



Tannery Wastes: Trivalent Chromium Case

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Abstract

The widely used applications of the Chromium metal compound in finishing metals, protection of wood, brass formation, electrical equipment designing, and sometimes as catalyst makes it available in different kinds of industrial waste. Industrial waste waters rich in chromium of different oxidations states, most important ones being Cr (III) and Cr (VI), have been a major concern for the environment in spite of application of various remediation technologies. Various reviews have been published for the removal technologies of Cr (VI) which is the most noxious oxidation state, however, Cr (III) also is a pertinent state to investigate owing to its toxicity as well as stability in different environmental compartments. Thus, this review explores the existence of different tanneries world over, the type of wastes generated, methods to remediate and dispose of the same, all in relation to Cr (III) and will be one of its kind and of great interest to researchers pursuing research in this field.

Keywords

Chromium (III); remediation; physical; chemical; biological methods

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Introduction

The heavy metal toxicity generated by various industries has a major effect on the life forms because heavy metals as such are not able to degrade again to less harmful products as is understood for different toxic organic compounds. The exposure of the chromium in the chrome industries due to chromium dust causes the skin irritation problem and mainly affects the respiration rate, which may often cause lung cancer. There are some findings related to chromium exposure causing severe haemorrhage (Huang and Wu 1977). Faust and Aly found the maximum chromium contamination of 0.05 ppm in drinking water (Faust and Aly, 1987). Stringent legislations on the quality of drinking water arose the major concern for developing the processes to treat chromium containing water, which comprise physical, chemical and biological methods. Adsorption of contaminated waste waters has been an extensively investigated option which comprised sorption on conventional activated carbon as well as alternative adsorbents obtained from wastes creating numerous methods of decontamination of Cr dosed waste waters (Gode and Pehlivan, 2003). Recent evidence suggests that Cr (III) species, although previously considered "kinetically inert," can readily bind to nucleic acids in vitro and can even act as

redox agents when complexed to a conjugated aromatic ligand (Warren *et al.*, 1981; Sugden *et al.*, 1990). In a study of in vitro replication of DNA, there is a 2 time more misincorporation of DNA polymerase due to the presence of Cr (III) in the sample (Sirover *et al.*, 1977; Tkeshelashvili *et al.*, 1981). These non-specific initiations increase the RNA synthesis with the in-vitro studies. This gives the idea that Cr (III) might have interrupted the gene regulation (Okada *et al.*, 1983). Here, in this review, the Chromium (III) release, the status of tanneries in the world and treatment/control methods in wastewater treatment processes has been summarized.

Tanneries in the world

The leather industry has a worldwide impact: Italy, U.S., Russia and the former Soviet Republic are the world-leading producers of leather (Tiravanti *et al.* 1997). In Pakistan, leather is the second most important export industry (Ashraf *et al.* 1997). There is a massive economic potential for the leather industry in the developing countries like China, Hong Kong, Thailand, Korea, and India, which already has an established industry (Khwaja *et al.* 2000). Figure 1 presents the first steps to hide treatment to obtain leather (Cabeza *et al.* 1998).

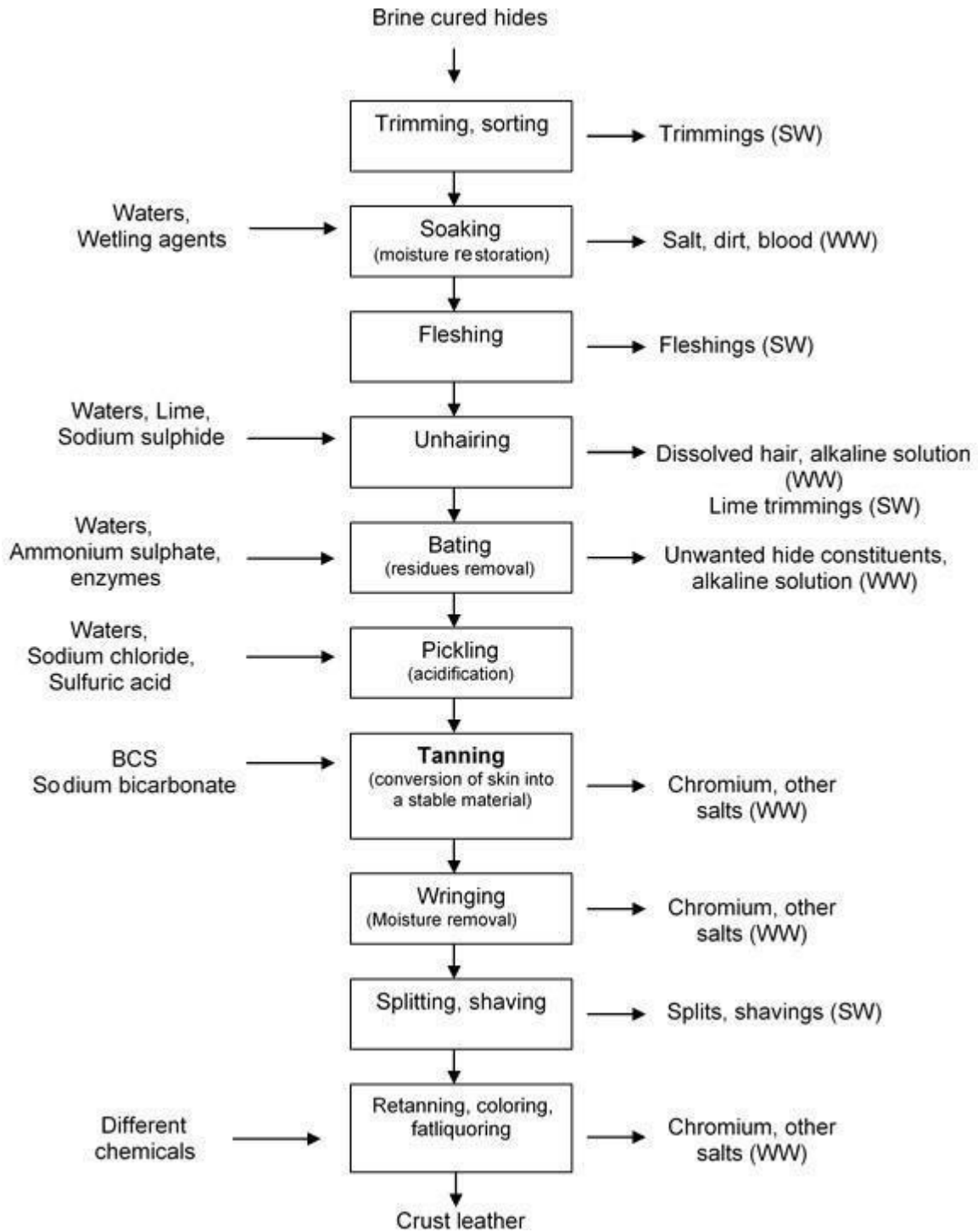


Figure 1. Chromium tanning in leather making process (WW: wastewater, SW: solid waste).

Tannages are classified as mineral and vegetable. The second one is used by 10% of the tanneries in the world while 90% applied the first method with chrome (Ram *et al.*, 1999). However, vegetable tanning does not match with the Cr-tanning process (Sreeram and Ramasami 2000).

Tanning is more easily described than defined as mineral tanning where the skin stabilization was achieved by some inorganic salts. Although many alternatives against mineral tanning were explored Cr-tanning is utilized mostly (Sreeram and Ramasami, 2000).

