Processing of spent tanning and chrome plating solutions for chromium recovery

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ABSTRACT

Use of chromium in metal plating and leather tanning industries gener-ates a lot of effluent containing Cr(III) and Cr(VI). Besides severe water pollution, substantial amount of chromium is lost due to the prevalent practice of removal-disposal technique followed world over. Processes based on recovery and reuse methodology are currently projected as ex-cellent means of meeting the environmental regulations while producing chromium salts/solutions for recycling. This paper details the composi-tion, conditions and quantity of spent liquors/effluents generated in elec-troplating and leather tanning industries and their treatment by removal-disposal as well as recovery-reuse methods. The approach based on pre-cipitation, ion exchange and liquid-liquid extraction particularly for chro-mium recovery is highlighted. The results of solvent extraction with D2EHPA and CYANEX 272 for chromium recovery from spent tanning baths are also summarised.

Keywords : Chromium, Chrome electroplating, Leather tanning, Metal recovery, Solvent extraction.

INTRODUCTION

Chromium is mainly used in the electroplating and tanning industries for surface treatment as well as finishing of metals/plastics and leather respectively. As a result of these applications chromium enters in the effluent streams [1-3] causing havoc to the environment. Due to stringent laws coming into existence the awareness of pollution related problems and their control are being increas-ingly focussed. Besides environmental aspects, sufficiently large amounts of metals are disposed-off resulting in enhanced burden on the depleting primary resources like ores and minerals. It is therefore essential to look for not only

removal-disposal approaches mostly employed as a cheapest technique but also to explore recover-reuse methods which can meet the twin objectives of achieving pollution norms and producing value added products from the waste stream thus conserving the natural resources.

Most of the electroplating industries are in the small scale unorganised sectors where environmental aspects [2] are not taken care. With the growth of automobile sector in India the consumption of chromic acid for electroplating is poised for a quantum leap. As such several thousand tonnes of chromic acid is consumed by a few thousand small and medium scale industries. As regards tanneries, there are more than 2500 units in our country with an annual capacity of processing 7.0 lakh tonnes of hides and skins [3,4]. With 80.0% of tanneries engaged in chrome tanning process, [5] the consumption of basic chromium sulphate (BCS) has increased from 25,000 to 40,000 T per annum [6] in the last decade (1984-1994). The leather production is expected to touch 4.8 billion ft^2 by the end of 2000AD and so is the environmental issues connected to such a growth.

ELECTROPLATING INDUSTRIES

The electroplating industries in India are mostly based on chromic acid bath. The composition and operating conditions [7] of the chrome plating bath from such solutions are summarised in Table 1. The conventional decorative, crack free, hard plating and black plating require chromic acid in the range 175-470 g/L with certain additions. The compositions of all sulphate Cr(III) bath commercialised in 1975 in western countries, are given in Table 2. The bath temperature in all the cases is 45-55°C excepting the black plating from Cr (VI) which operates at ambient temperature. The end solution of Cr(III) bath also contains some amount of Cr(VI) due to anodic oxidation whereas the chromic acid essentially produces end solution consisting of Cr(VI). The bath composition [2,8] of various streams in chrome plating industry is listed in Table 3. The chromium balance in chromic acid bath [9] is:

Chromic acid actually deposited	:	5.7 %
Miscellaneous losses including fumes exhaust	:	20.0 %
Drag out	:	74.3 %

Due to repeated use, the bath gets contaminated particularly with Fe and chlorine necessitating drag-out(bleed-off). The drag-out stream is normally purified in respect of above impurities and recycled back. It is discarded occasionally to control other contaminants. The rinse water is the stream generated during washing of the plated object. The volumes of drag-out electrolyte and

Table 1 : Composition and operating conditions
of the plating bath from chromic acid solutions

Type of deposit	Composition (g/L)				Operating condition		
	Chromic acid	SO_4^{2-}	SiF_6^{2-}	Sr^+/K^+	Temp (°C)	C.D. A/dm²	CE (%)
Conventional decorative							
(i) High efficiency	250	1	2	nil	45	15	15
(ii) Self regulating	250	1	2	4/14	45	15	15
Conventional crack free							
(i)High efficiency	450	2.5	1	nil	45	20	12
(ii)Self regulating	175	0.35	3	nil	45	16	18
Conventional macro cracked hard							
i)High efficiency	300	1.5	4	nil	55	50	22
ii)Self regulating	200	0.8	3	6/6	55	50	22
*Black chrome plating	300-470 (Cr^{3+}:8-10)	nil	$F^-+NO_3^-$ or acetate	-	16-32	30-50	15-30

