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Quantification of Pollution Discharges from Tannery Wastewater and Pollution Reduction by Pre-Treatment Station

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Abstract***: Leather tanning generates many complex and highly loaded effluents that require treatment before being discharged into receiving waters. Wastewater from tanneries usually contains high levels of salinity, organic and inorganic matter, dissolved and suspended solids, ammonia, organic nitrogen and specific pollutants (sulphide, chromium and other toxic metal salt residues). Wastewater characterization is an integral part of treatment and management strategies for industrial effluents. This paper outlines the results of detailed characterization of tannery wastewaters in Mohamedia city, Morocco. It evaluates aside from raw wastewater quality in terms of major polluting parameters, the effect of physical settling on wastewater characteristics and on heavy metal removal. The results showed that the COD and chromium were removed mainly through sedimentation: 83% removal of total COD with initial concentration of 27.6 mg/l, and 40-70% removal of total chromium from settled tannery wastewaters, at an initial concentration of 811.4 mg/1 and 223.7 mg/1 respectively. Other heavy metals were removed by the primary treatment (90% removal of total lead and 98% of total mercury at an initial concentration of 754 µg/l and 716 µg/l respectively).***

Keywords: Tannery Wastewaters, physical settling, Chromiu

1. Introduction

Industrial wastes are usually generated from different industrial processes. As a result the amount and toxicity of waste released from industrial activities varies with the industrial processes. Again, among all the industrial wastes tannery effluents are ranked among the highest pollutants [1]. Tanneries are one of the most prominent sources of chromium pollution to the aquatic environment. If not adequately treated, wastewater from tanneries contaminates surface water and sediments to a toxic level.

Tannery industry in Morocco is the significant contributor to the economy and provides large scale employment opportunity for people of economically weaker part of the society. In the factory of Mohammedia, the tanning operation in which organic or inorganic materials become more chemically bound to the available substance and preserve it from deterioration.

The main chemicals used include sodium sulphite and basic chromium sulphate including non-ionic wetting agents, bactericides, soda ash, CaO, ammonium sulphide, ammonium chloride and enzymes. Others chemicals are sodium bisulphate, sodium chlorite, NaCl, H2SO4, formic acid, sodium formate, sodium bicarbonate, vegetable tannins, syntans, resins, polyurethane, dyes, fat emulsions, pigments, binders, waxes, lacquers and formaldehyde. Various types of processes and finishing solvents and auxiliaries are also used [2]. It has been reported that only about 20% of the large number of chemicals used in the tanning process is absorbed by leather, the rest is released as waste as reported by Blacksmith Institute's [3]. The characteristics of tannery wastewaters vary considerably from tannery to other depending of its size, chemicals used for a specific process, amount of water used and type of final product produced by a tannery. Tannery effluents are characterized by high concentration of pollutants and a great variety of composition. There are considerable dissimilarities in the concentration range of pollutants in tannery wastewaters given by different authors [4]. The main inorganic pollutants are chloride, sulphate, ammonium ions, and sulfide ions... Moreover, the amount of organic pollutants is large-the COD value is usually several thousand mg/l of oxygen. Most of these pollutants are in soluble form, but a lot of them exist in suspension and only few are colloidal [5]. Heavy metal pollution, especially chromium pollution in wastewater sources from tannery has affected the life of many creatures on earth.

Chromium is an accidently occurring heavy metal that can exist in air, water, soil, and food, and common exposure pathways include ingestion, inhalation, and dermal contact. The primary health impacts from chromium are damage to the gastrointestinal, respiratory, and immunological systems, as well as reproductive and developmental problems. Chromium is a known human carcinogen. Its contribution to the pollution can affect all ecosystems and human health directly or through the food chain. Therefore, the determination of chromium in this study is of great importance since the effluents studied are discharged directly in sewerage without treatment. Example of this harm to the environment was in India, especially, Kanpur tannery industry, where in 2003 the main tanneries effluent disposal unit was dumping 22 tonnes slug of Chromium laden solid waste per day. In tannery industry, effluents are produced up to 64 kilo tonnes of wastewater per year [6]. These problems make the treatment of tannery wastewaters very difficult. Moreover, chemical and biological methods are considered to be very expensive in terms of energy and reagents consumption.

Treatment of various wastewaters is becoming more important due to the diminishing water resources, increasing wastewater disposal costs, and stricter discharge regulations that have lowered permissible contaminant levels in waste streams. Various treatments are used for tannery wastewater like physico-chemical methods such as sedimentation [7], électro floatation [8], coagulation floculation [9], filtration [10], and adsorption [11].

This work is concerned with the evaluation of the pollution caused by discharges from the tannery wastewaters in particular organic matter and metal pollution in effluent total and different stages of the process. The study also concerns the removal of organic and metallic element pollution by sedimentation.

2. Materials and Methods

2.1 Tanning (operations)

Two types of tanning operations based on tanning agents are chrome and vegetable tanning.