India capacitated around 2000 tanneries (Rajamani *et al.* 1995), while in Pakistan around 600 tanneries were calculated (European Commission Directorate-General Jrc Joint Research Centre, 2001). In Italy, the number of tanneries exceeds 1200 (Beccari *et al.* 1992). About 80%- 95% of tanneries in the world use Chrome tanning (Rajamani *et al.* 1995; http://www.anam.gob.pa/documentos/recopilacion/pdf/ic04.pdf). Chromium is considered as the most versatile and highly efficient tanning agent. It has a good processing speed; low costs and it gives a light color and greater stability to the leather. During tanning, an acidic Cr-oxide is used for the tanning of halide into the leather (Tobin and Roux, 1997). In this process, the absorption of the Cr (III) on a tissue and crosslinking of it to the collagen fibers were observed. Then, it forms a complex in between the collagen polypeptides and helps in the protection of the leather from the water penetration into it (Ashraf *et al.* 1997), nitrogen detachment from tissue and rotting (Tobin and Roux, 1997). It is reported as a sulfate form of chromium BCS (Basic chromium sulfate) is the main chemical to be used for tanning (Panswad *et al.* 2001; Sreeram and Ramasami, 2003).

Their effluents, particularly Chromium

There are three types of tannery effluents (European Commission Directorate-General Jrc Joint Research Centre, 2001):

- The currently discharged wastewater has not passed from any treatment process.
- Two types: solid tanned and solid untanned waste generated, which contains dust, salts, packing material, etc.
- Air emissions like ammonia emission during the drainage of acid and alkaline wastewater which also have adverse effects on workers; health.

The principal polluting chemicals (Sreeram and Ramasami 2000) used in tanning industry are Cr-salts, in the form of lime, sometimes sodium sulfide, ammonium salts, sulphuric acid, vegetable tannins (Schramm 1997), Fe₂O₃ and Al₂O₃ (Kowalski, 1994). The polluting residues generated are Cr-effluents, BOD (biochemical oxygen demand), COD

(chemical oxygen demand), SS (suspended solids), TSS (total suspended solids), TKN (total Kjeldahl nitrogen) (Panswad *et al.* 2001). About 30-60 liters of water per kg of the hide (Ramasami and Prasad, 1991). Organic compounds, like fats, proteins, and enzymes, are also rejected with Cr (Kocaoba and Akcin, 2002). During tanning, only 60% of Cr is adsorbed and the other 40% remains in the wastes (Fabiani *et al.*, 1997; Chakir, 2001). European bovine tanners produce about 400-kilo tonnes of solid sludge. In the U.S., around 60 KMT of Cr solid waste is generated each year; and about ten times this amount worldwide (Cabeza *et al.*, 1998). In Pakistan, about 937 tons per year of Chromium is wasted (Ashraf *et al.*, 1997). In Italy, 280 000 tons of Cr-containing (1-4%Cr) dry sludges are annually produced by tanneries (Simoncini 1989; Tiravanti *et al.* 1997). In Thailand, about 2.55 million cubic meters of wastewater, so 197.4 tons of Chromium were discharged in the environment in 1992 (Panswad *et al.* 2001). In Poland, 4 million cubic meters per year of tannery wastewater are generated (Kowalski 1994). In the absence of effluent treatment, Chromium concentration in tanning yard waste streams ranges from 1700-2500 mg/l (Ramasami 1996; Sreeram and Ramasami 2003). In Morocco, tannery effluents contain about 500 mg/l of chromium (Dahbi *et al.* 2002). Trivalent chromium is the predominant species in the effluents. Hexavalent Chromium concentration is 20 times less important than the Cr (III) one (Chuan and Liu, 1996).

Note: Other industries produce a large amount of Cr-contaminated wastes: Plating, cleaning and alloy preparation (Solisio *et al.* 2000), metal finishing industries (Chakir 2001), electroplating, acid electroplating, painting, dye and manufacturing, petroleum refining (Udy, 1956; Kocaoba and Akcin 2002), mining, cement industries, production of steel, photographic materials (Ramos *et al.* 1994; Dahbi *et al.* 2002), surface coating, fungicides, magnetic tape, metallurgy (Nriagu 1988; Sreeram and Ramasami, 2001).

Tannery waste pollutants generate the following problems (Wiegant *et al.* 1999): Cr-concentration reduces the possibility of agricultural reuse of sludge; the presence of organic pollutants brings the necessity of pre-treatment; the high content of sulfates hinders anaerobic treatment; a high SS concentration leads to a high amount of sludge and the need for corresponding facilities. Some solutions proposed by Wiegant *et al.* (1999) are: In-house Cr-recovery would allow the use of sludge as fertilizer; the anaerobic pre-treatment would be efficient after wastewater dilution or air oxidation (Macchi *et al.* 1991) (so the sulfate concentration and the sludge load would decrease); chemical pre-treatment would decrease the amount of SS and facilitate the maintenance; an aeration post-treatment would permit the effluent to reach standards for BOD, TS, and COD. Flow segregation is the most effective manner of effluent treatment (CATANCE, 2001). Also, segregation and treatment of

tannery wastes before treatment plant is advised (Macchi *et al.* 1991; Modrogan *et al.* 2003) because Cr can have damaging effects on waste biological treatment of municipal and industrial wastes (Pathe *et al.* 1996).

Chromium

The tanning industries and authorities always have an issue of debate about the toxicity of the chromium affecting the aquatic life. Industries says that it becomes non-toxic when in salt form while the authorities complain about the reduction in aquatic life forms because it causes toxicity in any form. The specific parameter of biotoxicity has been described concisely by Sreeram and Ramasami (2003). The oxidation state of this metal varies its implication (Dartsch *et al.* 1998). Chromium (III) was also investigated to participate in glucose metabolism and nucleic acid synthesis (Richard and Bourg, 1991; Mertz, 1998). But it is also able to crosslink with DNA or proteins, (Salnikow *et al.* 1992; Tsou *et al.* 1997; Balamurugan *et al.* 1999). The insoluble chromium metal ion is found in earth's crust is estimated as 122 ppm (Hartford, 1979). Its poor solubility and the formation of organic complexes limit the mobilization of its ions in fauna and flora. Cr (VI) also causes skin irritation respiration problems (Solisio *et al.* 2000) and is a well-established human carcinogen (Costa, 1991), hepato-toxic and nephro-toxic (Sreeram and Ramasami, 2001). The genotoxicity was also considered for the chromium (VI) in both in vitro and in vivo conditions (Singh *et al.* 1998). The oxyanions easily permeate the biological membranes by sulfate transport systems and reduced by cell's reducing agents which reduced it into Cr (III) from Cr (VI) (Arslan *et al.* 1987). In soils, manganese oxides this chromium oxidized reversibly. (Bartlett and James, 1979) while under specific conditions (in presence of acid and ferrous oxides or another electron donor such as organic matter), Cr (VI) may be reduced in Cr (III) (Bartlett and Kimble, 1976; Chakir *et al.* 2002).

The permissible limit of chromium in industrial wastewater is less than 0.3-2 (Ramasami *et al.* 1999) or 0.5 mg. L-1 of total chromium in liquid effluents (Maliotis, 1996) (1000 times less than the usual amount of Chromium in tannery waste, cf. previous paragraph). Numerous articles have been published on chromium toxicity and behaviour (Klein, 1966; Adamson, 1976; Benoit, 1976; Base and Mesner, 1976; Bharti *et al.*, 1979 ; Nakayama *et al.* 1981; Burrows, 1983; Moore and Ramamoorthy, 1984; Adriano, 1984, 1986; Stollenwerk and Grove, 1985; Carson *et al.*, 1986; Knocke and Kelley, 1987; Heary and Ray, 1987; Eary and Rai, 1987; Ciavatta *et al.* 1992; Runnels and Sheperd, 1992; Gao *et al.*, 1993; Stein and Schwedt, 1994; Ramana and Sastry, 1994; Kaim and Schwederski, 1994; Peräniemi and Ahlgrén, 1995; Rapoport and Muter, 1995; Kocaoba and Akcin, 2003).