* Limited usage

Table 2 : Composition and conditions of all-sulphate trivalent chromium bath*

1.	Chromium sulphate,$Cr_2(SO_4)_3$ or Chromium chloride, $CrCl_3$ + Ammonium formate	20g/L
2	Potassium sulphate	150g/L
3	Sodium sulphate	100g/L
4	Boric acid	60g/L
5	Malic acid	10g/L
6	Thiourea	0.1g/L
7	pH of bath	3.5-3.7
8	Temperature of solution	45-55°C
9	Current density	4-10A/dm²

* Advantages   : Limited toxicity of solution and environmental problem.
* Disadvantages : Limited usage, lesser acceptable colour of deposit and most susceptible to metallic impurities.

rinse water from a unit are 0.1-1.01 L/m² and 0.1-1.0 L/m² surface treated respectively. The composite discharge (Table 3) from such industries contains 0.15-0.60 g/L Cr at 1.7-2.5 pH which needs treatment. The solid sludge with 9-11% Cr is another product generated during plating, reduction/purification and neutralisation of waste waters; these are dumped as landfill or stockpiled.

Table 3: Composition of various streams in chrome plating

Stream	Chromic acid CrO_3 (g/L)	Cr(T) (g/L)	Cu(II) (g/L)	Zn(II) (g/L)	Fe(T) (g/L)	pH
Electrolytic bath	150-550	78-286	-	-	0.03-0.20	1.5-2.5
*Dragout electrolyte[0.1-1.01 L/m² surface treated]	100-300	50-150	0.002-0.20	0.004 -0.01	0.3-0.5	1.3-2.0
Rinse water (Running rinse [0.1-1.0 L/m² surface treated]	6-30	3-15	0.002-0.03	0.004 -0.01	0.003 -0.05	1.5-2.2
Diluted rinse discharge	0.22-2.0	0.1-0.9	0.002-0.02	0.001 -0.01	0.002 -0.02	1.5-2.4
Composite discharge solution	0.3-1.2	0.15-0.6	0.01-0.04	0.002 -0.01	0.02-0.04	1.7-2.5

* Drag out electrolyte needs purification for Fe and Cl and sometimes precipitated as sludge.

a   Composite water and rinse discharge need treatment for disposal/recovery. Composition of sludge:9-10% Cr, 1-2% Cu, 0.5-0.6% Fe and traces of Sn, Zn, Ni, etc.

TANNING INDUSTRIES

The environmental aspects with respect to tanneries need special attention as the toxicity level is governed by chromium content. Though the basic constituent of chrome tanning bath is Cr(III) yet some amounts of Cr(VI) is noticed in the spent bath [6]. Amongst the chromium species the Cr(IV)-Cr(VI) is reported to be as high as 25-30%. In the leather industry various effluents generated at different stages in the processing are listed in Table 4.

The table summarises the volume of spent liquor/effluent produced [10] for every 100kg of hide or skin treated, its pH, the suspended and total solid content (g/L) and the biochemical oxygen demand (BOD) in 5 days at 20°C. The volume of composite water including washings is 3000-3500 L/100kg of the hide tanned at pH 7.5-10 and BOD of 2000-3000. The existing practice of waste disposal from different streams is given in Table 5. The procedure followed by bigger tanneries as mentioned in the Table 5 is also questionable as the sludge making results in total loss of chromium; there is no appropriate care for processing of these effluents by smaller industries. The spent tanning baths for every 100 kg of hides and skin-treated, are 400-500 L in volume at a pH of 2.5-3.5

