



PRETREATMENT OF TANNERY WASTEWATERS BY AN ION EXCHANGE PROCESS FOR Cr(III) REMOVAL AND RECOVERY

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ABSTRACT

Conventional treatment of tannery wastewaters includes the physico-chemical treatment in order to precipitate metals (mostly Cr(III)). The landfilling disposal of mixed physico-chemical and biological tannery sludges is an economical and environmental problem, due to the saturation of possible sites.

A new process, namely, IERECHROM® (Ion Exchange REcovery of CHROMium), has been developed for removal, recovery and reuse of Cr(III) ionic complex from segregated tannery wastewaters. The process is based on the use of a weak electrolyte macroporous carboxylate resin, retaining the metal of reference together with other trace metals, including aluminum and iron.

A 10 m³/d fully automated pilot plant was assembled and a demonstration campaign was carried out at a medium size Italian tannery by using the IERECHROM process. The adoption of the IERECHROM process simplified the tannery wastewater treatment lay-out as the physico-chemical treatment was not necessary. A considerable decrease in the use of chemical compounds, a sludge production reduced by 80% with respect to the traditional treatment, and lower costs for sludge treatment and disposal were demonstrated. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Tannery; ion exchange; carboxylic resin; chromium; heavy metals; pilot plant; physico-chemical process; wastewater treatment.

INTRODUCTION

Current technologies are quite satisfactory in terms of purging tannery wastewaters from chromium and other heavy metals, but they systematically produce solid residues (sludges) containing toxic compounds whose final disposal is generally controlled landfilling with related high costs. Tanneries are among those industrial activities mostly blamed for the environmental impact: about 50% of the incoming chemicals (essentially Cr(III) salts) are disposed of as wastewaters or sludges from treatment operations. Italy holds, together with the United States, Russia and former Soviet Republics, the world leading production of leather. About 280,000 tons of Cr(III) containing (1-4% Cr) dry sludges (Simoncini and Ummarino, 1988) are annually produced by tanneries in Italy.

Chromium toxicity to mammals and aquatic organisms appears to be lower compared to other heavy metals, due to the general low solubility of Cr(III) compounds (Moore and Ramamoorthy, 1984; Adriano, 1984; Ciavatta *et al.*, 1992), low mobility in the environmental compartments and limited availability to living organisms. However, the possibility that organic ligands and/or acidic conditions in the environment increase Cr(III) mobility, that MnO₂ oxides, present in soils, favor the oxidation of Cr(III) to the more toxic and mobile Cr(VI) forms (Nakayama *et al.*, 1981; Heary and Ray, 1987), cannot be excluded. Accordingly, the practice of land application of tannery sludges for soil conditioning or soil manure must be discouraged. On the other hand landfilling operations must also be discouraged, in consideration of the progressive saturation of the sites. A new ion exchange process for selective removal, recovery and reuse of chromium was set-up and developed (Tiravanti *et al.*, 1994), with the aim of considerably decreasing the amounts of tannery sludges wasted into the environment. The process deals with the "segregated" streams of spent tannery baths and related leather washing waters. Fundamental aspects, together with applicative details of the process design, optimization and development at pilot scale level, to demonstrate process reliability and cost effectiveness, are illustrated in the paper.

MATERIALS AND METHODS

Table 1 shows the average composition of the spent tanning bath and the "segregated wastewaters" (spent baths diluted with leather washing waters).

Table 1. Average composition of spent tanning baths and segregated wastewaters*

	Spent tanning bath (mg/l)	Segregated wastewater (mg/l)
Cr(III)	3,500-4,000	100-1,600
Al(III)	80-150	2-60
Fe(III)	40-100	2-10
Ca ²⁺		100-300
Mg ²⁺		50-100
SO ₄ ⁻	10,000-12,000	300-600
NaCl	50,000-60,000	1,000-2,000
TOC (as CH ₃ COOH)	1,200-1,800	80-200
pH	2.5-3.5	3.5-3.8

* Exhausted tanning baths diluted with leather washing waters

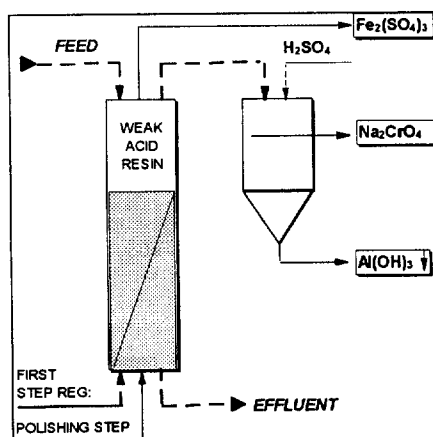


Figure 1. Conceptual lay-out of the IERECHROM process for selective separation and recovery of Cr(III) from segregated tannery wastewaters.

