

Utilization of Sudanese Magnesium Oxide to Increase Chromium Absorption Efficiency and Reduce Pollution

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Abstract

The optimization of common chromium tonnage with eco-friendly tanning materials have led to outstanding results, which related to the lowered pollution level in effluents and sludge. This work also is within the above line, aiming to obtain wet-blue leather by common chromium tanning process and fixed using Sudanese magnesium oxide as alternative to common fixated agents and exported one in order to reduce chromium in tannery effluent This workout on local raw gave excellent results on the level of leather and maintain the integrity of the environment

Introduction

Leather processing has emerged as an important economic activity in several developing countries. Awareness of environmental problems has increased considerably and during recent years protecting environment has become a global issue, where currently the leather processing industry their rationale and environmental problems is going through a phase change due to global environmental regulations which assumes the treatment of tannery waste, either by using advanced processing techniques, which is costly financially, or by using chemicals or environmentally friendly technologies to reduce the contribute of that pre-tanning and tanning processes which being about 80–90% of the total pollution load (BOD, COD, TS, TDS, Cr, S₂–, sludge, etc) [1]. Further, toxic gases like ammonia and hydrogen sulphide are also emitted. Volatile organic compounds, heavy metals, and carcinogenic aryl-amines from post-tanning and finishing operations are also creating severe concern [2]. Basic chromium sulphate used in the tanning process is not consumed fully and about 30–40% of it is washed away to the environment and thus creates severe environmental problem especially to the aquatic system [3]. Where a great deal of solid wastes as if lime sludge and chrome sludge from tannery and effluent treatment plants are being generated [4]. The results indicate that the residual chrome in chrome tanning and re-chroming wastewaters is the main origin of chrome in effluent. Meanwhile, a considerable amount of chrome is released from leather in almost all the post tanning processes, including washing, neutralizing, re-tanning with various retaining agents, dyeing, fat liquoring and acid fixation. As a result, more than 60% of the chrome added is discharged into wastewater [5]. So a right strategy to reduce chrome discharge in leather processing is to develop technologies that can increase efficiency of chrome-collagen interaction with reduced chrome offer, whereas several alkalinity salts are used to de-acidified to a pH of 3.7–4.0, such as sodium bicarbonate, sodium format and magnesium oxide which is more effective in chromium fixation and molecules distributing though collagen fibres. Magnetite was encountered in northern Sudan, where the field verifications proof the existence of magnetite rich micro-granite, which differs from the surrounding rocks [6]. Therefore, the study has focused on improvement of chrome tanning method in order to minimize the negative effects of chrome, such as high chrome exhaustion systems by utilize the magnesium oxide as the chromium fixation agent, whereas is capable of effectively minimizing the discharge of chrome and then can achieve absorption of 80%–90%.

Materials and Methods

The goat pelts were obtained from warehouse in Omdurman, Khartoum. Sudan. Reagents used for the experiment and analysis were of analytical grade.

Preparation of magnesium oxide material

The manganese ore was obtained from Engessana which latitude 600 Kilometres southern of Khartoum, then grinding and Ignition to 1300 °C in the muffle furnace in the presence of oxygen. Then cooled in desiccator and kept in polyethylene bag for further processes.

Experimental design

The experimental design was outlined in randomized complete design with three treatments; T1: traditional method; T2: method using exported MgO (Doltan Mg); and T3: method using local MgO, replicated three times.

The physico- chemical properties of doltan Mg and local MgO

The samples were prepared according to Indian standard then characterized according to. (ASTM [6 and 7] and physico-chemical properties of samples, MgO, CaO and SiO₂ were measured using Indian standard. [7].

Tanning trial

Green goatskins have been used for pre-tanning and chrome tonnage according to percentage declared in table (1), and the yielded leather saved as control leather. Then experiment was repeated two times using firstly doltan Mg and secondly local magnesium oxide receptively instead of sodium format. The samples of chrome bath of the previous trials each time were collected to determined chrome content and the obtained leathers were prepared to physicochemical tested.



Table 1: Tanning trail.