Table 4 : Analysis of tannery effluents at different stages

Effluent	Volume(L) for 100kg hide or skin tanned	pH	Total solid (g/L)	Suspended solid (g/L)	Biochemical O_2 demand (5days at 20°C)(mg/L)
Beam house processing					
(i) Soaking	250-400	7.5-8.0	0.8-2.0	0.25-0.4	1100-2500
(ii) Liming	650-1000	10.0-12.5	16.0-45.0	4.5-45.0	600-2000
(iii) Deliming	700-800	9.0-9.5	1.2-12.0	0.2-1.2	1000-12000
Tan yard processing					
(i) Vegetable tanning	200-400	5.0-6.8	8.0-50.0	5.0-20.0	6000-12000
(ii) Pickling	200-300	2.9-4.0	1.6-5.0	0.6-5.0	600-2200
(iii) Chrome tanning	400-500	2.5-3.5	2.4-12.0	0.3-1.0	800-1200
Composite (including washing)	3000-3500	7.5-10.0	10.0-25.0	10.0-16.0	2000-3000

and a BOD of 800-1200 mg/L. The average composition of spent tanning bath is listed in Table 6. The concentration of Cr(III) is in the range 0.5-4.0 g/L with an average of above 1.0 g/L Cr(III). The Cr(VI) is normally much smaller in concentration (0.001-0.005 g/L) but this amount is sufficiently high in the composite water. The concentration of Fe(III) and Al(III) present in the spent bath calls for their removal/recovery.

PROCESSING METHODOLOGIES

Thus the spent liquors prouced in the chrome electroplating and tanning industries are of two types.

(i) Drag-out electrolyte (spent) and rinse water and composite solution from electroplating.

(ii) Spent tanning bath from the chrome tanneries.

The tolerance limits [10] for disposal of industrial effluent/waste water into public sewer, on land for irrigation and in surface water/stream are given in Table 7. The pH in all the cases must be in the range 5.5-9.0 along with BOD at 20°C of 500 mg/L. Amongst the tolerable limits of different metal ions, chromium level should not exceed (mg/L) 2ppm for disposal in surface water/stream.The methods employed for the above spent liquor are described under the following approaches.

Table 5 : Practice of solid waste disposal from different streams in tanneries

Process steps in tanning	Solid waste generated	Utilization practice
Wet/dry salted skin	Salt dust	Disposal to on-land or into the sea
Soaking	Green fleshing	Drying and disposal for glue manufacture/animal feed
Unhairing and fleshing during liming with dissolved lime and Na_2S	Hair	Washing, drying and use for carpet and drugget/ woolen units
-Do-	Lime fleshing and trimmings	Drying and disposal for glue and gelatine making and animal feed etc.
Liming and deliming	Lime sludge	Used as building construction and soil conditioning
Vegetable tanning	Vegetable tan sludge	Used as fertilizer/soil conditioner.
Vegetable/chrome tanning	Shavings	Used in leather boards, reducing chrome liquors etc. · incineration along with sludge
Effluent treatment from tanning and composite solution	· Chrome tanning sludge	Disposal on land or into the sea

Table 6 : Composition of spent tanning bath for chromium recovery
Volume: 400-500L/100kg of leather processed

Constituent	Tanning bath(g/L)	Model solution(g/L)
Cr(III)	0.5-4.0	3.98-4.41
Cr(VI)	0.001-0.005	traces
Fe(III)	0.04-0.01	0.09
Al(III)	0.08-0.15	0.117-0.12
C(acetic acid)	1.2-1.8	1.5-1.56
Sulphate	10.0-12.0	12.0
NaCl	50.0-60.0	60.0
pH	2.5-3.5	2.65-2.70

Table 7 : Tolerance limits for disposal of industrial effluents/wastewaters

| Parameters of effluent discharge	For discharge in public sewer (IS:3306 -1965)	For discharge on land for irrigation (IS :3307-1965)	For discharge in surface water/stream (IS:2490-1963)
pH	5.5-9.0	5.5-9.0	5.5-9.0
BOD(5days at 20°C) max.	500 mg/L	500 mg/L	500 mg/L
Solid(max.)	600 mg/L (suspended) 2100 mg/L (dissolved inorganic)	2100 mg/L (dissolved inorganic)	100 mg/L (suspended)
Temp.(max)	45°C	Ambient temp.	40°C
Metallic/toxic ions (mg/L)	2.0 Cr, Ni&CN⁻. 1.0-Pb, 3.0-Cu, 15.0-Zn,2.0-B	2.0-B	0.2-CN', 2.0-F', 1.0-As,Cd,B,Cr,Cu, Hg.Pb,Se,Ni,As,Zn (one/all)
Sulphates & chlorides(mg/L)	3100&600	1000&600	2.0 (sulphides) 1.0(residual Cl_2)
Oil, grease & phenolic compounds (mg/L)	5100(phenol)	30(oil & grease)	10(oil), 1.09(grease), 0.2(phenol)