2.1.1 Vegetable Tanning

Vegetable tanning employs the use of extracts from the bark of various trees as the tanning agent. Since the introduction of chrome tanning, vegetable tanning has decreased in importance. Soles of shoes have been traditionally naturally tanned; however, since the introduction of synthetic materials for shoe soles, natural tanning has further decreased in importance. Natural tanning is also used to produce leather used in crafts. Many of the basic steps used in the chrome tanning process are also present in natural tanning. The sequence in which these steps are employed is somewhat different, and there are few finishing operations associated with natural tanning. The processing of hides prior to vegetable tanning begins with a soak in lime to loosen the hair. Tanning is essentially the reaction of collagen fibers in the hide with tannins, chromium, alum, or other chemical agents.

2.1.2 Chrome Tanning

After pickling, when the pH value is low, chromium (III) salts are added. To fixate the chromium, the pH is slowly increased through addition of a base. The process of chromium tanning is based on the cross-linkage of chromium ions with free carboxyl groups in the collagen. It makes the hide resistant Tanning involves a complex combination of mechanical and chemical processes. The general flow sheet for tanning process is given in Fig. (1).

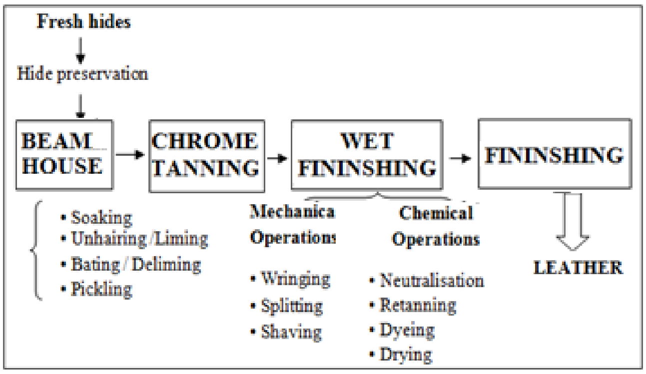


Figure 1: Simplified leather production chain

2.2 Sampling

The wastewaters are pre-treated by primary, secondary and tertiary decantation. The figure 2 shows the different steps of the pre-treatment station in a tannery located at Mohamedia city in Morocco.

Water samples were collected manually over three days period from:

- The collection basin B3 (Fig. (1)) that release directly to the sewerage system, at hourly interval, numbered from 1 to 7;
- The end of five important stages of the process during a cycle of production.

Sampling bottles were rinsed in the laboratory with distilled waste and rinsed again with sampled water just before collection. Solid samples (sludges and leather waste) were taken from ten different points on the whole factory (Fig. (2)). Samples were kept in a cooler (+4°C).

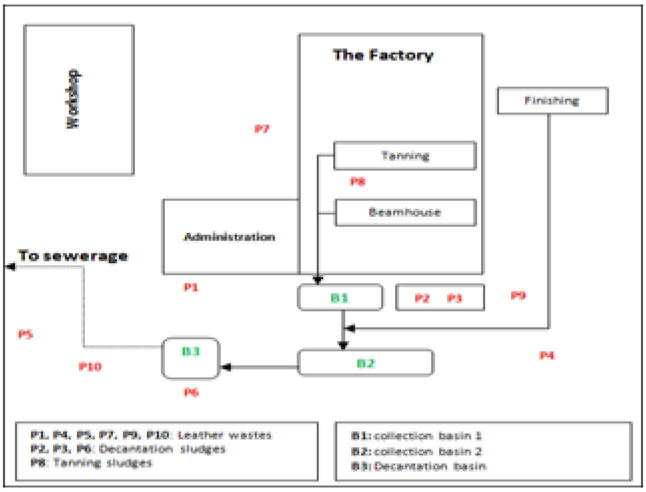


Figure 2: Schematic description of the sampling points

2.3 Analytical Methods

2.3.1 Liquid samples

Eight physicochemical parameters were analyzed in water: pH, conductivity and turbidity were measured in situ respectively by conductivity meter HI 98360 and turbidity meter (HI 93703 microprocessor turbidity meter). COD, BOD5, MES, sulphates, sulphides… were performed according to the standard methods (AFNOR, 1999). After one hour of sedimentation, the beaker contents are transferred into Imhoff cones, settled sludges were removed from water and the volume is recorded according to volumetric method (Eaton, 1995). In order to determine the concentration of heavy metals (Chromium, Cadmium, mercury, lead…) the samples undergo mineralisation.

Mineralisation wastewater [12]: 10.5 ml of concentrated hydraulic acid and 3.5 ml concentrated nitric acid were added to 50 ml of the wastes. The samples were left for 16 hours and, then, heated for 2 hours up to the appearance of white fumes. After cooling, the solution was placed in measuring flasks of 50 ml capacity and made up to the mark with distilled water.

2.3.2 Solid Samples

Sludges and leather wastes were drained and then homogenised separately in a porcelain mortar before the mineralisation step.