Weak and strong electrolyte, i.e., sulphonic and carboxyl resins, were tested in the laboratory. The resin finally used was the macroporous carboxyl resin Purolite C106, which was the more efficient and potentially more resistant to fouling from soluble organic substrates (proteins, long chain fatty acids, surfactants) present in tannery effluents, and more resistant to the mechanical breakage of the resin beads as well (Skriba and Kunin, 1988).

Preliminary experiments showed that exchange kinetics of Cr(III) species in solution were relatively slow. For this reason exhaustion of the resin column was carried out at flowrates of 4 BV/h. Among different regeneration protocols for the exhausted resins adopted throughout the experiments, (elution with acidic, basic solutions, alone or sequentially or with reverse procedure) the best results were obtained with elution of alkaline $\text{H}_2\text{O}_2/\text{NaOH}$ solutions, followed by polishing of the resin with 1M H_2SO_4 . Figure 1 shows the lay-out of the process.

A 10 m³/d pilot plant (operative total retention capacity of 1.75 kg Cr/cycle) was designed and assembled to demonstrate process reliability on a larger scale, thanks to the financial support of the Italian Leather Authority (UNIC) and of the Italian Ministry of Environment. The plant is made of two ion exchange columns containing 100 l of resin each; two precipitators for Cr, Al, Fe hydroxide separation and recovery; two filters; one degasser and several service reservoirs for feeding, product, and regenerant solutions. It operates on segregated wastewaters of tannery industry, including spent tanning baths and leather washing waters. The detoxified effluent (average Cr concentration: <2 mg/l, below the maximum allowable limit for Italian legislation) is sent to the wastewater treatment installation.

The resin was regenerated in a closed loop system through which the metals were separated and recycled. In a first regeneration step hydrogen peroxide 0.15 M in sodium chloride 0.5 M (for additional savings) and sufficient alkalinity (NaOH 0.5 M) to pH 12 was used (15 BV + 15 BV recycled) to elute chromium and aluminum from the resin, after oxidation to chromates and hydrolysis to aluminate, respectively. In a final polishing step of the resin ferric species were eluted by using 1M H_2SO_4 (5BV); the resulting ferric sulfate solution was reused as a flocculating agent. Aluminate species were separated from chromate by $\text{Al}(\text{OH})_3$ precipitation. After filtration, the precipitate was redissolved with H_2SO_4 and reused in the general wastewater treatment plants as a flocculating agent. The residual Cr(VI) solution was directly reused in the tannery industry, after reduction to Cr(III) with sodium sulfite in acidic media. Furthermore, a more concentrated solution was obtained by Cr(OH)₃ precipitation and recycling. Before the new exhaustion step, the resin was reactivated by elution of 1M NaOH followed by hydrolysis with softened water.

The mobile plant was assembled on a trailer, to carry out demonstration campaigns at several tannery installations. During the tests, analytical controls were performed to all units. In particular, total metal concentrations in the liquid-phase were determined by AA spectrophotometry on a Mod.1100B from Perkin Elmer or by Inductively Coupled Plasma emission (ICP) spectrometry using a Mod.40 Plasma System, also from Perkin Elmer. All the other parameters were analyzed according to Standard Methods (1993).

RESULTS AND DISCUSSION

Exhaustion behavior of the resin

Strong electrolyte sulphonic resins showed poor performances toward chromium removal from tanning wastewaters; accordingly they were soon replaced by carboxylic resins.

Exhaustion of the carboxylic resin was run on partially hydrolysed H/Na-form at controlled pH conditions (pH 8.5-9). Reference pH range is sufficiently high to avoid hydrolysis and inactivation of the functional groups toward chromium species, but sufficiently low to avoid precipitation of metal hydroxides onto the resin beads. Hydrolysis of the carboxylate groups was controlled by washing the Na-form resin with softened water (30 BV).

Figure 2 shows the exhaustion/regeneration breakthrough curves for resin Purolite C106 in reference to the segregated wastewater reported in Table 1.