Alternatives to Chromium

Many metals have potential tanning properties but the only metal salts, other than Cr(III), suitable are Aluminium,

Silicone, iron, Ti, Zr, and Ce (Chakravorty and Nursten, 1958; Sreeram and Ramasami, 2003). Some organic tanning agents are or could be used in the leather industry e.g.: vegetable tannins, synthetic tanning materials, aldehyde-based tannins (Wojdasiewicz *et al.*, 1992; Slabbert, 1999; Sreeram, T. Ramasami, 2003). Syntans, resins, and polyacrylates are agents used with tannin of Chrome and vegetable.

In order to catalyze the process, the biocatalyst could be replaced with the advanced biochemistry, which specifically aims for the leather industry. It also helps in the reduction of the use of a large quantity of chemical replaced by a smaller quantity of biochemicals and becomes less hazardous to the workers also.

Thanikaivelan *et al.* (2003) propose a technique used for the tanning in a three-step process: dehairing, the opening of fibers and tanning catalyzed at pH 8.0 by biocatalyst. Sometimes, post-tanning and neutralization steps are also added to ensure no unused salt discharged to waste stream (CATANCE, 2002).

Effluents management

Incineration

This technique is recommended for small amounts of sludge but only with a suitable incinerator equipped with the proper flue-gas-purification system (Modrogan *et al.*, 2003). Jones (1978) filed a patent on a process for incinerating of tannery waste solids containing organic material and Chromium. The waste is fed in the combustion zone of an industrial furnace at a low temperature (800-1200 °F) to convert a part of the organic material to gases and the chromium to ash. The gases are removed from the combustion zone and subjected to further oxidation while the ash is taken out of the furnace. By controlling temperature and waste composition, the Chromium in the ash can be obtained in trivalent or hexavalent form (extracted with solvent for reuse in the tanning process). Trivalent Chromium is recovered as a chromic oxide in an improved stable form for landfill or storage. Incineration is not feasible because of a GHG emission and low yield of energy (Sreeram and Ramasami, 2003).

Marine discharge

It was commonly used but heavy metals in wastes bring out environmental issues (Xiang *et al.*, 2000).

Landfilling

It was the most common way of dealing with tannery wastes. But the costs increase with the cost of transportation and the fewer landfill sites available (Cabeza *et al.*, 1998). In Europe, landfilling of sludge becomes increasingly difficult because the landfill area is not sufficiently available. This way of management will become more and more difficult. In some

places, it is already forbidden (Cabeza *et al.*, 1998). That's why other alternative routes are needed for the treatment options.

Land application

Tannery sludge has been widely used (Cabeza *et al.*, 1998) as fertilizer because it is rich in proteic matter: Fe(II) and organic matter stabilize Cr(III) but acidic conditions and organic ligands improve its mobility (Adriano, 1986) and manganese oxides oxidize it in Cr(VI) (Nakayama *et al.*, 1981). The application of sludge in agriculture in Europe is a generally accepted practice, although not in every country. The restrictions are due to chromium contamination of soils by pesticides, and other pollutants containing chromium. Schramm, 1997 also described that the legislation limits should be imposed on the use of the heavy metals so that it will not be found in sewage sludge in higher quantity (Schramm, 1997). Nonetheless, tannery waste use in agriculture is restricted because the saturation of sites occurs (Tiravanti *et al.*, 1997) and it is a rather expensive (the tanner has to finance it) and environmentally inappropriate management technique (Cabeza *et al.*, 1998). In some place, it is already forbidden (Sreeram and Ramasami, 2003).

Chromium effluents treatments

Effluent treatment is crucial for long-term tannery profitability (Song *et al.*, 2000) but recycling processes and viability of the disposals depends respectively on the quality and market of the waste and by-products (CATANCE, 2002). The tannery waste treatment is generally subdivided into the following operations: screening, equalization, sedimentation, removal of sulfides (by chemical precipitation), biological oxidation (by activated sludge) (Beccari *et al.*, 1992). Following, there are few suggestions for the waste fractions, other than Chromium, management: recycling of the salts, organic solvents, compact dust, landfill of wet scrubber sludge.

There are options for recycling chromium floats up to 50%. In Italy and Portugal, chromium recycling units are established and re-used for tanneries. Germany also has these kinds of units in a place where chromium be used for tanning (CATANCE, 2002). In the recent decade, the exhaustion rate improvement helped in releasing very small quality of the chromium waste (Beccari *et al.*, 2001). Some tanneries use high-exhausting Chromium salts process.

Chemical methods

Pyrolysis

A patent (Muralidhara, 1982) has been filed for a process for chromium values and potential energy recovery from liquid and solid leather tannery wastes. It comprises: pyrolyzing the tannery wastes to produce a burnable fuel product used to supply energy for the system and recovering Chromium compounds from the solid residue.

Hydrolysis

In the years of the 1970s and 1980s, the leather waste hydrolysis for the recovery of amino-acids was developed for to use them in fertilizers (Cabeza *et al.*, 1998). Erickson *et al.* (1995) filed a patent, which improves the process with chromium removal by use of steam and precipitation methods. Guardini (1984) also proposed the chromium oxide removal as a solid waste from the polypeptides and their use for plants and animal feeds. Another de-tanning process involves the use of caustic soda, lime, and other alkali solutions (Heidemann, 1991; Rose *et al.*, 1999 Taylor *et al.*, 1997).

Leaching

Chromium is recovered from sludge by acid extraction. Different mineral acids (HNO_3 , HCl and H_2SO_4) were tested by Shen *et al.* (2001) and H_2SO_4 seems to be more efficient. It is, by the way, the most commonly used (Macchi *et al.*, 1991).

Oxidation

Macchi *et al.* (1991) technique are based on acid sludge extraction followed by oxidation of Cr (III) with H_2O_2 ; Cr (VI) is then separated from other cations (Fe, Mg, Al, and Ca) and reduced to Cr(III), which is recovered as Cr-hydroxides. 80% Cr-recovery of total Chromium content in tannery sludge is obtained. This process combined with air oxidation (to remove sulfides) will decrease the H_2O_2 requirement. Chemicals costs and the fact that the yield depends on iron and manganese concentration are some disadvantages but Cr (VI) containing steps are the more limiting factors.

Precipitation/Filtration

It is the same done by the use of the alkali, and the chromium gets precipitated and recovered by filtration. If stronger alkali is used for precipitation, the rate of coagulation increases (CATANCE, 2002). Figure 2 illustrates the following process: after leaching, Chromium precipitation by alkali, the dewatering and the redis solution by H_2SO_4 and generation of $\text{Cr}_2(\text{SO}_4)_3$ (Panswad *et al.*, 2001).

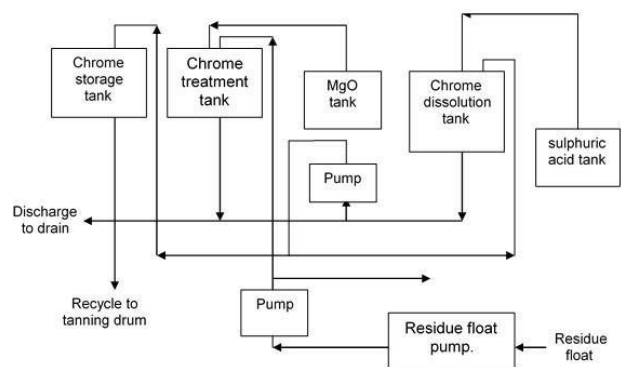


Figure 2: Tanning Chrome recycling system.

