather exposed to 80 °C and UV radiations for 72 hours [18]. Font and co-workers reported higher concentrations of Cr (VI) of 40 mg/kg after exposing un-retanned leathers to UV light for 325 hours [33]. After the retanning process, the levels of Cr (VI) increased to 292.7 mg/kg. The pronounced increase can be attributed to the excess Cr (III), not chemically linked to the carboxylic group of collagen and hence easily oxidizable to Cr (VI) [9]. Furthermore, the use of sodium and ammonium bicarbonates during neutralization and basification or wetting-back processes prior to the retanning process provide mild oxidation agents, especially at high pH, that necessitate the formation of Cr (VI) in retanned wet blue leathers [33]. The results agree with those reported by Colak and others of 136.3 mg/kg for chrome-retanned leathers exposed to 80 °C heat and UV radiations for 170 hours [20]. Font and colleagues reported 65 mg/kg of Cr (VI) when naphthalene sulfonic acid-

retanned leather was exposed to UV light for 8 days [33]. The levels of Cr (VI) decreased to an average of 91.46 mg/kg after the dyeing process. This implies that the majority of the unbound and unfixed chromium from the retanning process had been drained away from the fibrils as a result of washing and neutralization [31]. Therefore, the dyeing process minimizes the free soluble and total chromium that is likely to be converted to Cr (VI) during ageing. After the fatliquoring process, the concentrations of Cr (VI) rose to an average of 201.23 mg/kg. The increase could have been enhanced by the fatliquors in the leather crusts. In the presence of UV radiation and heat, the fatliquors decompose into a system of unsaturated carbon-carbon conjugated double bonds in the fatty acids, both free and esterified, which initiate reactions that generate reactive oxygen species [11,35]. These reactive oxygen species easily oxidize the Cr (III), which in turn forms Cr (VI) [10,35].

Mitigation of Cr (VI) formation using Abm and carrageenan

Table 4 shows the absorbance values for aged and non-aged leathers and crusts, treated with and without Aloe barbadensis miller mixed with carrageenan.

Table 4. Absorbance of post-tanned leathers and crusts (132 hours UV+ 24 hours at 80 °C)

		Without ABM		With ABM	
		Non-aged	Aged	Non-aged	Aged
Tanned	With DPC (A_1)	0.046	0.048	0.039	0.023
	Without DPC (A_2)	0.046	0.047	0.039	0.023
Retanned	With DPC (A_1)	0.033	0.033	0.072	0.071
	Without DPC (A_2)	0.023	0.017	0.072	0.071
Dyed	With DPC (A_1)	0.058	0.022	0.047	0.058
	Without DPC (A_2)	0.058	0.017	0.047	0.058
Fatliquored	With DPC (A_1)	0.036	0.078	0.022	0.035
	Without DPC (A_2)	0.036	0.067	0.022	0.035

The Cr (VI) levels were calculated and tabulated in Table 5.

Table 5: Calculated values of Cr (VI) (mg/kg)

	Without *Aloe*		With *Aloe*	
	Non-aged	Aged	Non-aged	Aged
Tanned	-	18.3	-	-
Retanned	183	292.7	-	-
Dyed	-	91.46	-	-
Fatliquored	-	201.2	-	-

The Cr (VI) levels in wet blue leathers and crusts processed with Abm mixed with carrageenan, both aged and non-aged, were below the detection level, implying that the levels of Cr (VI) in these samples were below 3.587 mg/kg (the detection limit determined from the calibration curve). The Abm and carrageenan mixture proved to be effective under all the ageing conditions employed in this study. Using tannic acid, Colak et al. demonstrated that the inhibitory effect improved with the increase in the concentration of the acid and the levels of Cr (VI) were in the range of 1.5 to 5.3 mg/kg at the concentration of 3% [20]. The results of using tannic acid, published by Colak et al., indicated that the inhibitory effect improved with the acid concentration ranging from 0.1 to 3% [20]. At 3%, the levels of Cr (VI) were in the range 1.5-5.3 mg/kg. Bayramoglu et al. used walnut leaves, hazelnut shells, olive shoots and thyme and the Cr (VI) formation rate was reduced by 45, 51, 80, and 80 %, respectively, on the samples aged for 24 hours at 80 °C and UV irradiation for 72 hours [18]. Therefore, the inhibition rate of *Aloe barbadensis miller* and carrageenan against the formation of Cr (VI) as observed in this study is superior.

The effectiveness of the antioxidant activity of Abm can be attributed to the high content of antioxidative components, such as polyphenols, indoles, alkaloids, tetradecanoic acid, methyl ester, squalene, ascorbic acid, tocopherol, campesterol and coumaric, limonene, carvone and pigments [22,24,36-41]. The catechins in Abm have been reported previously to possess the ability to reduce the covalent modification of collagens induced by the reactive oxygen species [42]. The antioxidant activity of Abm has been determined by DPPH assay (%) to be in the range of 87.65 to 88.31% and 65.65% of α-tocopherol [44-46]. Furthermore, we hypothesize that the efficiency of the inhibition may have been related to the synergistic action of the compounds in both Abm and carrageenan rather than a single fraction or extracts [46].