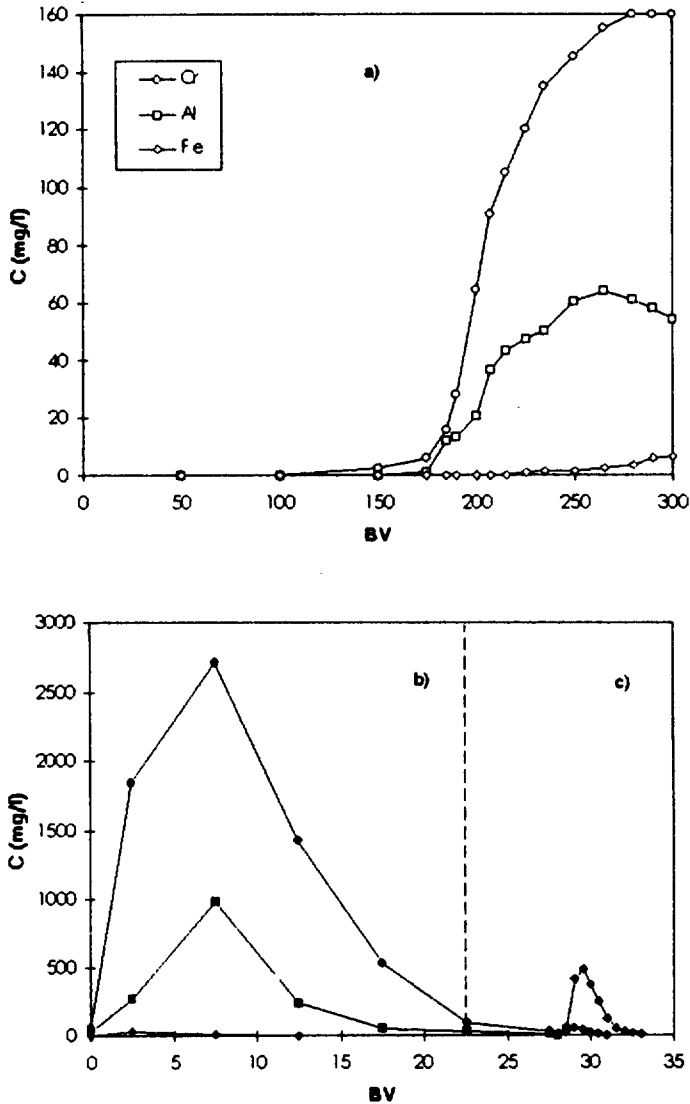


Figure 2. Typical breakthrough curves for the carboxyl resin Purolite C-106 with reference to the Cr(III)/Al(III)/Fe(III) system in the segregated tannery wastewaters. (a) Exhaustion; (b) First step (upflow) regeneration with hydrogen peroxide in alkaline media; (c) second step (downflow) regeneration with sulfuric acid 1 M. Initial Cr concentration = 160 mg/l; T = 20°C; pH = 3.5.

The metals retention is attributed to the strong interactions with carboxylate groups, via mechanisms other than ion exchange, such as covalent bonding through stable carboxy-metal complexes, as indeed reported in the literature for ferric ions (Chanda *et al.*, 1988). As a consequence of the affinity of carboxylate groups for ferric species the retained aluminum is "rolled up" by ferric ions (see Fig. 2).

Table 2 reports the operative exchange capacities for Cr and Al at the respective breakthrough, whereas only partial data is given for iron having not reached complete exhaustion of the resin during the experiments.

Table 2. Operative exchange capacities of resin Purolite C106. Operative exchange capacity (mol/Lr)

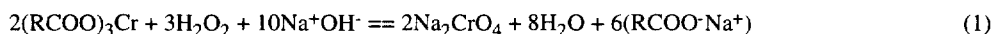
H-Cycle	Cr(III)	Fe(III)	Al(III)
3.36	1.05	0.03*	0.2

* Refers to the ferric ions actually retained by the resin at the chromium and aluminium breakthrough (Fig. 2)

Regeneration behavior of the resin

In situ oxidation of the Cr(III) species to chromate was investigated by using hydrogen peroxide in alkaline (pH 12) media. The hypothesis was that chromate ions formed, as anionic species, would be rejected by the functional groups, by the Donnan effect (Helfferich, 1962).