- Slow precipitation with magnesium oxide gives a dense sludge, which allows for decanting and also helps in maintaining pH below 10 (CATANCE, 2002). The MgO is also suitable for use due to its high settling ability and high alkalinity (Rao *et al.*, 1999). The previous figure shows a MgO using process (Panswad *et al.*, 2001). Cabeza *et al.* (1998) used MgO on shavings to get a Chrome cake and isolate potentially valuable protein products (gelatin and collagen hydrolysate); the procedure is described in Figure 3.

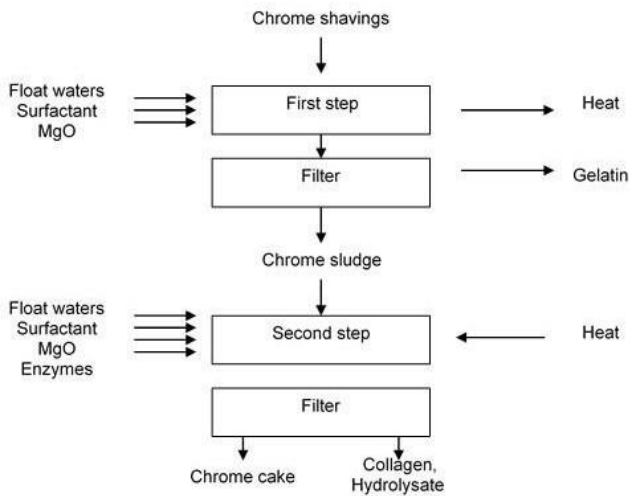


Figure 3: Schematic representation of the Chrome shaving

Wiegant *et al.* (1998) used MgO for recovery of Chrome from tanning effluents (figure 4). Khwaja *et al.* (2000) precipitated Chromium from spent liquor with MgO (figure 5). Basic magnesium carbonate can also be used.

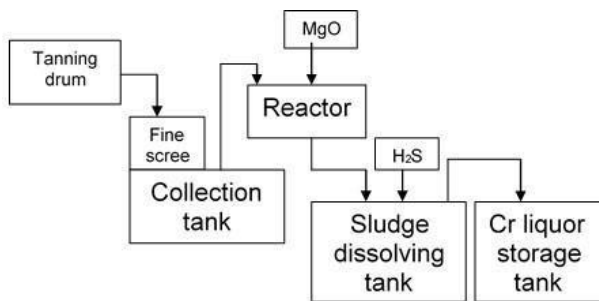


Figure 4. The layout of a simple Chrome recovery unit.

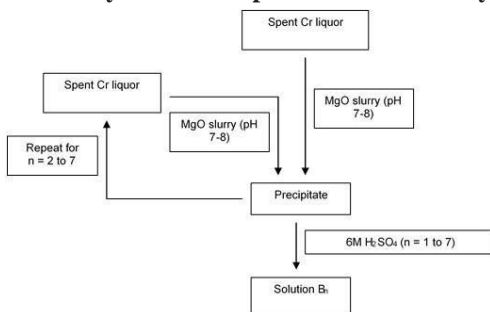


Figure 5. Sample pre-treatment.

The disadvantages are: Commercial MgO has calcium impurities (which lead to calcium sulfate that coprecipitate with Cr-hydroxide); large amounts of $MgSO_4$ are generated (which render the groundwater harder); Mg-soap is made from the oils and fats coming from the tanning process (Sreeram *et al.*, 2000); a long settling time is needed; and a large amount of sludge is produced (Chakir, 2001).

- Sodium chemicals: Sodium sulfide and sodium hydrogen carbonate (Chakir *et al.*, 2002) have been proposed for Cr-removal but the more common chemicals used are sodium carbonate (Panswad *et al.*, 2001) and sodium hydroxide (Pathe *et al.*, 1996; Panswad *et al.*, 2001; Modrogan *et al.*, 2003; Nacheva *et al.*, 2003; Shen *et al.*, 2003). Figure 6 illustrates the NaOH precipitation of Chrome that allows Cr-recovery from 75 to 90%.

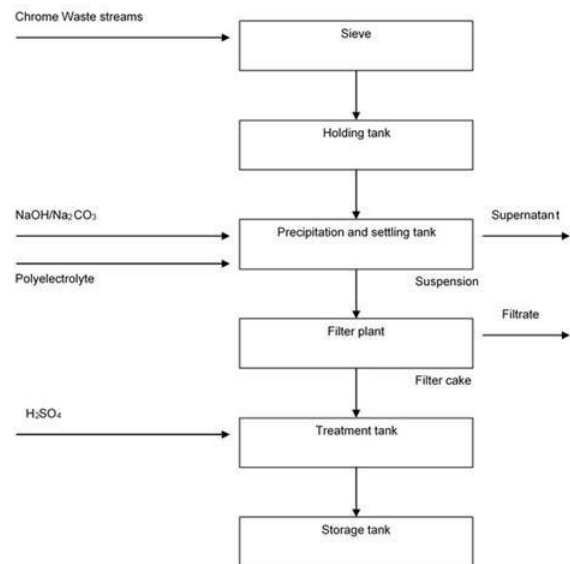


Figure 6: The NaOH precipitation of chrome recovery.

Cabeza *et al.* (1998) used precipitation with NaOH and filtration technique, showed in Figure 7, to recover purified Chromium from the chrome cake they obtained. The disadvantages are that a long settling time is needed, the filtration is difficult (Kowalski, 1994) and a large amount of sludge is produced (Chakir, 2001).

- Calcium hydroxide (Nacheva *et al.*, 2003) and calcium carbonate (Chakir, 2001) are also used. The technique (Figure 2) allows obtaining a Cr-recovery of 99% with $Ca(OH)_2$ (Panswad *et al.*, 2001). But a long settling time is needed, the filtration is difficult (Kowalski, 1994) and a large amount of sludge is produced.

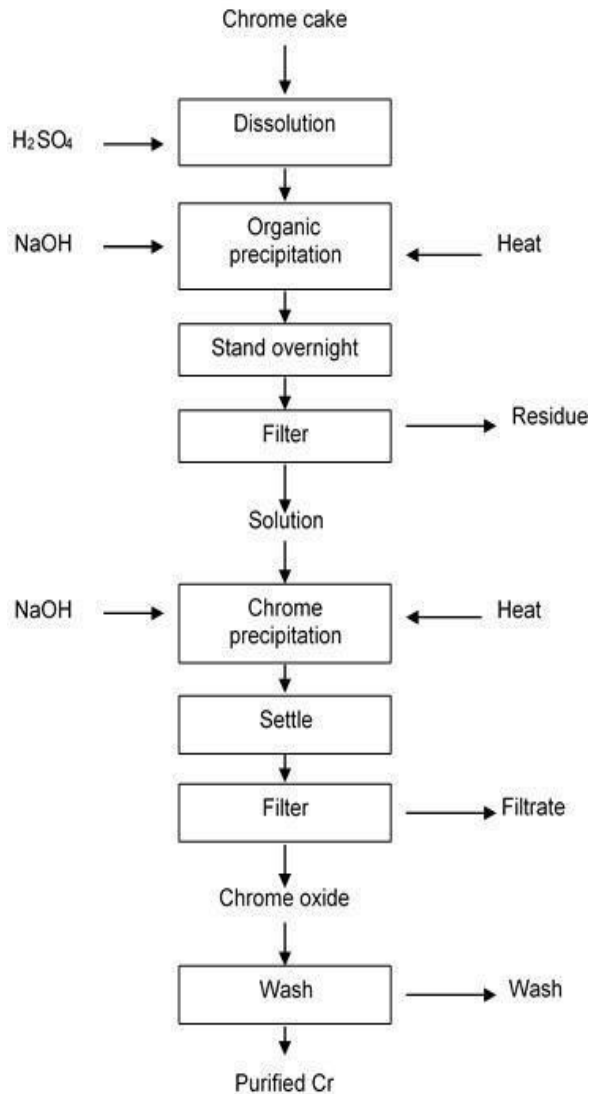


Figure 7: Chrome cake purification procedure.