(i) Removal-disposal scheme
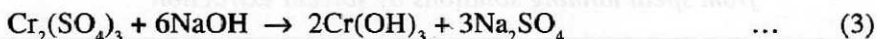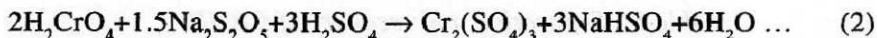
(ii) Recovery-reuse scheme

i) REMOVAL-DISPOSAL SCHEME

This is the most commonly used procedure to remove chromium content of the rinse and composite water of the plating industry and often used for treating the composite water of the tanneries. The unit operation in vogue are - reduction-precipitation, and precipitation besides evaporations and ion exchange for recovery in the plating industry.

Reduction-precipitation method: The ferrous sulphate is extensively used for reduction of Cr(VI) to Cr(III) in the pH range 2.5-3.0.

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} \qquad \ldots \quad (1)$$
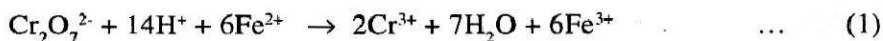
Other reductants used [8] are sulphur dioxide, sodium metabisulphate, barium sulphide, iron and zinc. The Cr(III) is then precipitated as hydroxide by the alkali treatment [11].

$$2H_2CrO_4 + 1.5Na_2S_2O_5 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3NaHSO_4 + 6H_2O \dots \quad (2)$$

$$Cr_2(SO_4)_3 + 6NaOH \rightarrow 2Cr(OH)_3 + 3Na_2SO_4 \quad \dots \quad (3)$$

The major problem with this approach is that the sludge formed is bulky and light and has poor settling properties. When barium sulphide is used as reductant, the volume of sludge produced after lime addition is smaller and more easily dried than all other agents. Though the Cr(III) precipitated as hydroxide is considered less toxic to aquatic species, but its conversion and mobility to Cr(VI) due to weathering/biooxidation/oxidation process by MnO_2 can be the cause of concern in the longer duration.

Precipitation: The chromic acid of spent plating solution may be precipitated by the addition of barium chloride/hydroxide as barium chromate

$$Ba(OH)_2 + CrO_3 \rightarrow BaCrO_4 + H_2O \quad \dots \quad (4)$$
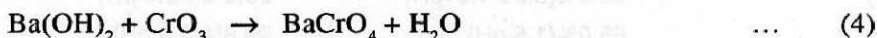
An excess barium salt is avoided as soluble barium is itself poisonous. The precipitate is sensitive to lime addition as neutral pH is required for the sludge formation.

In the leather industry the methods used are reduction-precipitation and precipitation for removal, and solvent extraction and ion exchange are mostly considered for recovery though the process involving electrolysis, membrane and foam separations and reverse osmosis are also being developed. In India tanneries of large and medium size have adopted precipitation methods [3,12,13] to treat the composite water for pH, suspended and total solids and BOD. The use of coagulants and flocculants has also been reported [14]. Tannery effluent can be treated by activated sludge process by mixing the composite water with sewage and fine carbon [10] to reduce BOD. This approach requires long aeration period. The coagulation-flocculation approach [4] uses calcium hydroxide(1.8-3.5 g/L), ferrous sulphate(1.0-4.0 g/L) and aluminium sulphate (1.5-3.2 g/L) to achieve the acceptable water quality on treating the composite water. The treatment of segregated washwater streams in the tanneries is another very promising procedure as it allows maximum flexibility (Table 5) with respect to recovering various products for recycling/safe disposal.

ii) RECOVERY-REUSE SCHEME

Though some attempts were made [15,16] to recover chromium values from the sludge already generated/stockpiled, it is an established opinion to follow the recovery and reuse methodologies. The techniques for the purpose are based on evaporation in the plating industry and ion exchange (IX) and solvent extraction

Table 8 : Separation and recovery of Cr(III)
from spent tanning solutions by solvent extraction