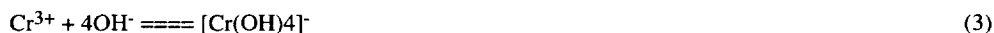
Quantitative regeneration was obtained (Petruzzelli, 1992) according to the oxidation reaction:



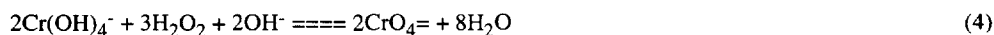
It is likely that the overall mechanism proceeds initially via the $\text{Cr}^{3+}/\text{Na}^+$ exchange reaction:



followed by hydrolysis of metallic ions in alkaline media:

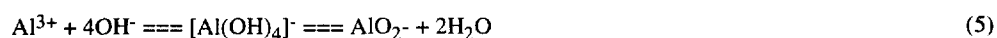


and subsequent oxidation reaction:



As hydrolysis and oxidation reactions proceed, they shift to the right the exchange reaction (2), thus favoring Cr elution. However, an outer shell of carboxylate groups is formed on the resin beads, thus hindering further migration of hydroxide ions in the solid phase by the Donnan effect. The overall reaction (1) proceeds at decreasing rates as hydroxide ions, necessary for the hydrolysis reaction (3) and oxidation reaction (4) are depleted at the solid-phase. Accordingly, long tailings in the regeneration curves were indeed observed (see Fig. 2).

In the proposed mechanism, sodium hydroxide plays various roles, i.e., as a counterion source for the ion exchange reaction (2), and as alkalinizing agent for the chromium hydrolysis reaction (3) and for the oxidation reaction (4). Sodium hydroxide plays a role even in the separation of metals from the spent regeneration eluates. In moderately alkaline media (i.e. $10 < \text{pH} < 12$) ferric species are not hydrolyzed and retained by the resin whereas aluminum is quantitatively co-eluted with chromates, due to the hydrolysis reaction to aluminate:



Final elution of ferric ions is then obtained by 1M H_2SO_4 solution as shown in Fig. 2. At the end of the regeneration, the resin is ready for the subsequent exhaustion step after reactivation with 1M NaOH, followed by hydrolysis with softened water.