Binary extraction/Electrodeposition

Oximes, amines (with high molecular weight) and alkylphosphorus compounds are the usual extractants but they suffer from poor selectivity or extractant loss (Gupta *et al.*, 2002). Cyanex 301 has been used for Cr(III) extraction, which is reported to be difficult (Ritcey and Ashbrook 1979). Khwaja *et al.* (2000) explored Cyanex 301 for separation of Cr(III) from other associated metals Figure 8 (Which follows figure 5) presents the SCL treatment. However, the major drawback of this chemical is its foul smell, even diluted (Gupta *et al.*, 2002). Pandey *et al.* (1996) compared Cyanex 272 with other extractants. Gupta *et al.* (2002) studied Cr(III) and Ni (II) recovery: after MgO precipitation and H₂SO₄ dissolution they used Cyanex 923 for extraction and separation from other metal ions (Al(III), Fe(III), Mn(II), Co(II), Cu(III), Zn(II), Pb(II)). The purification step is based on electrodeposition.

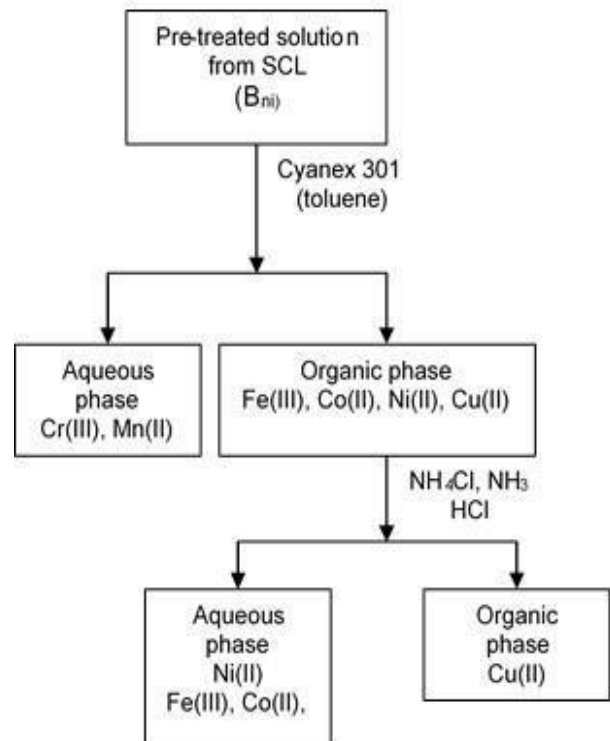


Figure 8: Flow sheet for SCL waste solutions purification using Cyanex 301 (Toluene).

Ion exchange

Ion exchange is considered a very effective pre-treatment for liquid tannery wastes (Loizidou *et al.*, 1969; O'Dwyer and Hodnett, 1995; Kocaoba and Akcin, 2002). Cr(III) can be removed as an ion pair as of perchlorate mixture by TBP (Agett and Udy, 1970); di-2-ethylhexyl phosphonic acid (Rice, 1983) or theonyl trifluoro acetone (TTA) (Ave *et al.*, 1971), but those extractions are low. Chaudry *et al.* (1997) proposed the following supported membrane technique, a unit process with simultaneous extraction and stripping steps: the extractant is supported in a microporous hydrophobic film Cassano *et al.* (1997) worked on a precipitation of chromium by a membrane derived with pressure and to remove chromium at a higher rate before tannery waste release. The salt removal by the neutralization process developed by Rao *et al.* reduces the sodium chloride and sulfate concentrations. The electro dialysis techniques like AMV and CMV also offers the neutralization process without any problem in process control. Tiravanti *et al.* (1997) developed the IERECHROM process (Ion Exchange Recovery of CHROMium). In which, the weak microporous electrolytes having carboxylate resins are used for the metal removal with other non-specific metals. They used fewer chemicals and decrease of sludge production by 80%, leading to lower cost for its treatment and disposal. Figures 9 and 10 describe the configuration of waste treatment without and with IERECHROM process.

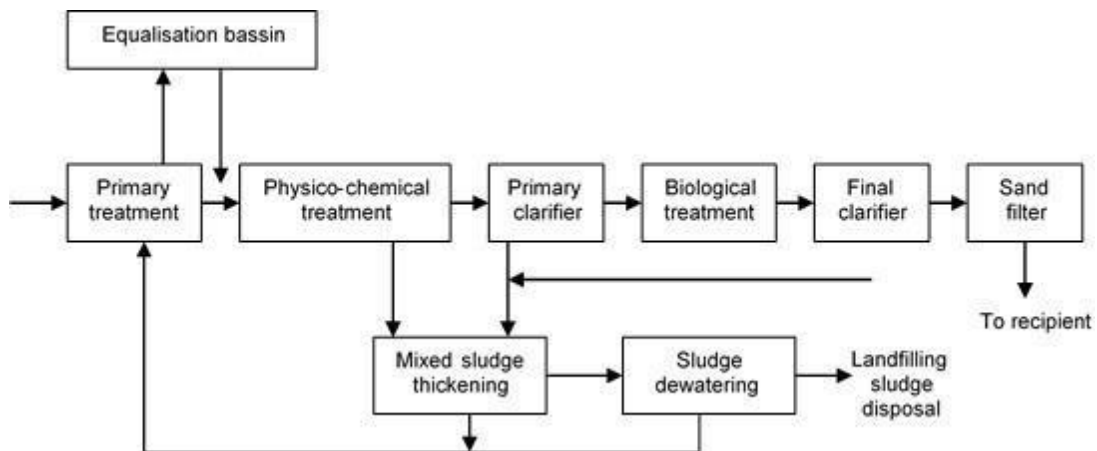


Figure 9: Flow diagram of a conventional tannery wastewater treatment plant configuration