Process	%	Product	Time	Remarks	PH	
					Skin	Float
Washing	200	Water At 28°C	30'			
Drain						
Unhairing	150	Water At 28°C				
	6	Lime	60'			
	3	Sodium Sulphide	60'	Overnight And Run 10'/H		Ph = 12.5
Next Morning	Run	10'		Drain/Wash/Drain/Reliming	Next Morning	
Drain/Wash/Drain	200	Water At 28°C	10'			
Reliming	100	Water At 28°C				
	2	Lime	30'			Ph = 12.5
Drain/Wash/Drain	200	Water At 28°C	30'			
Drain/Wash/Drain	200	Water At 28°C	10'			
Neutralization	100	Water At 28°C				
	1.5	Ammonium Sulphate	60			Ph = 8
Drain/Wash/Drain	100	Water At 28°C	20'			
Batting	80	Water At 30°C				
	1	Orbon	30'	Check Fft	Ok	Ph=7,0/7,2
Drain/Wash/Drain	200	Water At 28°C	10'			
Drain/Wash/Drain	200	Water At 28°C	10'			
Pickling	60	Water At 28°C				
	0.1	Fungicide				
	10	Salt	10'	Bring To Bé =6		
	0.5	Formic Acid (1 : 5)	30'+30'			
	1	Sulphuric Acid (1 : 10)	30' + 30'	Stop Overnight		
Next Morning						
Run			10'		Bcg=Yellow	Ph=3,0/3,1
	4	Chrome 26/33	60'			
	4	Chrome 26/33	180'			
	2	Sodium Formate	40'		Bcg=Blue	Ph=3,8/4
Mechanical Operations		Pile Up / Sammy / Shave / Re-Tannage				

Physico- chemical properties of chrome bath liquor

Waste water characterization was done for the physico-chemical quality parameters; pH, and total chromium content according to ASTM [8-9].

The mechanical properties of leather

The samples were prepared according to SLP1&2 then the specimens were subjected to conditioning according to SLP3 and shrinkage temperatures SLC406 were measured according to (SLP 7) [10].

Statistics Analysis

The data mechanical, physicochemical analyzed using the statistical package for science (SPSS) at a significant level $p = 0.05$ using (ANOVA) [11].

Results and Discussion

The samples of magnesium oxide were analysed (Local and export), the components of both samples such as magnesium, silicon, calcium oxide and compound oxides were distinguished for discussion the purities of samples and results in table.2, which displayed that local magnesium oxide sample contained high percentage of calcium and silicon oxides compared to the exported magnesium oxide sample, when compared to the requirements of the ISO of the magnesium oxide.

Table 2: Physio-chemical property of magnesium oxide.

Name	Type	Chemical Analysis (%)					Physical Property		
Mg O Name Mg O		Mg O	Ca O	Si O ₂	Fe ₂ O ₃	Al ₂ O ₃	Sieve Analysis Mesh	Flow Rate s/%	Tap Density g/cm ³
	1	≥96	≤1.0	≤2.0	≤0.5	≤0.5	40-325	150±15	2.28-2.50
	2						80-325	160-180	2.24-2.34
	3						40-325	150±15	2.28-2.50
	D Mg	97	0.6	1.7	-	-	40-325	150±15	2.28-2.50
	Local	69.9	20.4	9.1	-	-	40-325	150±15	2.28-2.50
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Chrome tonnage is the most common type of tanning in the world. Chrome tanned leathers are characterized by top handling quality, high hydro-thermal stability and excellent user properties but chrome waste from leather processing poses a significant disposal problem. Conventional chroming process generally involves in pickling, chroming and basifying, and there are several defects existing in the process 8-10% salt and 1.0-1.2% sulphuric acid were used in pickling, which results in higher contents of chlorides, sulphates and chemical oxygen demand (COD) in the effluent. The uptake of chromium in conventional chroming is lower (70-80%), a considerable amount of chromium left in the effluent may result in environmental problems. To increase the chrome absorption and decreased the chromium which discharged thus the experiments were designed utilized the local and exported basification agents and the results showed that local agent has good ability of de-acidified and development the chromium sulphate fixation into the fibres and supported strong bonding and increased the strengthen of the collagen-chromium bonds (ionic, covalent and co-ordinate bonds) compared to the common fixation materials. Alkalinity salts commonly was used to raise the pH of the bath after chromium tonnage from 2.5 to 3.8-4 and the mechanism of fixation was chemically illustrated by introducing hydroxyl groups (-OH) into the chromium coordinate-valance shells instead of crystallization water molecules and changed the basicity of the complex.

Table 3: Bond length

Description	T1	T2	T3	mean	Std.D	Sig
Tensile strength kg/Cm ²	210	202	207	-	-	-
Tearing strength kg/Cm	95	89	90	-	-	-
Elongation at Break %	40	44	39	-	-	-
Grain strength kg/Cm	63	60	62	-	-	-
Chrome content of tanned bath/ g/L	0.25	0.152	0.155	0.186	0.717	0
Shrinkage temperature of leather	102	102.5	102	102.2	0.752	0