Mineralization of sludge and leather wastes: 7 ml of concentrated hydraulic acid and 2.5 ml concentrated nitric acid were added to 1g of the solid wastes. The samples were left for 16 hours and, next, heated for 2 hours up to the appearance of white fumes. After cooling, the solution was filtered and placed in measuring flasks of 50 ml capacity; the insoluble residue was washed by a solution HNO3 0.5mol/l and made up to the mark with this solution. Metallic elements (Cr, Cd, Pb, Hg, Cu, Ni, Fe, Zn) were measured by ICP-AES.

3. Results

3.1 Wastes characterization: Process Wastewaters

The samples were collected from a tannery located in the factory of Mohammedia, Morocco. Different wastewater streams are generated at different times and as a result, the effluent characteristics in the main drain vary significantly. The results show that the physical chemical parameters analyzed and metal contamination (Table I and Table II) along the steps of the process varies significantly from one stage to another. However, these parameters vary slightly for the same step and during the three companies taking. Averages of measured parameters for all samples taken from the end of process steps are given in Table I and Table II.

Table 1: Characterization of tannery wastewaters (Process waters)

	pH	Cond.(ms/cm)	Turb. (NTU)	SS (mg/l)	COD (g/l)	BOD5 (mg/l)	sulfate (mg/l)	sulfide (mg/l	BOD_5/COD
Soaking	6,8	27	3050	3000	8,28	0	2825,6	13.43	0
Unhairing/Scudding	10	22	4500	14200	44,16	2800	3005,1	22,04	0.07
Deliming/Bating	8,6	10,9	2664	1000	7,36	0	8979,5	22,04	0
Pickling	3,4	45,6	733	100	2,76	2000	11748,7	29,05	0.73
Tanning	3,6	52,6	220	100	4,6	0	28748,7	2.5	0

Table 2: Concentration of metallic elements in tannery wastewaters (Process waters)

	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn
Soaking	0,004	0,202	0,12	8,27	0,01	0,007	0,73	1,85
Unhairing/Scudding	0,004	0,38	0,204	7,86	0,15	0,06	0,35	2,02
Deliming/Bating	0,003	0,83	0,067	2,7	0,317	0,006	0,24	0,73
Pickling	0,004	3,20	0,061	1,80	0,012	0,005	0,24	1,63
Tanning	0,005	4325,75	0,008	1,96	0,649	0,032	0,14	0,66

All values are in mg/l of wastewater

3.2 Wastewaters from collection basin (Fig. (2), B3)

Averages of measured different parameters and metal contamination for all samples taken from the collection basin (B3) are given in Table III and Table IV. The hourly samples are numbered from 1 to 7 (T1 to T7).

Table 3: Characterization of tannery wastewaters (wastewaters from collection basin)

Times	*pH*	*Cond. (ms/cm)*	*Turb. NTU*	*SS (mg/l)*	*COD (g/l)*	*BOD5(mg/l)*	*Sulfate (mg/l)*	*sulfide (mg/l)*	*BOD_5/COD*
T1	6,9	3,95	705	2600	5,52	-	876,9	37,17	-
T2	4,7	15,5	1150	1600	4,6	125	6825,6	38,97	0.03
T3	4,9	19,8	3100	1600	5,52	100	6876,9	39,57	0
T4	5,4	13,5	3750	9400	27,6	100	4646,2	38.27	0
T5	9,1	17,5	3800	1500	11,96	850	3620,5	31,66	0.07
T6	9,6	9,4	2450	500	11,96	750	1800,0	39,37	0.06
T7	8,3	6,0	1150	2000	5,52	200	2646,2	26,55	0.04

Table 4: Concentration of metallic elements in tannery wastewaters: Collection basin

	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn
T1	0,004	34,20	0,04	2,34	0,09	0,014	0,14	0,35
T2	0,005	682,08	0,02	2,004	0,12	0,01	0,13	0,32
T3	0,005	811,41	0,07	3,020	0,72	0,02	0,11	0,57
T4	0,003	110,1	0,07	5,96	0,45	0,07	0,085	0,86
T5	0,004	223,73	0,1	4,17	0,17	0,04	0,06	0,94
T6	0,005	74,35	0,07	8,09	0,17	0,03	0,14	0,92
T7	0,003	29,215	0,04	1,64	0,01	0,007	0,76	2,4

All values are in mg/l of wastewater

The production unit generates wastewater quality variable over time, the effluent of a sample varies to another. This variation is due to the changing composition of waste collected along different process steps.

3.3 Analysis of metallic elements in Sludge and leather wastes

The analysis of heavy metals is a very important task to assess the potential environmental and health risk associated with the sludge coming from wastewater. So, it is necessary to determine total elements to give an accurate estimation of the potential environmental impact and to obtain suitable information about their toxicity. Metallic elements in solids samples (Sludge and leather) from different steps are given in Fig. (3) and Fig (4).