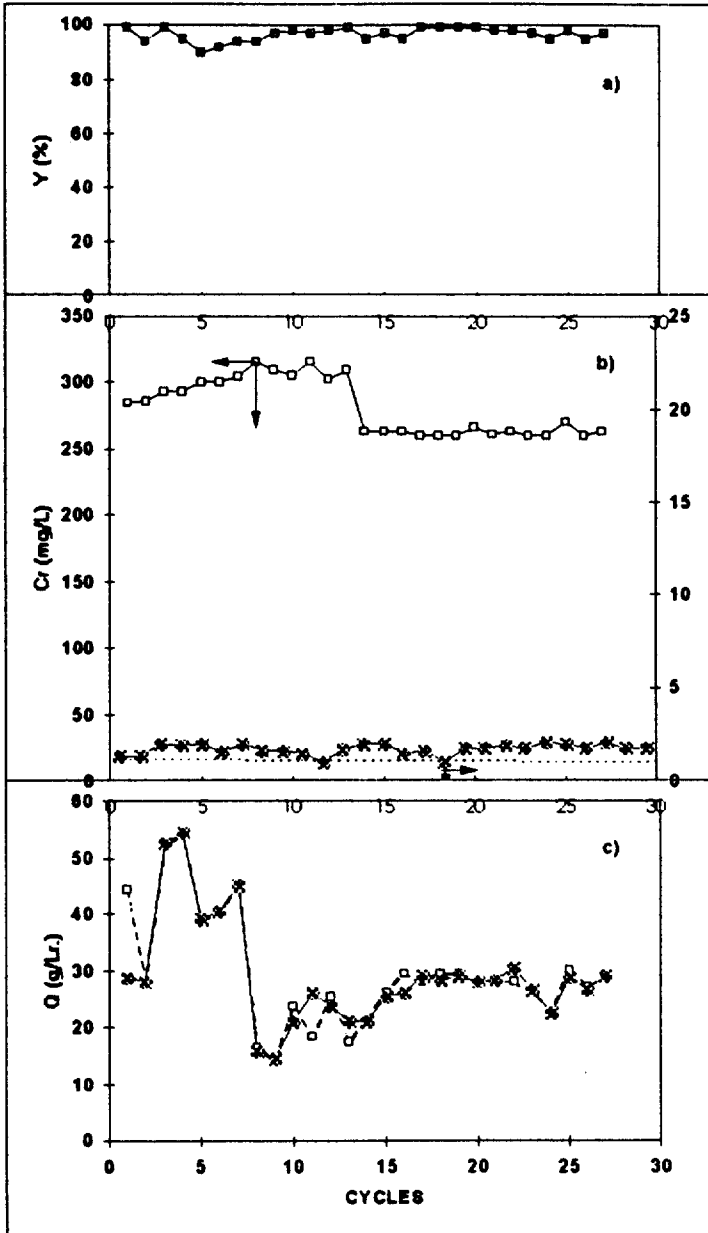


Figure 3. Typical cyclic performances of the 10 m³/d mobile plant fed with real segregated wastewaters from a tannery. (a) % of chromium removed; (b) average influent (□) and effluent (x) chromium concentration; (c) Exhaustion (□) and regeneration (x) capacities of the resin. MAC = Maximum Allowable Concentration for Italian legislation.

The IERECHROM process: field tests on pilot plant scale

Tests on the pilot plant have been operated for several months directly in medium size tanning industries in northern Italy and in France. During the tests, the operating conditions were varied by increasing the Cr

concentration of the segregated water to be treated, up to 1600 mg/l. The exhaustion times were changed while the regeneration times were maintained constant. The performances of the plant, in terms of exhaustion-regeneration curves, were similar to those obtained in the laboratory investigations. As an example, Fig. 3a shows the fractional chromium removal efficiencies, steadily above 98% (Cr initial concentration of 160 mg/l). Figure 3b shows the cyclic performances of the resin in terms of average influent and effluent chromium concentration; the effluent concentration results to be steadily below the maximum allowable concentration (MAC) for chromium discharge in waterbodies as enforced by the Italian legislation. Figure 3c shows the operative cyclic performances of the resin in terms of exhaustion-regeneration capacities, Q_{Cr} . The coincidence of the two superimposed lines, referring respectively to the exhaustion and the regeneration performances, confirm the absence of chromium accumulation in the resin phase and, most important, the capacities remain satisfactorily constant. Both findings indicate an acceptable resin stability under the drastic conditions imposed during regeneration. In this context, degradation of the resin under oxidative conditions was observed in the long run; this represents only an acceptable cost for the resin make-up without influencing the overall process reliability. Generally speaking process performances can be summarized as follows:

- 90% of the influent chromium, purified (>99.9%) from metals and organic compounds, is recovered as $\text{Cr}(\text{OH})_3$;
- Aluminum is recovered partially (37.5%) in the polishing step and the remaining (62.5%) precipitated in the various steps of the process as $\text{Al}(\text{OH})_3$;
- 93% of ferric species is recovered in the polishing step;
- 50% of organic compounds (TOC) remains in the effluent; the fraction retained by the resin is eluted during regeneration and coprecipitated with $\text{Al}(\text{OH})_3$.

Treatment of wastewaters when IERECHROM process is used

Experiments were carried out to demonstrate the advantages, if any, of the adoption of the IERECHROM process on the treatment of tannery wastewaters. The medium size tannery where field tests were carried out was equipped with a conventional wastewater treatment plant (wwtp) having a capacity of about 150 m³/d. The wwtp consisted of a primary treatment, a physico-chemical treatment for sulfide oxidation, metals precipitation and COD removal, a primary sedimentation, a biological (activated sludge) treatment, a final clarifier and effluent filtration. The flow diagram is shown in Fig. 4. The mixed (physico-chemical and biological) sludges were thickened, dewatered by belt press and disposed by controlled landfilling.

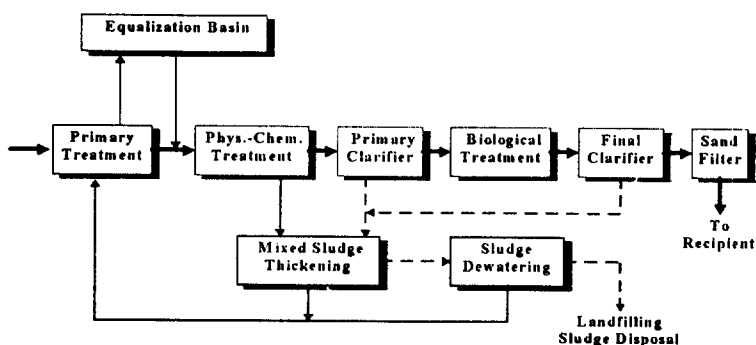


Figure 4. Flow diagram showing the configuration of a conventional tannery wastewater treatment plant.