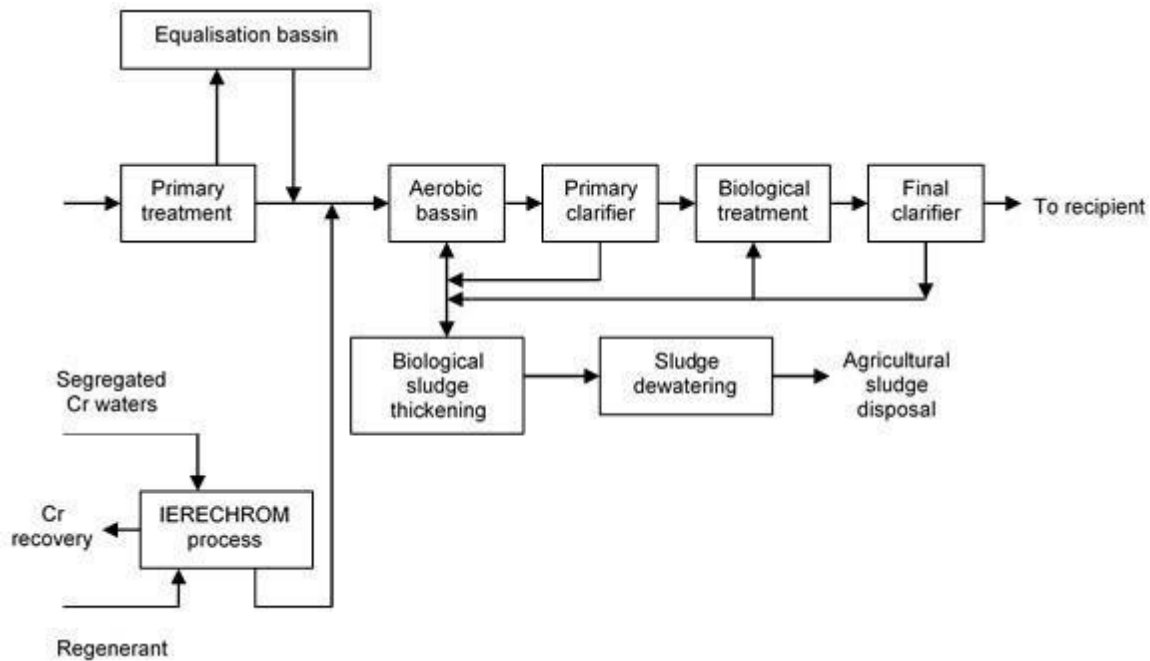


Figure 10: Flow diagram of the advanced treatment including the recovery of metal by IERECHROM process.

Kocaoba and Akcin (2002) compared carboxylic resins because they offer a slow rate kinetics of absorption and high rate of the apparent capacity (Petruzzelli *et al.*, 1995; Pasullean *et al.*, 1995). Exchange resins are categorized as Amberlite IRC 76 and 718 (weakly acidic exchange resins) and Amberlite IR 120 strongly acidic exchange resins) were studied. Further studies were done on IRC 718 and kinetic of Chromium (Kocaoba, and Akcin, 2003). Chanda and Rempel (Chanda and Rempel, 1997) studied Cr removal from binary mixtures with other metals, using poly(ethyleneimine) as a chelating resin to prepare a gel-type granular sorbent. They compared this templated gel-filling process with a commercial resin Chelex-100; a high selectivity of Cr(III) in

the presence of Ni(II) was observed and NaCl and Na₂SO₄ enhanced the sorption. A lot of works (Hayashi, 1974; Pocięcha, 1974; Gorensson and Moberg, 1975; Tahir *et al.*, 1998; Dahbi *et al.*, 2002; Kocaoba, and Akcin, 2003) have been done on ion exchange treatment for Cr wastes, however, these techniques require high capitals and operational costs.

Other methods

Polymers use

Anionic polymers are used as flocculant because they agglomerate iron and Chromium into large size particles for precipitation (Calvin *et al.*, 1981; Nojiri *et al.*, 1989; Pathe *et al.*, 1996).

● Leaching/Electro-winning

Vegliò et al. (2003) worked on the recovery of Cu, Ni, Mn, Pb, Sn, and W from electronic waste along with galvanic wastes produced from leaching and electro-winning process; this could be applied to Cr-recovery in tannery wastes.

Adsorption

Chemicalsorbents

Kowalski (1994) focused his work on high concentration of organic compounds that disturb Cr(III) removal from tannery wastes. Based on the precipitation/filtration method, he highlighted the fact that Cr(OH)₃ sedimentation and

filtration in wastewater are practically impossible after Ca(OH)₂ or NaOH treatment. Even flocculents, like polyacrylamides, starch, surface-active agents or FeCl₃, were without effect. Al(SO₄)₃ showed some efficiency but only after several dilutions of the wastewater. Kowalski (1994) directly mixed cement and wastewater and used the process described in Figure 11; good sedimentation and filtration were observed and the process has been developed in tanneries.

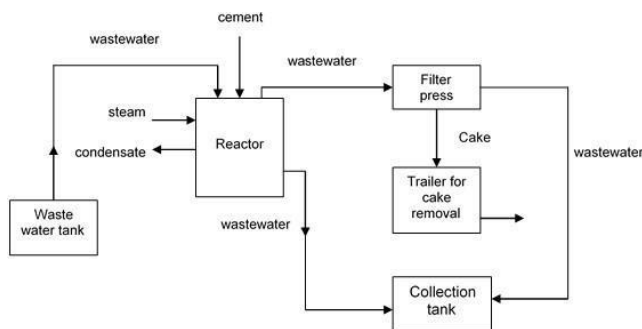


Figure 11: Flow diagram of the treatment plant of wastewater containing Chromium

Biochemical sorbents

Chitosan (Kowalski, 1994) (from seafood processing wastes) and xanthate (Masri *et al.*, 1974) (easy and cheap to prepare or from xanthated sawdust (Bricka and Hill, xxx) are suggested for Cr(III) sorption in Bailey's review (1999) on low-cost sorbents for heavy metals. Biopolymers have also been proposed for Cr(III) adsorption (Bailey *et al.*, 1999); Teixeira and Araújo, 1996) used alginate gel beads for Cr removal from aqueous tannery solutions. Pandey *et al.* (2003) proposed the use of humic acid containing calcium alginate (HACA) beads as an additional and more effective detoxification step to the lime sulphuric acid process (of tannery wastes treatment. The non-toxic reduction of the chromium by HACA beads is selective and efficient sorption technique. (Skogerboe and Wilson, 1981; Singaram, 1994; Elovitz and Fish, 1995 Appel and Torma, 1993; Wittbrodt and Palmer, 1995). The process consists in tannery effluent passing through a chromatography column and keeping in contact during 24 hours; two columns were compared, one

with CA beads and the other with HACA beads; the second one removed 54% of Cr (against 39% for the first one). The author considers the use of CA beads along with HA in continuous fixed bed columns, as a promising technique. Eromosele and Bayero (2000) suggested cellulosic graft copolymers for Chromium adsorption from the aqueous waste.

Biological sorbents

- **Activated carbon:** (Grases, 1972; Urbini, 1974; Divet, 1974; Adrian and Hodges, 1973; Landringan and Hallowell, 1975; Huang, 1975; Toledo *et al.*, 1994; Ramos *et al.*, 1994, 1995; Morozova, 1995; Eromosele

and Bayero, 2000): It has been the most popular adsorbent in wastewater treatment (Babel *et al.*, 2003). Polishing a method of using activated carbon and ion-exchange resins (Alves *et al.*, 1993). The oxidized granular activated carbon (GAC) is an efficient Cr³⁺ sorbent because of the attractive interaction between its large negatively charged surface and the positive metal ion charge (Park and Jung, 2001). But activated carbon remains an expensive material compared to a large number of other sorbents (Alves *et al.*, 1993; Dahbi *et al.*, 2002; Babel and Kurniawan, 2003).

