

# **A review of the green chemistry approaches to leather tanning in imparting sustainable leather manufacturing**

## **Supplementary Materials**

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**Table S1.** Tanning performance of leather treated by improved Cr tanning process.

Tanning agents	Type of leather	Tanning agent consumption (l/Kg)	Chemicals consumption (g/Kg)	Water consumption (l/Kg)	Shrinkage temperature (°C)	Tensile strength (MPa)/Elongation (%) / Tearing strength (N/mm)	Ref.
<u>Chrome-tanning with other metals and zeolites</u>							
BCS + FS	Cowhides	15.4 + 6.6	20.0	n/a	110.0	26.4 / 74.0 / 75.6	67
BCS + BAS + FS	Cowhides	11.0 + 7.7 + 3.3	20.0	n/a	109.0	24.7 / 53.0 / 81.0	
BCS + BAS + ZrS	Cowhides	11.0 + 7.7 + 3.3	21.0	n/a	119.0	43.0 / 84.0 / 79.1	
BCS + sodium zeolites (lab-scale)*	Pickled sheepskin	80.0 + 30.0	110.0	2.74	105.0	n/a	68
BCS + sodium zeolites (pilot-scale)*		76.4 + 30.0	116.4	0.93	104.0	24.4 / 46.0 / 94.0	
BCS + re-tanning with acrylic and phenolic syntans and fatliquoring*	Raw goatskin	80.0	-	-	110.0±1.0	25.6 ± 0.5 / 76.0 ± 3.0 / n/a	69
<u>Cr tanning with Cr adsorption increasing additives</u>							
BCS + PBA nanoparticle dispersion, then re-tanning/fatliquoring with syntan and sulphited oil*	Pickled cowhide	80.0 + 40.0	135.0	n/a	126.0±1.2	27.9 ± 0.6 / 84.0 ± 4.0 / n/a	32
BCS + oxazolidine	Cowhides	90.0 + 10.0	180.0	1.8	105.0±2.0	25.0 / n/a / 57.9	66
BCS + TLWP	Pickled cow pelt	60.0 + 60.0	140.0	1.0	106.0±0.5	27.0 ± 0.3 / 58.0 ± 1.0 / 57.0 ± 1.0	69
BCS + AVP-ZnO	Cowhides	35.0 + 30.0	165.0	n/a	92.4	n/a	70
BCS + AVP-ZnO, then re-tanned with the same	Cowhides	35.0 + 30.0/30.0 + 20.0	215.0	n/a	124.7	24.7 / 80.0 / 141.7	
BCS + AVP-MMT	Salted goatskin	30.0 + 20.0	n/a	n/a	104.3	16.0 / 76.0 / 55.0	71
BCS + HBAP	Pickled pigskin	80.0 + 40.0	350.0	n/a	107.5	n/a	73
BCS + RSTW-PEG	Cowhides Goatskin	60.0 + 50.0	n/a	n/a	n/a	24.1 ± 0.4 / 56.0 ± 1.0 / 49.1 ± 1.0	76
<u>Cr adsorption increase by sonication</u>							
BCS tanning under sonication (300 Watt/28 KHz) Cr* treatment using	Pickled goatskin	20.0 g/l <sup>d</sup>	n/a	n/a	105.2	13.8 / 40.1 / 56.2	77
Sonicated Cr treatment using BCS*	Cowhides	60.0 g/l <sup>d</sup>	n/a	n/a	104.5	n/a	80
Sonicated (150 Watt/40KHz) Cr* treatment using BCS	Pickled cowhide	50.0 g/l <sup>d</sup>	n/a	n/a	116.0±1.0	n/a / 33.2 ± 1.3 / 70.0 ± 4.0	81
Sonicated Cr treatment using BCS + microwave*	Pickled goatskin	20.0 g/l <sup>d</sup>	n/a	n/a	103.8	15.4 / n/a / 34.2	82
<u>Waterless tanning</u>							
Waterless tanning with BCS in propylene carbonate	Cowhides	50.0	70.0	0.15	100.0	n/a	88
BCS in SC-CO <sub>2</sub>	Cattle skin	90.0 g/l BCS + 120.0 g/l NaCl + 5.0 ml formic acid + 8.0 ml/l sulphuric acid for 2.5 hr under 6.0 MPa pressure <sup>d</sup>			100.0	n/a	91
Tanning in 2:1 urea and KCr(SO <sub>4</sub> ) <sub>2</sub> ·10H <sub>2</sub> O deep eutectic solvent	Cowhides	The Cr content of leather was 3.52%			83.0	30.3 / 42.5 / n/a	92
<u>Cr tanning in combination with tannins, syntans, resins, and other crosslinking agents</u>							
Cr-syn/PAA/PMA, then fatliquoring	Delimed goat skin	15.0	80.0	1.5	118.0 ± 2.0	32.9 ± 1.0 / 78.0 ± 4.0 / 84.3 ± 5.0	33
<i>Cassia alata</i> tannin + BCS	Raw goatskin	65.0 + 25.0	145.0	n/a	95.0	12.0 / 53.5 / 49.2	34
( <i>Cassia alata</i> tannin + <i>Cassia alata</i> tannin induced Ag NP) + BCS	Raw goatskin	65.0 + 25.0	145.0	n/a	107.0	21.7 / 66.5 / 60.6	