The use of ion exchange which removes metals made the physico-chemical treatment unnecessary so that a different flow sheet was adopted. The chromium containing waters (spent baths and related washing waters,

10% of total, Cr initial concentration of 1600 mg/l) were segregated and treated by the IERECHROM process. The remaining waters (90% of total) and the treated effluent from ion exchange were sent to the wwtp (Fig. 5). In particular the physico-chemical treatment tank was converted into an aeration tank (250 m³) including the sulfide oxidation step. The pH was buffered at 7.5-8 and phosphates were added at the beginning to balance the demand of the biomass. After primary sedimentation the waters were then sent to the activated sludge treatment and to the final clarifier and sand filtration. The sludges in the aerobic basin and in the activated sludge tank were recirculated while the excess sludge was thickened, dewatered and sent to agriculture disposal.

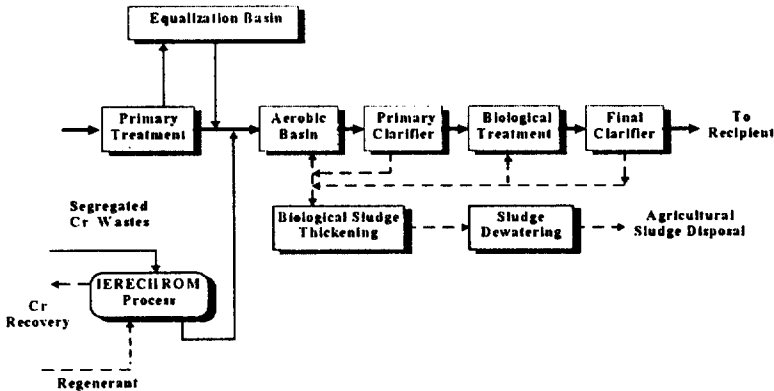


Figure 5. Flow diagram showing the configuration of the advanced treatment including recovery of metals by IERECHROM process.

Table 3. Summary of experimental average results obtained for the conventional and the advanced treatment process for tannery wastewaters

Parameter	Raw wastewater*	Conventional process (A)		Advanced process (B)	
		Phys-chem. process	Biological process	First aeration process	Biological process
pH	4-7	7.5-8	7-8	7.5-8	7-8
Suspended solids	400-600	90-140	30-40	180-240	60-90
COD	4000-6000	400-700	40-70	1200-2000	100-220
Chromium(A)	100-150	<1	N.D.		
Chromium(B)	<5			0.25-0.35	0.1-0.2
N-NH ₃	30-45	10-15	3-10	10-20	2-8
N-NO ₃		5-10	7-13	7-15	5-9
N-NO ₂		0.2-0.4	0.1-0.15	0.4-0.6	0.15-0.25
Non ionic surfactants	35-55	10-20	0.5-1.5	10-15	1-2
Anionic surfactants	1-2	0.5-1	0.15-0.3	0.5-0.8	0.15-0.3
Sulfite	<1	N.D.	N.D.	0.3-1.0	0-0.5

(A) Conventional process made of the following units: physico-chemical treatment, biological treatment, sludge dewatering and landfilling disposal (see Fig. 4)

(B) Advanced process made of the following units: pre-treatment with ion exchange for Cr recovery, oxidation process, biological treatment, sludge dewatering and agriculture sludge disposal (see Fig. 5)

* The raw wastewater is the same for the two plant configurations, with the exception of Cr containing wastes which, in the advanced process, are pre-treated by ion exchange for Cr recovery.

N.D. = not detectable

Table 3 reports a summary of the results obtained with the plant configuration of Fig. 5 during 3 months operation and, for comparison, all those previously obtained by treating waters with the conventional lay-out (Fig. 4).