- **Bone charcoal:** It is obtained from the calcination of bovine bones in the absence of air. Dahbi *et al.* (2002) studied its Cr (III) adsorption capacity in an aqueous solution similar to Moroccan tannery effluents. They reached an efficiency superior to 90% and suggested HCl and NaOH treatment to increase Cr retention. Bone charcoal is also a good Cr(VI) sorbent.
- **Clay:** Bentonite (Park and Jung, 2001) adsorbs chromium instantaneously, and its efficiency increases with pH. Kaolinite and montmorillonite clay minerals Cr(III) sorption are really pH dependent (Griffin *et al.*, 1997). Natural zeolite clinoptilolite has a quick and efficient ion exchange process with Cr(III) (Loizidou *et al.*, 1962). Chakir (2001) proposed expanded perlite as Cr(III) sorbent for tannery effluents (perlite is an inert volcanic rock, containing 70% of silica, which expands when it is quickly heated): it removed 40% of Cr(III) when bentonite removed 96% and more rapidly. Wallastonite-fly ash was also studied (Panday *et al.*, 1984).
- δ -Al₂O₃ and γ -Al₂O₃ (Wherli *et al.* 1990; Chang *et al.* 1994): it is a two-step process for Cr(III) adsorption. With δ -Al₂O₃, after adsorption of the ions, there is the loss of an H₂O molecule from the metal centers of the adsorbate ions. With γ -Al₂O₃, H⁺ is released from the surface hydroxyl groups SOH and Cr(III) is attached to the protonated site of the surface complex.
- **Fungi:** Fungi are well studied for metal sorption ability (Tobin *et al.*, 1990; Gadd, 1993). Tobin and Roux (1997) have compared *Mucor meihi* biomass to ion exchange resins for a tannery effluent treatment. They observed a very good removal capacity, which increases with the

Cr-concentration (it may be due to the complex adsorption process involving multiple types of binding (Gadd and de Rome, 1988; Brady and Tobin, 1995). They also related the high efficiency of a resin. Mucorales are an example of high chitin and chitosan containing substances with amino groups attached, and they suggested that the amine groups contribute to the uptake level of the biomass. One drawback is that the basic-acid desorption treatment damages the biomass.

- **Living biomass:** The biomass of cells is highly used as adsorbent because of larger surface area. Dead cell biomass or lyophilized inactive biomass are also considered for it (Chong and Volesky, 1996, Vegliò and Beolchini, 1997) and live cells biomass has less adsorption capability for metals (Jewell, 1994). Some bacteria like *Streptomyces noursei* (Mattuschka and Straube, 1993) and the *Halimeda opuntia* as alga (Volesky, 1992) were specifically investigated for the Cr removal. The bacterium *Sphaerotilus natans* (Lodi *et al.* 1998; Solisio *et al.*, 2000) showed the higher removal rate at low pH i.e. 3.5-4.0. *Pinus Sylvestris* bark: Some researches have used the bark of numerous pine classes (Randall *et al.*, 1974; Randall *et al.*, 1976; Vasconcelos, 1989, 1990; Castanheira and Durão, 1990; Deshkar *et al.*, 1990) for heavy metals contaminated waters. Alves *et al.* (1993) focused their work on *Pinus Sylvestris* bark for tannery wastewater chromium removal. The efficiency of the Cr removal increased with the use of alkali and the passing of air additions.
- **Other natural sorbents:** Lee *et al.* (1995) used naturally as well as copper coated moss columns for aqueous solutions. Various peat (Coupa and Lalancette, 1976; Wolfgang, 1980; Gosset *et al.*, 1986; d'Avila *et al.* 1989; Bulewicz *et al.* 1997) and sphagnum moss peat (Henke *et al.*, 1989) have been studied for metals and Cr-removal. Other natural sorbents are peanut shells, skin, rice husk, straw, and walnut cover (Smith *et al.*, 1977), coconut husk (Sharma and Forster, 1993), fly ashes (Friedman and Waiss, 1972; Panday *et al.*, 1984; Tan *et al.*, 1993) and coal ash (Masaru and Hideo, 1997). Flowing plasma gas was also used for the Cr conversion (Grover and Narayanswami, 1982).
- **Industrial wastes:** Recently, they have been studied with great interest in heavy metal polluted effluents (Lister and Line, 2001; Babel and Kurniawan, 2003; Selvaraj *et al.*, 2003) (because of the economic and ecological advantages). Biogas residual slurry (BRS) removed 78% of Cr(III) of tannery effluents (Namasivayam and Yamuna, 1999). Fe(III)/Cr(III) hydroxide wastes were also used to treat Cr containing wastewater (Namasivayam and Yamuna, 1994).

Biological methods

Bioleaching

An alternative to the common chemical extraction, a large amount of sulfuric acid (Shen *et al.*, 2006) is used, termed bioleaching. This process has been mainly studied with sulfur-oxidizing bacteria (SOB) (Tyagi *et al.*, 1988; Tyagi *et al.*, 1993; Tyagi *et al.*, 1996, 1997; Blais *et al.*, 1992a). Tyagi *et al.* (1988) highlighted for reducing the cost by 80% than chemicals way. Moreover this process is able to carry out simultaneous sludge digestion and metal leaching (Blais *et al.*, 1992a).

Shen *et al.* (2002, 2003) applied the microbial leaching for Cr solubilization and also studied by the use of indigenously grown (Jain and Tyagi, 1992).

Digestion

The aim of digestion is to remove the BOD (Biochemical Oxygen Demand) of the effluents. There are two types of digestions processed, the aerobic (Ram *et al.*, 1999) and the anaerobic (Vijayaraghavan and Murthy, 1997; Abdel-Shafy *et al.*, 1997). The wastewater quality is improved while the Chromium and other metals are concentrated in the resultant sludge.

Bioremediation

The process consists of: the effluents are aerobically biodegraded by indigenous bacteria (yeast and *Pseudomonas*); after a manual filtration, the effluent is dehydrated; the liquid phase is filtrated (Mediaflex) and sent to sludge storing tanks and the solid phase is solidified for elimination (Serrener consultation inc., 1994).

Flotation

Ghazy and Moustafa (Ghazy and Moustafa, 2001) studied the flotation-separation by using PAC (power activated charcoal) and oleic acid as adsorbents. They concluded that it is very cost-effective method than the commonly used ones for the removal of metals (Kobayashi *et al.*, 1975; Hiraide and Mizuike, 1975; Mizuike and Hiraide, 1982; Wilson and Clarke, 1983; Sonawane *et al.*, 1983; Mizuike, 1983; Huang *et al.*, 1988; Zouboulis *et al.*, 1995; Lazaridis *et al.*, 2001). It could be noted that PAC has a large surface area and distributes more easily and uniformly in water but it is difficult to separate it from suspensions for its reuse.

Other methods

● Direct recycling of Chrome liquors

The direct recycling of the chrome liquor with the fresh liquor is the easiest method (Ram *et al.*, 1999). The spent liquor is reconstituted by addition of acid masking agent and salt. The reconstituted spent liquors have been used for lowering the total chrome concentration. Sometimes the base is also added as constituents. (Ohsugi and Thorstensen, 1970; National Research Council of Canada, 1976). This recovered spent chrome liquor is again treated with acid to prevent chrome staining. (Davis and Scroggie, 1980). It is very easy to combine a tannery Cr-recovering process already used with direct recycling (Figure 12 (Davis and Scroggie, 1980). Undiluted spent chrome liquor is advised for greatest savings in salt use and recommended for the small tanneries (European Commission Directorate-General Jrc Joint Research Centre, 2001).

Figure 12 also showed the total recycling of Chrome and salts liquors (Cranston *et al.*, 1999).