Cr (III)-loaded nanoparticles of PEGMA-co-AA-co-GMA and then fatliquoring treatment	Pickled sheepskin	20.0 <sup>b</sup>	243.0	7.3	101.5	12.4 / 98.8 / 30.5	38
Cr-acid complex formulation, then re-tanned/fatliquored with syntan	Wet salted goatskin	40.0	370.0	2.0	>100.0	23.3 ± 0.9 / 72.6 ± 1.2 / 68.8 ± 0.9	93
Pickling with oxazolidine + BCS	Pickled goatskin	40.0 + 70.0	130.0	n/a	107.5	22.9 / 82.7 / 71.2	94
BCS + acrylic resin/montmorillonite	-	60.0 + 20.0	160.0	2.0	89.0	17.7 / 8.9 / 29.1	95
BCS + SiNP-pMMA-BA (1% Si NP)	Pickled buffalo	30.0 + 40.0	170.0	2.0	100.0	48.5 / 72.0 / n/a	97
BCS + SiNP-pMMA-BA (5% Si NP)	hides	30.0 + 40.0	170.0	2.0	115.0	41.0 / 56.0 / n/a	
MgAl-LDH + BCS	Pickled goatskin	40.0 + 20.0	60.0	n/a	94.0±3.0	19.3 ± 0.6 / n/a / 26.1 ± 0.7	99

N.B. The calculation of BCS, BAS, ZrS, and FS was based on their Cr<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub> contents respectively, and also the weight of wet skins.

<sup>a</sup>No re-tanning/fatliquoring treatment or fatliquoring but dosage was not provided.

<sup>b</sup>The authors did not provide re-tanning and fatliquoring chemical consumption provided.

<sup>c</sup>The nanoparticles contain 4% Cr. The dosage is equivalent to 20 g Cr/kg pickled wet leather containing 200% water.

<sup>d</sup>Soaked in this solution for 5 to 6 min.

<sup>e</sup>Calculated based on Cr content.