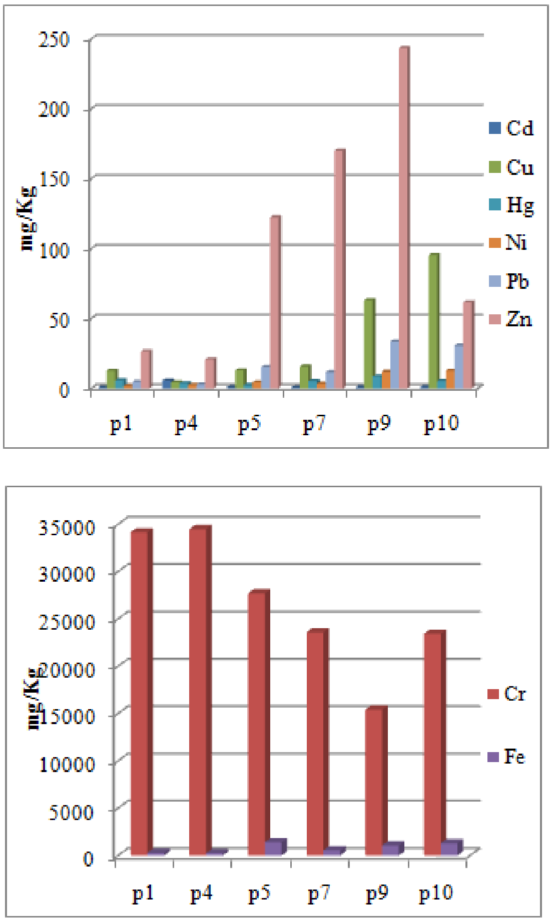


Figure 3: Metallic elements in leather wastes

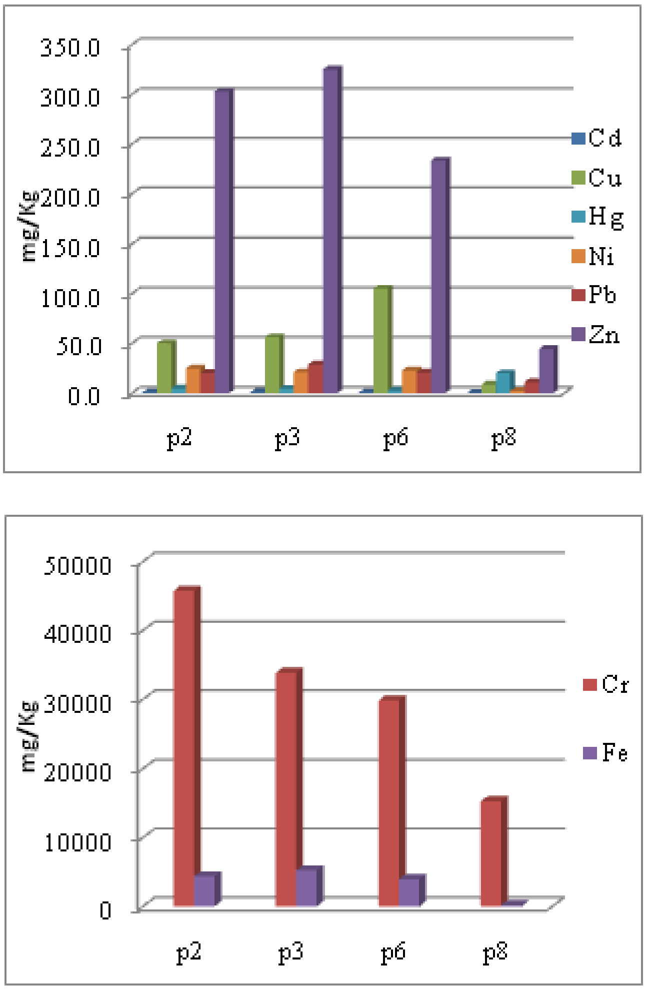
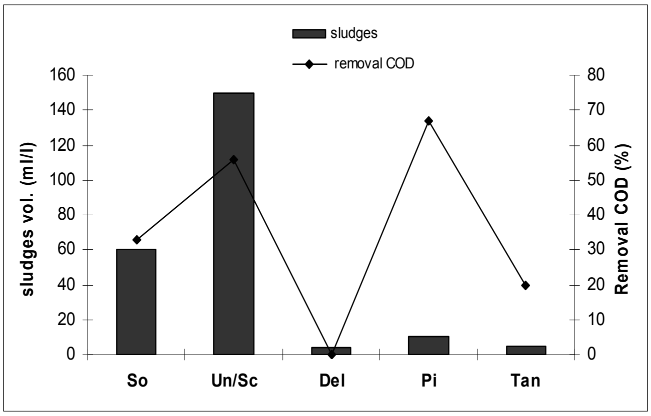