Studies have explained several mechanisms behind the inhibiting effect on the formation of Cr (VI) in leather crusts. Firstly, the antioxidant components affect the formation of Cr (VI) by delaying or preventing the oxidation of the substrate by stabilizing, deforming free radicals, or by chelating metals [47-48]. The antioxidants have been known to prevent or interfere with oxidative reactions in collagens by scavenging the free radicals and donating free electrons [7,50]. Scavenging free radicals and donating free electrons hinders the formation of reactive oxygen species and reverses the oxidation process [34]. The phenolic structures have hydrophobic benzoid rings and, in this case, a hydrogen bond is formed between the N-H group of collagen and the C=O group of antioxidants [50-51]. Phenolic hydroxyl groups are good hydrogen donors that react with oxygen and reactive nitrogen species in a termination reaction, thereby breaking the cycle of generating new radicals [50]. This way, the phenols inhibit the radical-mediated oxidation process and interfere with the covalent modification of the collagens already induced by the reactive oxygen species [42]. Secondly, the presence of antioxidants

hinders the absorption of UV radiations because of the aromatic residues of collagen, such as phenylalanine and tyrosine, thereby minimizing the collagen's sensitivity to UV [20,51]. In this present study, the two mechanisms hold, therefore explaining the high inhibitory action of Abm.

Autoxidation alone is sufficient to initiate the formation of Cr (VI) in retanned wet blue leathers to detectable levels due to high content of unbound Cr (III) salts. Although the levels of Cr (VI) in dyed wet blue leathers were the lowest, all the aged leathers far exceeded the permissible value of 3 mg/kg as per REACH Annex 17 and CEN/TS 14995. The levels of Cr (VI) in leathers processed with Abm/carrageenan were below the detection limit. Therefore, the formation of Cr (VI) in leathers should not be considered as a definitive barrier to chrome-tanning technology in the leather industry, human health and environmental management. In light of the pertinent issues related to Cr (VI) in the leather industry, more investigations are required to ascertain the synergy action between Abm and carrageenan. The study also recommends a lower percentage of chromium sulphate during chrome retanning process in order to minimize the unfixed Cr (III) and hence prevent spontaneous oxidation and minimize accelerated oxidation. The potential toxicity of Abm in leather should be investigated in future research. The results will contribute to the eco benign and sustainable leather production under the superior chrome-tanning technology. This will form the basis for technological direction by the policy makers and environmentalists in addressing perennial environmental problems in the leather tanning industry and the downstream sector.

CONCLUSION

In the present study, the effects of post-tanning processes (retanning, dyeing and fatliquoring) on the formation of Cr (VI) in leathers were determined. Autoxidation alone is sufficient to initiate formation of Cr (VI) in retanned wet blue leather to detectable levels due to a high content of unbound Cr (III) salts. Ageing the samples for 24 hours at 80 °C and 132 hours under UV radiations increased the levels of Cr (VI) in all the leathers to detectable levels, with the highest level recorded in retanned leathers followed by fatliquored leather crusts. Although the levels of Cr (VI) in dyed leathers were the lowest, all the aged leathers far exceeded the permissible value of 3 mg/kg as per REACH annex 17 and CEN/TS 14995. The levels of Cr (VI) in leathers processed with Abm and carrageenan were below 3.587 mg/kg. After ageing (being exposed to heat at 80 °C for 24 hours and UV radiations for 132 hours), the levels of Cr (VI) were below 3.587 mg/kg. The incorporation of Abm and carrageenan showed a high efficiency in inhibition of the formation of Cr (VI) in leathers under the ageing conditions described in this study. Therefore, the formation of Cr (VI) in leathers should not be considered as a definitive barrier to chrome-tanning technology in the leather industry, human health and environmental management. In light of the pertinent issues related to Cr (VI) in the leather industry, more investigations are required

to ascertain the synergy between Abm and carrageenan. The study also recommends a lower percentage of chromium sulphate during chrome-retanning process in order to minimize the unfixed Cr (III) and hence prevent spontaneous oxidation and minimize accelerated oxidation. The results contribute to the eco benign and sustainable leather production under the superior chrome-tanning technology.

Author Contributions

Conceptualization – Nalyanya KM, Rop RK, Onyuka AS and Birech Z; methodology – Nalyanya KM, Rop RK, Onyuka AS, Birech Z and Kamau P; formal analysis – Nalyanya KM, Rop RK, Onyuka AS, Birech Z and Kamau P; investigation – Nalyanya KM, Rop RK, Onyuka AS, Birech Z and Kamau P; resources – Nalyanya KM, Rop RK, Onyuka AS, Birech Z and Kamau P; writing-original draft preparation –Nalyanya KM; writing-review and editing – Nalyanya KM, Rop RK, Onyuka AS and Birech Z; visualization –Nalyanya Km; supervision – Rop RK, Onyuka AS and Birech Z. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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