**Table S2.** Tanning performance of chrome-free leather tanned by chemical cross-linking.

Tanning agents	Type of leather	Tanning agent consumption (l/Kg)	Chemicals consumption (g/Kg)	Water consumption (l/Kg)	Shrinkage temperature (°C)	Tensile strength (MPa)/Elongation (%)/Tearing strength (N/mm)	Ref.
Glutaraldehyde + Tara tannin followed by re-tanning with polyaryl sulphate	Pickled sheepskin	250.0	627.5	6.0	92.0±1.0	23.0 ± 1.8 / n/a / 51.0 ± 7.8	41
Syntan + Mimosa tannin + oxazolidine, and then fatliquoring/dyeing	Calfskin	150.0 + 40.0 + 200.0	494.0	9.5	98.0	16.6 / n/a / 44.0	42
Glutaraldehyde + Mimosa tannin + oxazolidine, and then fatliquoring/dyeing	Calfskin	10.0 + 40.0 + 200.0	354.0	9.5	104.0	21.0 / n/a / 50.9	
THPS + Tara tannin + glutaraldehyde, then re-tanned and fatliquored	Pickled sheepskin	15.0 + 100.0 + 20	475.0	3.5	88.0 ± 1.0	16.2 ± 0.5 / 58.0 ± 2.0 / n/a	111
Glutaraldehyde + syntan followed by re-tanning/fatliquoring with acrylic syntan and vegetable tannin <sup>a</sup>	Salted goatskin	25.0 + 20.0	213.0	n/a	85.0	15.6 / 44.1 / n/a	112
Glutaraldehyde tanning followed by re-tanning with melamine resin	Salted goatskin	110.0	110.0	0	90.0±4.0	15.0 ± 2.0 / 72.0 ± 6.0 / n/a	115
Lysine + glutaraldehyde and then re-tanning with melamine resin	Salted goatskin	10.0 + 20.0 + 40.0	85.0	0.5	120.0±8.0	18.0 ± 3.0 / 56.0 ± 6.0 / n/a	
Glyoxal	Pickled goatskin	60.0	60.0	n/a	82.0	n/a	116
EHBP-D + BAS	Pickled goatskin	80.0 + 60.0	340.0	2.0	108.6±1.1	15.0 ± 3.7 / 93.8 ± 6.3 / 30.6 ± 6.3	122
BDA + Acrylic resin + Amino resin + mimosa + BAS	Pickled sheepskin	20.0 + 30.0 + 20.0 + 40.0 + 10.0	320.0	19.5	88.0	17.5 / 85.0 / 15.0	127
THPS + syntan followed by re-tanning & fatliquoring twice	Salted goatskin	20.0 + 20.0 + 60.0 + 135.0	681.0	27.0	91.0	n/a / 28.5 / 28.4	128
POSS-NH <sub>2</sub> + THPS	Salted goatskin	60.0 + 25.0	90.0	n/a	83.0	17.1 / 102.2 / 74.5	129
HHTT-EGDE-CP	Pickled sheepskin	120.0	474.0	17.0	78.8	13.5 / 68.2 / 54.2	130
AEHET		120.0	464.0	17.0	75.7	7.9 / 73.4 / 23.9	
COS-GTE tanning followed by fatliquoring	Sheep hides	150.0	418.0	9.0	83.5	10.1 / 62.6 / 47.4	131
AAMV tanning, then re-tanning and fatliquoring	Pickled sheepskin	80.0 + 50.0 + 40.0	310.0	n/a	70.0	13.0 / 60.0 / 54.0	133
Tara tannin + BAS + glutaraldehyde, then re-tanning/fatliquoring with syntan	Cow upper skin	200.0 + 170.0 + 10.0 + 2.00	607.0	13.5	103.0	n/a	134

N.B. The calculation of BAS was calculated based on its Al<sub>2</sub>O<sub>3</sub> content and also on the weight of wet skins.

<sup>a</sup>The chemical consumption does not include fatliquoring chemicals.

<sup>b</sup>No re-tanning and fatliquoring treatment.