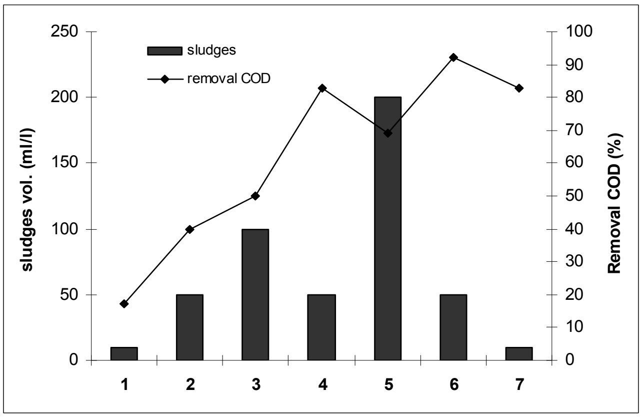
Figure 4: Metallic elements in sludges

3.4 Effect of physical settling

The treatment of tannery wastewaters highly polluted can be difficult in the presence of toxic compounds, so, before discharging, it has to be submitted to pre-treatment devoted to the reduction of the concentration of these polluants, a special problem is constituted by the removal of COD and heavy metals, particularly chromium. In this step of work, we study the possibility of pollution reduction by simple sedimentation. During the preliminary tests, the most important parameters (COD, turbidity, pH, conductivity, SS, sulfates and sulfides) were determined to analyze the efficiency of a simple sedimentation. Averages of measured parameters for all samples are given in Table V (a: Process wastewaters, b: Basin wastewaters). Raw wastewaters collected from the basin of collection (B3) and from process stages are settled for one hour. The effect of settling on COD removal according to settled sludge is shown in Fig. (5).



(a)



(b)

Figure 5: Rate of reduction according to sludges settled
(a): process wastewaters; (b): basin wastewaters

Table 5: Effect of settling on pollution reduction (a): process wastewaters; (b): basin wastewaters

		pH	Cond. (ms/cm)	Turbi. (NTU)	COD (g/l)	Sulfate (mg/l)	Sulphide (mg/l)
T1	Raw	6,9	3,95	705	5,52	876,9	37,17
	Settled	7,1	3,9	490	4,6	800	4,41
	Removal (%)	--	1,27	30,50	16,67	8,8	88,14
T2	Raw	4,7	15,5	1150	4,6	6825,6	38,97
	Settled	4,9	3,04	380	2,76	3697,4	28,65
	Removal (%)	--	80,39	66,96	40,00	45,83	26,48
T3	Raw	4,9	19,8	3100	5,52	6876,9	39,57
	Settled	4,9	6,09	620	2,76	4928,2	0,6
	Removal	--	69,24	80,00	50,00	28,34	98,48
T4	Raw	5,4	13,5	3750	27,6	4646,2	38,27
	Settled	5,7	10,87	1652	4,6	2466,7	26,05
	Removal (%)	--	19,48	55,95	83,33	46,91	31,93
T5	Raw	9,1	17,5	3800	11,96	3620,5	31,66
	Settled	10,9	10,7	920	3,68	3543,6	0,6
	Removal (%)	--	38,86	75,79	69,23	2,12	98,10
T6	Raw	9,6	9,4	2450	11,96	1800	39,37
	Settled	10,7	7,8	793	0,92	1774,4	1
	Removal (%)	--	17,02	67,63	92,31	1,42	97,46
T7	Raw	8,3	6	1150	5,52	2646,2	26,55
	Settled	8,5	5,07	510	0,92	1723,1	8,72
	Removal (%)	--	15,50	55,65	83,33	34,88	67,16

(a)

		pH	Cond. (ms/cm)	Turbi. (NTU)	COD (g/l)	Sulfate (mg/l)	Sulphide (mg/l)
Soaking	raw	6,8	27	3050	8,28	2825,6	13,43
	settled	7	3,9	1840	5,52	1235,9	2,5
	Removal (%)	--	85,56	39,67	33,33	56,26	81,38
Unhairing/ Scudding	raw	10	22	4500	44,16	3005,1	22,04
	settled	11	3,04	940	19,32	1056,4	6,11
	Removal (%)	--	86,18	79,11	56,25	64,85	72,28
Deliming/ Bating	raw	8,6	10,9	2664	7,36	8979,5	22,04
	settled	9,1	6,09	1150	7,36	8594,9	5,61
	Removal (%)	--	44,13	56,83	0,00	4,28	74,55
Pickling	raw	3,4	45,6	733	2,76	11748,7	29,05
	settled	3,5	10,87	144	0,92	7569,2	15,03
	Removal (%)	--	76,16	80,35	66,67	35,57	48,26
Tanning	raw	3,6	52,6	220	4,6	28748,7	2,5
	settled	3,6	10,7	40	3,68	22145,4	1,2
	Removal (%)	--	79,66	81,82	20,00	22,97	52,00

(b)

The COD and chromium were removed mainly through sedimentation (83% removal of total COD with initial concentration of 27.6 mg/l). The effect of settling on principal heavy metal removal is shown in Fig. (6).