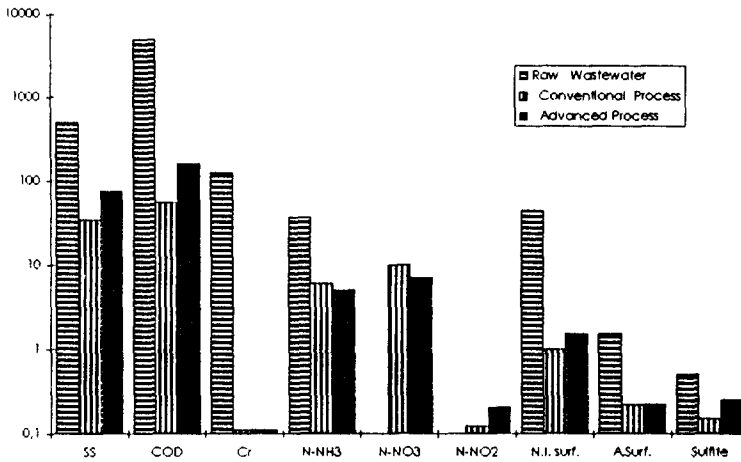


Figure 6. Concentrations of some parameters of the raw wastewater and of the final effluents from the conventional and advanced process.

Table 4. Comparative economic evaluation for the two studied flow diagrams (costs expressed as US\$/m³ of treated water)

Item	Conventional treatment	Advanced treatment with Cr recovery
Manpower	0.35	0.11
Chemicals	0.67	1.37
Sludge transport and disposal	1.18	0.26
Analytical monitoring	0.14	0.16
Amortization (10% in 10 years)	0.12	0.26
Maintenance	0.36	0.06
Electric energy	1.01	0.61
Taxes	0.14	0.14
TOTAL	3.95	2.97

The data, reported in Fig. 6, show that the overall removal efficiencies of the two configurations are almost the same. The final effluent concentrations were, in both cases, below the limits imposed by the current Italian legislation. As a conclusion, the following technical improvements for the advanced process were evidenced:

- no need for physico-chemical process and related consumption of chemicals;
- reduction of about 80% of the amounts of sludges produced having relatively low chromium concentration (< 0.1% d.w.) to be compared to 3-4% of the conventional plant;
- possibility for this low Cr content sludge to be used in agriculture;
- recovery of chromium directly to the tanning processes or for other uses.

A technical-economical evaluation for the two different schemes of the plant is reported in Table 4. The main costs of the conventional treatment, which are in the order of 2.5-3% of the total annual tannery budget, refer to (in increasing order) manpower, operation, chemicals and controlled landfilling sludge disposal costs, due to the presence of Cr. Looking at the advanced flow-sheet, the main economies are for manpower (0.11 vs 0.35 US \$/m³) electric energy (0.61 vs 1.0 \$/m³) and transport and sludge disposal (0.26 vs 1.18 \$/m³). As a conclusion, the final cost of the advanced process including investment costs is lower than the traditional one (2.97 vs 3.95 \$/m³), without taking into account the revenue due to chromium recovery and reuse. A proper economic analysis, however, cannot exclude the evaluation of the cost-benefits deriving from the avoidance of the impact related to minimized introduction of such toxic wastes into the environment, which would represent the key point of this technology.

CONCLUSIONS

The lack of knowledge of the geochemical behavior and fate of chromium in the environment limits the agricultural use of tannery sludges containing chromium. A practical alternative based on conservative ion exchange technology has been developed. The process deals with spent chromium tanning baths and related leather washing waters representing only 10% of the wastewater discharged from the productive lines. Segregation of the wastewaters is an important point for the process reliability in terms of metals recovery and reuse. The IERECHROM process is based on the use of a macroporous carboxylic resin, allowing for removal and separation of about almost pure (>99.9 %) chromium from other interfering metals and organic compounds for reuse.

During regeneration steps, chromium and aluminum are separated and the latter can be reused as coagulant in the general wastewater treatment plant. A final polishing step allows ferric sulfate to be recovered from the resin and reused as flocculating agent.

The application of IERECHROM technology to tanneries allows a drastic reduction in the amounts of chromium discharged into the environment. Experiments showed that about 90% of chromium actually discharged can be recovered. It has been calculated that, in Italy, about 1000 tons of chromium/year would be reused.

When this process is adopted, the tannery wastewater treatment station can eliminate the physico-chemical treatment step for metals removal, still obtaining the effluent concentrations below the limit imposed by Italian legislation. The sludges produced have less than 0.1% chromium content and are just 1/4th in volume of that of a corresponding conventional wwtp. Detoxified sludges can be used for soil conditioning or in the compost production or safely disposed in agriculture.

A technical-economical evaluation showed that the final costs of the water treatment, when recovery of Cr(III) is applied, are lower than the conventional one, without considering the revenue due to Cr recovery and reuse.

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