**Table S3.** Tanning performance of chrome-free leather tanned by cross-linking with dialdehyde polymers.

Tanning agents	Type of leather	Tanning agent consumption (l/Kg)	Chemicals consumption (g/Kg)	Water consumption (l/Kg)	Shrinkage temperature (°C)	Tensile strength (MPa)/Elongation (%) / Tearing strength (N/mm)	Ref.
SAD + fat liquoring	Pickled sheepskin	80.0	212.0	34.0	89.4	22.1 ± 2.7 / 42.5 ± 7.0 / 114.6 ± 4.4	3
ZrS + oxidised starch (with 60% H <sub>2</sub> O <sub>2</sub> ), then re-tanning with mimosa and syntans, and fatliquoring	Pickled cattlehides	175.0 + 48.0 + 70.0	590.0	30.5	87.3 ± 0.5	15.6 ± 0.7 / n/a / 76.9 ± 2.5	126
SPDA (4% solution) tanning followed by fatliquoring	Pickled sheepskin	80.0	250.0	13.0	79.0	19.7 ± 1.8 / 107.9 ± 8.1 / n/a	139
CMC-D + SAD	Pickled cattle pelt	40.0 + 7.0	47.0	n/a	81.0	n/a	140
SAD		7.0	7.0	n/a	79.0	n/a	
H-CMC + SAD		40.0 + 40.0	80.0	n/a	72.0	n/a	
CMC-D, then fatliquoring with synthetic fatliquor	Pickled cattlehides	40.0	100.0	10.0	78.8	7.07 ± 0.23 / n/a / 22.95 ± 0.31	142
CMC-D + chitosan		40.0 + 20.0	120.0	10.0	85.0	n/a	
CMC-D + chitosan, then fatliquoring with synthetic fatliquor		40.0 + 20.0	190.0	19.5	80.0	3.43 ± 0.60 / n/a / 16.16 ± 1.13	
CMC-D + LMC-III, then fatliquoring with synthetic fatliquor		40.0 + 20.0	190.0	19.5	80.0	12.7 ± 1.5 / n/a / 28.8 ± 0.5	
TGD	Pickled sheepskin	80.0	656.0	8.0	86.7	n/a	143
SAD		80.0	656.0	8.0	83.9	n/a	
CDD		80.0	656.0	8.0	82.0	n/a	
Al-m-CCA (equal to Al <sub>2</sub> O <sub>3</sub> ) + ZrS	Pickled cattle pelt	15.0 + 40.0	215.0	1.0	84.5	12.1 / 25.0 / 37.5	144
Al-m-MCA (equal to Al <sub>2</sub> O <sub>3</sub> ) + ZrS	Pickled cattle pelt	150.0 + 40.0	210.0	2.0	86.0	n/a	145
Zr-m-HCD + ZrS	Pickled cattle pelt	n/a + 20.0	n/a	2.0	75.2	n/a	146
Al-m-HCD (equal to Al <sub>2</sub> O <sub>3</sub> ) + ZrOCl <sub>2</sub>	Pickled cattle pelt	10.0 + 30.0	100.0	2.0	87.0	n/a	146
(SBCD) + re-tanning with syntan followed by fatliquoring	Salted goatskin	100.0 + 160.0	420.0	3.0	73.0 ± 2.0	19.9 ± 1.3 / n/a / 40.6 ± 0.9	147
CSD <sup>b</sup>	Pickled sheepskin	100.0	160.0	5.0	77.9	8.6 / 72.0 / 14.5	148
CSD-g-EGDE + HMTA <sup>b</sup>		100.0 + 5.0	165.0	5.0	85.2	10.9 / 85.0 / 29.6	
TA-d-PEG <sup>b</sup>	Cowhide	160.0	160.0 + NaHCO <sub>3</sub>	6.0	80.8 ± 0.2	15.3 ± 0.1 / 66.8 ± 0.2 / 44.2	149
			for neutralisation				
CSD tanning followed by fatliquoring with several natural and synthetic fatliquoring agents	Pickled goatskin	200.0	350.0	9.0	61.0 ± 1.0	28.2 ± 2.9 / 72.9 ± 10.1 / n/a	150

N.B. The calculation of BAS and ZrS were calculated based on their Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> contents respectively and also on the weight of wet skins.

<sup>a</sup>The chemical consumption does not include fatliquoring chemicals.

<sup>b</sup>No re-tanning and fatliquoring treatment.