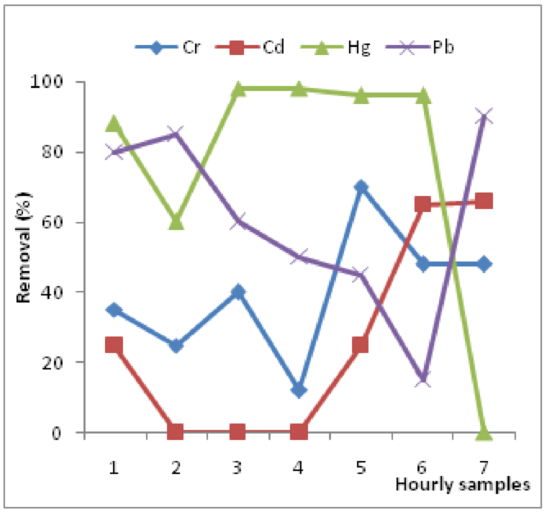


Figure 6: Principal metallic element pollutants removal in the basin collection effluents (B3)

40-70% removal of chromium from settled tannery wastewaters, at an initial concentration of 811.4 mg/l and 223.7 mg/1 respectively. About 90% removal of total lead and 98% of total mercury at an initial concentration of 754 µg/l and 716 µg/l respectively. Whereas cadmium, sedimentation is not profitable.

4. Discussions

4.1 Wastes Characterization

Tanning involves a complex combination of mechanical and chemical processes. The heart of the process is the tanning operation itself in which organic or inorganic materials become chemically bound to the protein structure of the hide and preserve it from deterioration. The substances generally used to accomplish the tanning process are chromium. Tanneries that perform the complete tanning procedure produce mixed wastewaters. The composition of this wastewater is not solely the result of separate waste streams that merge together. In general the wastewaters are basic, have dark brown color and have a high content of organic substances that vary according the process steps and according to the chemical used. In this study terms of COD, BOD5 and TSS along different steps of the process (5 steps) recorded significant values ranging respectively from 2760 to 44160 mg/l and 0 to 2800 mg/l, 100 to 14200 mg/l (Table I).

The physic-chemical characteristics of wastewater collected over time from the sedimentation basin (B3) vary from 4600 to 27600mg/l, and 100-850 mg/l (Table III) respectively COD, and BOD5, these effluents are rich in suspended solids (maximum value, 9400 mg/l, is observed at the time of release of Unhairing). The maximum values of COD, BOD5 and TSS were observed in wastewater collected from basin B3, which is related directly to the sewerage. These concentrations are comparable to COD results by Kongjao and al. [13]. This high load of organic matter is mainly due to biogenic materials skins and organic chemicals used. In addition to the organic load, the effluent is rich in minerals. The electrical conductivity that reflects the ion concentration of the medium shows the average results of between 10.9 and 52.6 mS / cm for the wastewater collected in the various steps of the process (Table I) while the conductivity values for 7 times samples from one basin varies between 3.95 and 19.8 mS/cm. These values are important in conductivity due to the use of large quantities of salts during the manufacturing process. Sulphate concentrations for the different steps of the process vary between 2820 mg/l and 28750 mg/l (Table I), whereas concentrations in the basin B3 varies between 877 and 68770 mg/l (table 3). Many authors use the BOD5/COD ratio as biodegradability index [14]. Wastewater can be considered readily biodegradable if it has a ratio value that varies between 0.4 and 0.8 [15]. The BOD5/COD ratio is generally less than 0.5. Therefore, the biodegradability of the influent was found to be low, according to the criteria of Ahn and al. [16]. However, BOD5 is a controversial parameter, when it is applied to tannery wastewater, since it contains many inhibitors of BOD5 [5]. The pH values varied with the current step, they range from 4.7 to 9.6. The characteristics of tannery effluent vary considerably from a tannery another depending on the size of the tannery, chemicals used for a specific process, and amount of water used and type of final product produced by a tannery [17].

Some of tannery wastewater characteristics are given in Table VI. This result shows a great variability in the quality of the influent, depending on the type of hides and skins and the region from which they came, at the time of the sampling.

Table 6: Characteristics of different types of tannery wastewater

References	*COD mg/l O2*	*BOD5 mg/l*	*Cr total mg/l*
Tamilchelvan and Dhinakaran, 2012[18]	11680	3410	1.8
Apaydin et al. 2009 [19]	3700	1470	---
Aboulhassan et al. 2008 [20]	1 429 ± 317 2 723	253 ± 209 369	81,3 ± 34 47,2
Kongjao et al. 2008 [13]	4100-6700	630-975	11.5-14.3
Floqi et al. 2007 [21]	6168-11032	965-1631	4.75-49.2
Ganesh et al. 2006 [22]	4800± 350	---	95±55
U.kurt et al. 2006 [23]	2810	910	62
Lefebvre et al. 2005 [24]	2200	---	---
Szpyrkowicz et al. 2005 [25]	2426	---	29.3
Leta et al. 2004 [26]	11153.67	2906	32.87
Thanigavel 2004 [27]	5650	---	---
Koteswari et Ramanibai 2003 [28]	8000	930	11.2
Orhon et al. 2000 [29]	2155	---	50.9
Yatribi and Nejmeddine 2000 [30]	Epilage-Pelanage: 20000 Tannage : 7020	7000 2400	- 70
Ram et al. 1999 [31]	3114	1126	83
Present work (B3)	4600-27600	100-850	34,16-811,4