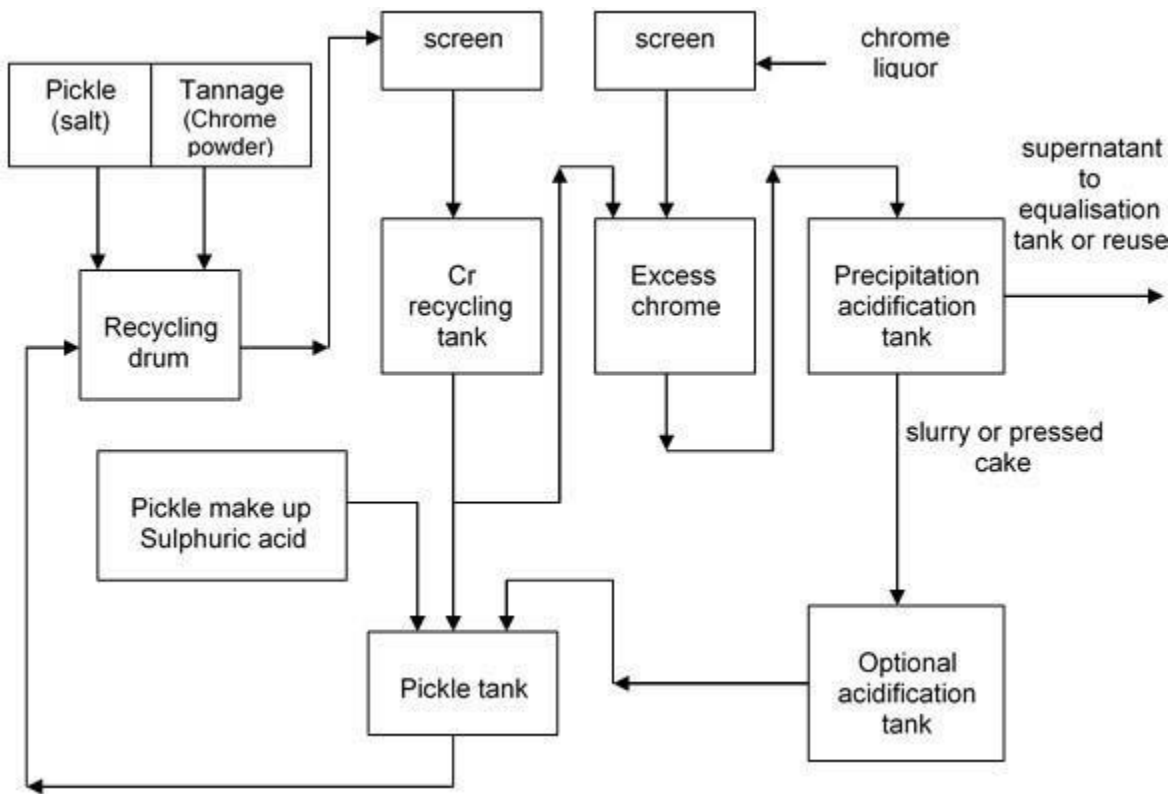


Figure 12. Direct chrome reuse and recycling process (<http://www.tft.csiro.au>)

Figure 13 showed the process of total recycling of chrome, in which chromium is collected first in clarifier1, then to flash evaporator to clarifier2 for salts precipitation and then concentrated second clarified chrome liquid is used for tanning process again.

● **Sedimentation**

It is a possible pre-treatment and for example, Song *et al.* used a settling column to clean tannery wastewater. They observed, in water, TSS removal and a reduction of COD, BOD, and Cr., which was concentrated in the residual sludge. Modrogan et al (2003) also used sedimentation after equalization and homogenization in a settler.

● **Semi-continuous method (adapted from Sreeram *et al.*, 2000)**

Figure 14 shows a schematic of the reactor set-up. The Cr (III) solution and alkali are pumped into the neutralization tank with hydrostatic pressure applied. The mixture is filtered and passed to settle and separated to obtain a precipitate.

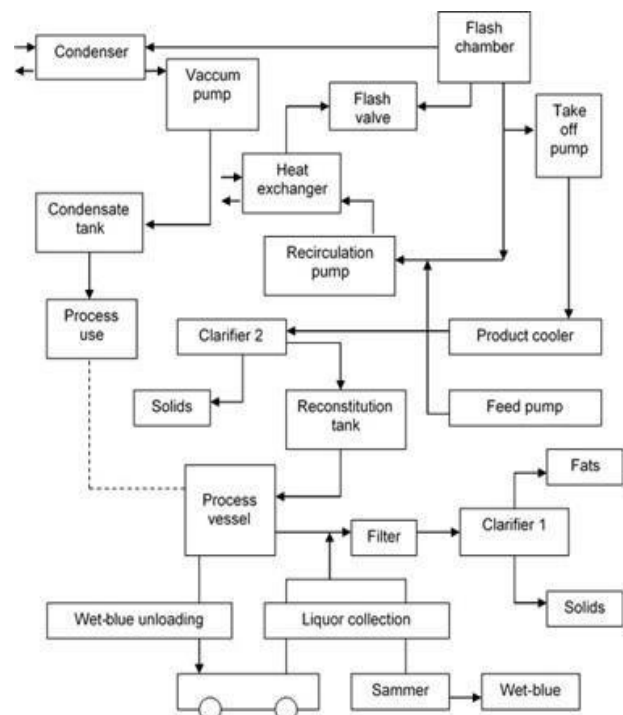


Figure 13: Schematic representation of the flow of the chrome removal and recycle in clarifiers

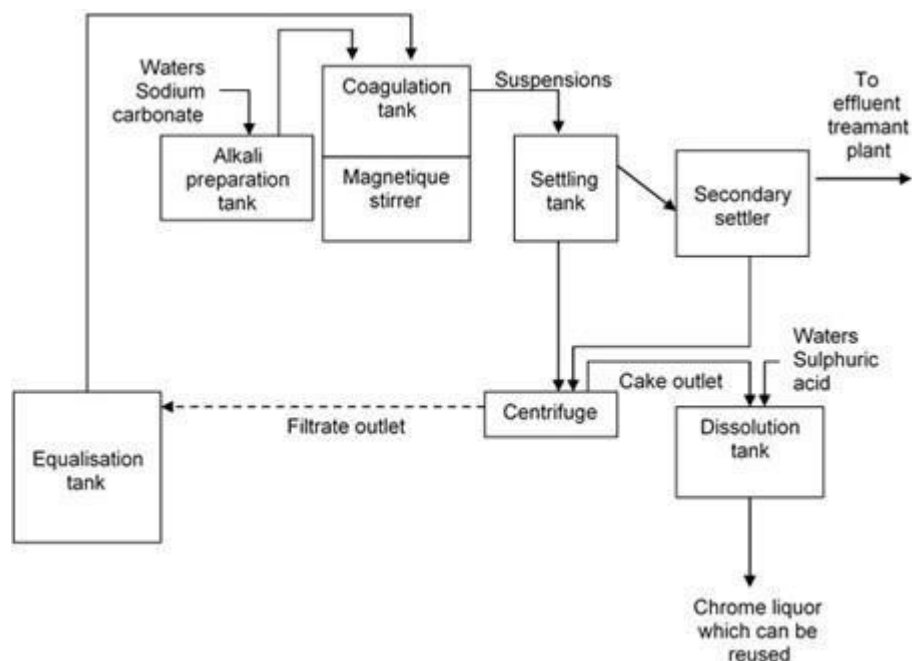


Figure 14. A semi-continuous Chromium (III) hydroxide recovery plant.

Conclusions and Future Outlook

Chromium is the major metal component found in the tannery waste. For the removal and simultaneous recovery of the chromium for its safe use and disposal, various methods and techniques have been discussed here in this review. These advanced technologies also helped in the reduction of its quantity spread in out streams which is the main causes of the health-related problems for the tannery workers. Various processes exist for the treatment of Cr (III) laden wastewaters, which include, physical, and biological treatment processes. Out of the processes cited, bioleaching has gained immense importance as Cr (III) can be precipitated as hydroxide and is not assimilated by cells. Despite tremendous leaps in the Cr (III) removal, there are many vital points to be considered, especially with respect to re-compartmentalization of pollutants which might require hybrid or sequential treatment processes, example, physical followed by biological treatment.

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