Item	Solvent : D2EHPA	Solvent : CYANEX 272
Solvent composition	15%D2EHPA, 10% isodecanol in kerosene	15-25% CYANEX 272, 10% p-nonylphenol in kerosene
Form of solvent	50% ammoniated solvent	50% ammoniated solvent
Equilibrium pH for Cr(III) extraction	3.0-5.0	>5.0(Higher solvent % forms emulsion)
Maximum extraction	2.5%(1.5 pH)	Nil(upto 2.5pH)
Cr(III)	95.0%(3.95-4.01pH)	95.0%(>5.0 pH)
Al(III)	68.0%(1.5 pH)	99.8%(3.0 pH)
Fe(III)	99.0%(1.5 pH)	98.1%(3.0 pH)
Recovery of metals by stripping (time:5min)	80% Cr(III) by3MHCl, 85%Cr(III) by 8MHCl (in 4 stages), 86%Fe(III)&76%Al(III) by 3M HCl, 90%Fe(III) & 88%Al(III) by 6M HCl(in 1 stage)	70% Cr(III) by 6M HCl, 85% Cr(III) by 8M HCl (in 4 stages), 72% Fe(III)& 27% Al(III) by 3M HCl 99%Fe(III) & 90% Al(III) by 8M HCl (in 1 stage),
Favoured methodology for separation and recovery	(i)Extraction and recovery of Fe(III) & Al(III) at an eq. pH 1.5	(i) High extraction and recovery of Fe(III) and Al(III) at pH 3.0
	(ii) Subsequent extraction and recovery of Cr(III) at above pH 3.0 followed by stripping with HCl.	(ii) Subsequent extraction and recovery of Cr(III) at pH 5.0 followed by stripping with HCl

(SX) for the processing of both types of solutions .

Evaporation: Chromic acid recovery from the rinse waters from plating units is also industrially used [17-18]. The process depends on either vacuum or atmospheric evaporation and in some cases preceded by ion exchange to remove foreign metals. The recovered chromic acid may be used for plating.

Ion exchange: Ion exchange has been increasingly used to cope with waste

disposal and regeneration of solutions. Some of the resins available are suitable for adsorption of chromium (VI) from rinse and composite waters [19]. The newer resins have better loading and recovery characteristics, yet the perfect regeneration properties of these resins are still researched though,these have emerged as viable option. Ion exchange technology is currently applicable for removing impurities from spent plating bath as well as recovering total chromium from spent liquors of chrome plating and tanning. A recent process reported [20] involves electrooxidation of Cr(III) to Cr(VI) and its recovery by IX thus eliminating sludge formation.

Solvent extraction: This is a versatile and effective technique for extraction/separation/enrichment and recovery of desired metals [21]. There are limited information on extraction and recovery of Cr(III) and Cr(VI) from industrial effluent [22-24] and no details are available for the recovery of this metal on commercial scale. Earlier Wu et. al., [25] reported the preliminary studies for treating chrome tanning solution containing 0.5-1.0 g/L Cr(III) using P_2O_4 - a phosphatic solvent. In our recent investigation [26], an attempt was made to recover metals from a model tanning bath containing (g/L)3.98-4.41 Cr(III),0.09 Fe(III) and 0.117-0.12 Al(III) (Table 6). The results on separation and recovery of Cr(III) are summarised in Table 8 using the commercial reagents viz. di-2-ethylhexyl phosphoric acid and Cyanex 272.

These results highlight the two different conditions for the metal extraction and stripping by the solvents. For D2EHPA, Al(III) and Fe(III) recovery at pH 1.5 followed by Cr(III) extraction at pH 3.0 is worked out where as Cyanex 272 operates at pH 3.0 and pH 5.0 for the respective metal separations. Upto 85% Cr(III) recovered can be recycled for retanning purpose.

CONCLUSIONS

The drag-out electrolyte and rinse solution as well as composite water in chrome plating and spent tanning bath, and composite solution in the tanneries can be processed to recover chromium. The existing "removal- disposal (precipitation) process" followed in the organised sector, though, results in mitigating the pollution problems to a large extent, the Cr(III) sludge generated and used for landfill can not guarantee the oxidation and mobility to Cr(VI) due to weathering process. This calls for metal recovery from such sludge. It is also necessary to treat these solutions from smaller sector in single processing unit. The "recovery-reuse scheme" based on evaporation, IX and SX needs to be fully developed and exploited depending upon the compatibility of the existing industries. This approach is extremely attractive in view of its applicability on all scales of operation.

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