4.2 Metallic Elements

The metal concentration recorded showed that the industrial discharges are very contaminated with metal. This heavy load of metal in addition of organic matter causes an impoverishment of dissolved oxygen, hence the high levels of COD. These high concentrations are due in particular to the use of chromium sulphate as a tanning agent and aluminum sulfate used in step deliming. Sulfate ions in acidic medium or low oxygen will lead to hydrogen sulfates at the sewerage. Trivalent chromium is considered non-toxic and relatively immobile in nature. Hexavalent chromium is easily soluble in water, very toxic and mobile [32]. Chromium concentration during the various steps of the process shows a very high value at the tanning step 4325.75mg/l. In addition, the analysis of chromium for samples over times shows values ranging between 29.2 and 811.4 mg/l with mean value of 280.7 mg/l (table 4) which could have a high impact on the antibacterial activity. The concentration of Cadmium varies between 3 and 5 µg/l for the five steps of the process as well as for samples over time. Mercury concentration varies between 10 µg and 649 µg/l along different steps of the method so that the values of Hg detected in the water decanted (B3) represents a maximum of 720 µg/l and at least 10 µg/l. High concentrations of Hg have been observed particularly in tanning discharges that could be explained by the use of impure tanning reagents.

The total chromium content of tannery effluents can reach values much larger [33]. Chromium content in the effluent will be transmitted in the environment where it can undergo oxidation reactions to convert to Cr (VI) [34]. Conventional chrome tanning results in wastewater containing at high as 1500-3000 mg/l of chromium [35]. The tanning industry is an especially large contributor of chromium pollution in India [36]. It was estimated that in India alone, ~ 2000–3000 tonnes of chromium escape into environment annually from the tanning industries, with chromium concentration ranging between 2000 and 5000 mg/l in the aqueous effluent, compared to the recommended permissible limit of 2 mg/l [37]. Chromium has low acute and chronic toxicity to humans at high doses. Chromium toxicity is dependent on chemical speciation and thus associated health effects are influenced by chemical forms of exposure. Cr (VI) compounds are much more soluble than Cr (III) and are much more toxic (mutagenic and carcinogenic) to microorganisms, plants, animals and humans. The excess of Cr (III) is proven to be a potential soil, surface water, ground water and air contaminant under specific condition [35]. Pollutant load in organic matter and heavy metals depends on the concentration of pollutants in wastewater and water consumption by process. Table 7 provides an overview on water consumption in individual processing operations during the tanning process. Depending on the type of applied technology (conventional or advanced) the water consumption varies extremely. Technologies that can be regarded as advanced in comparison to conventional methods involve processes usually termed low-waste or cleaner technologies (high exhaustion, chrome fixing). In Morocco, tanning industry consumes large quantities of water and generates large amounts of waste and wastewater.

Table 1: Consumption of water and wastewater production

References	*Consumption of water (m3/tone of hides)*	*Wastewaters (m3/tone of hides)*	*Solid wastes (Kg/tone of hides)*
Gutteres et al. 2008 [38]	10.5-28	---	---
Trujillo et al., 2008 [6]	---	175 tone/day	22 tone/day
Suthanthararajan et al. 2004 [39]	30-40	---	---
Thanikaivelan et al. 2004 [40]	---	34-45	---
Center of Promotion of Sustainable Technologies, 2003 [41]	15-40	---	---
Ramirez et al. 2003 [42]	35-40	---	---
Rao et al. 2003 [43]	30-40	---	---
Infogate GTZ, April 2002 [44]	conventional technology:3-5 advanced technology: 0,5	-	-
Environmental commission of IULTCS, 1997 [45]	34-56	---	---
Nandy et al, 1999 [46]	---	30-35	---
Buljan, 1994 [47]	25-45	---	450-600 (225kg/ton leather waste)
El Boushy and Van der Poel, 1994 [48]	---	---	165
RIVM 1992 [49]	24-41	35	---
Clonfero, 1990 [50]	---	310	---

Leather processing involves a huge quantity of water in its different stages and therefore it generates a considerable amount of wastewater, which demands high investment and operational costs for effluent treatment to satisfy the discharge standards required by the environmental legislation [51].

4.3 Solid samples

Concentration ranges of heavy metals even in sludges and leather wastes are shown in Table VIII

Table 8: Heavy metals concentration in leather wastes and sludges

	Cr (10^3)	Fe (10^3)	Cd	Hg	Pb	Zn	Cu	Ni
Leather	15 – 35	0,25 – 1,35	0,5– 5,0	5,0– 8,5	4,5 – 33,5	20,0– 24,5	100 – 95	1,5 – 12,5
Sludges	15 – 45	0,15 – 5,0	0,5 – 1,2	2,5 – 20	11,5 – 29,0	44,5 – 325,0	9,0 – 120,0	2,5 – 25,0

All values are in mg/Kg of dry matter.