The bond length is very important here whereas the Cr-OH coordinate bond is longer than the Cr - H₂O links, therefore the size of the basic chromium sulphate molecules become very big and is imprison inside the fibre spaces and thus physically

the big chromium complexes does not license out through the skin pores, and this is explain that the shrinkage temperature of the leathers samples is more acceptable and to be found within the limits of the specifications of the standard requirement, moreover the results table. 2 proved that the magnesium oxide de-acidification treatments were reduced the chromium load to about half compared to common de-acidification, and thus conservation the environment. The mechanical properties of producing leather (Table 2) were indicated that the strengths of produced leather were acceptable according to the requirements of the standard specifications of shoe upper leather. In spite of that tensile strength of leather actually know the combined force up to which all the fibres in unit cross sectional area and in the direction of stress can jointly stand without breaking, but naturally the tensile strength does not say anything about the total number of fibre's which shared the applied force during testing and the strength of those fibre's individually for this reason the tear strength was determined. Because in these cases only few fibres are ruptured at a time, so they give some idea about the strength of leather fibres. If the tear strengths of leather are compared with its tensile strength, then some rough idea about the fibre's density per unit leather cross sectional area can be obtained, in this case where Table (3) presented that tensile strength and the tear strength of produced leather are both higher than the requirement of leather box for shoe upper according to the standard, moreover the tear strength value indicates that the fibres of the original raw hide are strong and a good. The percentage of elongation at break was measured to discuss the leather elasticity and the results showed that it is more acceptable compared to standard requirement of chromium-tanned leather.

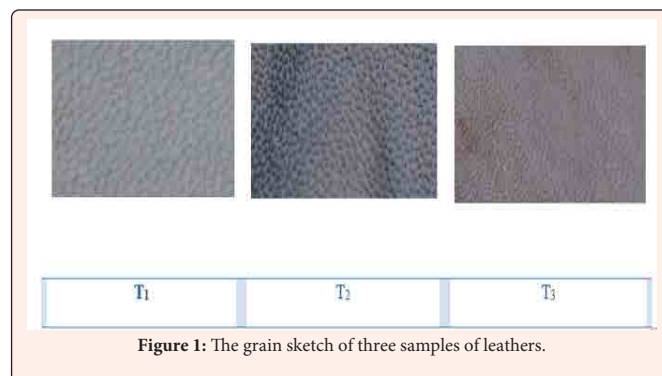


Figure 1: The grain sketch of three samples of leathers.



The structure of the grain of leathers were show in photo.1, the grain of leathers which produced utilizing T1, T2 and T3 experimental were consistency and had similarity in shape and size of pores, these enhances the physical analysis results of obtained leathers. The use of local material after purification can have an economic feasibility, the magnesium oxide solubility in water is 300 g / 100 ml and gives a clear alkaline characteristic, the pH of a saturated solution is 9.5 - 10.5. This solubility increases when added to the bath containing diluted sulphuric acid and react Which has its solubility is 25.5 g / 100 ml at 20 °C and PH of a saturated solution is 6, this is improved the ability of chromium to penetrate and stabilize into pelt fibre's, The local sample of magnesium oxide is a contaminated agent which contented calcium oxide where its solubility in water is 0.189 mg / 100 ml at 20 °C and decreases according to increases of temperature and has a strong alkaline property, the pH is 12.4, these solubility increased when added to the pickle bath which contains sulphuric acid they reacted together, the reaction is exothermic may cause drops of the shrinkage temperature of the skin, and therefore deposit insoluble calcium sulphate (solubility in water 2.4 g / liter at 20 °C) in the inter-fibrillary space of the grain layer which is cause roughness and crack-ness to the leather. High pH value of calcium oxide caused a non-graded increasing of external chromium basicity, therefore, maximum amount of chromium was fixed up to the grain and flesh side, which prevented further penetration of chromium into the pelt. Moreover, this type of uneven distribution of chromium causes stiffness, pepperiness of the finished leather and roughness of the grain surface. Therefore, when used local de-acidification agent the powder dissolved in boiling water and then filtered to isolate calcium oxides which poring soluble in a hot water and silicon oxide insoluble where formed the impurity of the sample and then added to the bath of tonnage. In addition, with this the economic viability of the local material increases whenever its purity has increased and thus it can give a good quality leather that can be compared to leather produced using imported raw materials and contributes to the environmental impact by reducing the load of wastewater with chrome. Utilizing this ore consumed an additional amount compared to export one, which represented as the impurities percentage in the sample, which were separated using previous method mentioned to obtain reasonable purity, moreover wastes an extended amount of time to conduct treatments and additional energy to heat the water.

Conclusion

Chromium fixation using local magnesium oxide gave excellent leather with distinctive physical and chemical properties compared to the common and exported fixation, moreover contributed to reducing pollution by increasing the absorption and fixation of chromium inside the fibres. Utilization the Sudanese magnesium oxide that reduced the load of chromium in effluent and preserved the environment from pollution, need higher purification rate of impurities to get the perfect combination.

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