Environmental contamination with toxic heavy metal ions in the industrial wastes is one of the major concerns of developing countries. Industrial effluents loaded with toxic metal ions are released in the environment without any treatment. The sludge and leather wastes, as expected, are very high in heavy metals particularly in chromium. The analysis of the sludge showed that it contained high amounts of trace elements especially chromium, cadmium, mercury and lead, which all have a negative impact on plant growth [52]. The level of chromium was high (30 mg/g) and above the maximum level which should be present in the soil (100 mg /kg). The lead content in the sludge was high (20 mg/Kg) compared to the maximum allowable level of lead content in the soil 15 mg/Kg [53]. From the above results it appears that the sludge from the tannery was at an acceptable level, except for chromium and cadmium (Table I).The mobility of trace metals, their bioavailability and related eco-toxicity, depend strongly on their specific chemical forms or ways of binding. Consequently, these are the parameters that have to be determined, rather than the total element contents, in order to assess toxic effects and to study geochemical pathways. The presence of heavy metals in the sludges produced restricts their use for agricultural purposes [54].

4.4 Effect of Physical Settling

Tannery effluents are generally treated biologically for the removal of biodegradable organics before discharge to receiving waters. Schrank et al. (2004) [55] has suggested that many organic compounds contained in wastewater are resistant to conventional chemical and/or biological treatment. The choice of wastewater treatment process depends on several factors like efficiency, cost and environmental capability [56]. However before carrying out studies to investigate the options for the cost-effective treatment of tannery wastewater, it is necessary to first examine the behaviour of the pretreatment.

In terms of COD, decanting is more effective for discharges of liming step that presents a serious pollution (COD 44000 mg/l, and SS 14200 mg/ l). One hour settling eliminates almost 60% of COD and produces a large volume of sludge (150 cm3). While for the water basin, the efficiency is recorded at time 4 (T4) (with initial COD 27600 mg/l and SS reaching 9400 mg/l), the COD removal exceeds 83%. In other study, whitin 1 hour of settling process, the removal efficiency for COD of mixed effluent had levelled out at 37.7% [7]. It appears that a significant proportion of the poorly degradable matter in tannery wastewater is removed by sedimentation. The effect of physical settling on the other parameters is shown in Table V.

The removal efficiency of chromium, cadmium, lead and mercury over time by settling are presented in Fig. 6. The concentration of chromium decreases of 40% in T3 with a initial concentration of 811.4 mg/l, leaving 486.8 mg/l of chromium in the supernatant, which explains the high values of chromium concentration in sludges (15-45 mg/Kg of dry matter). Within 1 hour, the removal efficiency of Cd is very low, while for Hg and Pb reach 98% and 90% respectively. These metals tend to precipitate out with the protein during the sedimentation. Other studies on chromium recovery and treatment from tannery effluents and sludge have been reported elsewhere [7, 20].

The different pH's and the different compounds influence each other's solubility. In composite wastewater, compounds precipitate while they stay dissolved in the wastewaters from the separate processes. In order to carry out effluent treatment in the most effective manner, flow segregation is useful to allow preliminary of concentrated wastewater streams, in particular for sulphid and chromium containing liquors. Although a reduction of water consumption does not reduce the load of many pollutants, concentrated effluents are often easier and more efficient to treat. A disadvantage of sedimentation is the generation of high volume of sludge.

5. Conclusion

The goal of this study has been to investigate the possibility of removing pollutants from tannery effluents. The results illustrate that sedimentation in leather tanneries can affect strongly the final physic chemical parameters and heavy metal composition of the effluent.

The results of Cr content of both the sludge and leather wastes indicate that it may not be safe to dispose the sludge on barren land and in water bodies as well as land filling. Settleable solids are removed rapidly in laboratory tests and pilot- and full-scale results show good correlation between removals of settleable and suspended solids. The proportion of settleable solids in crude wastewater increases with increasing suspended solids. There is significant linear correlation between removal of suspended solids and organics in primary sedimentation. Coarser components, such as sand and pelage and high concentrations of settleable solid can be removed from wastewater by sedimentation. The concentration of chromium decreases by 40% in T3 with an initial concentration of 811.4 mg/l, leaving 486.8 mg/l of chromium in the supernatant, that explain the high values of chromium concentration in sludges (15-45 mg/Kg of dry matter). Within one hour, the removal efficiency of Cd is very low, while for Hg and Pb reach 98% and 90% respectively. A significant proportion of the poorly degradable matter in tannery wastewater can be entrained by settleable matters. Even so, further treatments are needed prior to discharge not only in terms of environmental impact (COD, chromium) but also in terms of economics.

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