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CHARACTERIZATION OF TANNERY WASTEWATERS FOR PRETREATMENT – SELECTED CASE STUDIES

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ABSTRACT

Wastewater characterization is an integral part of treatment and management strategies for industrial effluents. This paper outlines the results of detailed characterization studies on three different tannery complexes. It evaluates, aside from raw wastewater quality in terms of major polluting parameters, the impact of physical and chemical settling on wastewater characteristics. Emphasis is placed upon homogenization and sulfide removal potential. Chemically treated wastewater is further studied for assessing COD fractionation, presently used as significant modelling information for biological treatability. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Chemical treatment; chromium removal; COD fractionation; settling; sulfur removal; tannery effluents; wastewater quality.

INTRODUCTION

A reliable wastewater characterization is a prerequisite for an acceptable treatment strategy for industrial wastewaters. This is especially true for tanneries which exhibit significant differences in their line of activity, generating effluents of very specific and complex natures.

Wastewater management approaches for tannery effluents usually involve subcategorization. Subcategories are defined to differentiate wastewater quality, treatment technology and applicable effluent limitations in terms of meaningful parameters. The significant groupings in this approach have to be identified on the basis of local trends in the tanning industy. Recently, six different subcategories have been proposed for tannery effluents in Turkey (Tünay *et al.,* 1995). Evaluation of a number of experimental surveys indicates that the critical differentiation of wastewater characteristics from different subcategories is the presence or absence of major parameters such as chromium and sulfide, rather than the magnitude of conventional parameters like BOD, COD and suspended solids; such parameters show significant fluctuations from one plant to the other within the same subcategory, mainly because of different processing experience and habits. Lately, there has been a worldwide initiative to locate tanneries together in what is called *organized industrial districts.* Presently, 16 organized tanning industry districts are in operation in Turkey. These districts present an excellent opportunity to collect reliable information on effluent character, as they homogenize quality variations from individual plants.

In this study, a detailed wastewater characterization was performed for three major tannery complexes in Turkey: The *Istanbul Organized Leather Tanning Industrial District* (district 1), created after the relocation of the historical Kazlicesme/Istanbul tanneries in Tuzla with a potential capacity that would generate a wastewater flow rate of 36000 m^3 d^{-1}, presently houses 107 tanneries processing both cattle hide and sheepskin; at present, the wastewater flow is only 13000-14000 m^3 d^{-1}. The *Çorlu Leather Tanning Industrial District* (district 2) incorporates 87 tanneries processing predominantly sheepskin with an effluent quantity of similar magnitude. Finally, the *Biga Tanneries District* (district 3) is of much smaller size with only 46 plants all processing sheepskin, with a wastewater flow rate of 1800 m^3 d^{-1}.

Wastewater characterization may also be used as a significant index in assessing the performance of physical and chemical pretreatment before biological processes (Tünay *et al.,* 1994). In this study, the size distribution of COD, estimated as the main parameter for tannery effluents, was evaluated in three groups defining total, settled and dissolved fractions. The observed results for COD and other significant parameters were compared with the performance of plain and chemical settling studies carried out in laboratory and full-scale units. Emphasis was placed upon the performance of homogenization in terms of COD and sulphide removal. The nature of organics reflected by the COD content of the pretreatment effluent was also investigated to assess biological treatability.

EXPERIMENTAL RESULTS

Raw wastewater quality

The characteristics of raw wastewater were monitored for more than a year both in districts 1 and 2; fewer data were available from district 3. The results presented in Table 1 show that effluent quality from the three tannery complexes exhibit striking similarities in terms of their overall organic matter and suspended solids contents, reflected by an average COD concentration of 5000 mg l^{-1} and a suspended solids concentration of 2200 mg l^{-1}. The statistical evaluation of COD distribution for districts 1 and 2 is plotted in Fig. 1.

Table 1. Characterization of raw wastewaters

Parameters	**District I (Tuzla)**		**District II (Çorlu)**		**District III (Biga)**	
	Mean	Range	Mean	Range	Mean	Range
Total COD	5094	3235–7420	4947	2513–8781	4850	3180–6270
Soluble COD	2336	1040–3810	1770	1284–3125	2150	1320–2950
BOD_5	1760	600–2600	-	-	-	-
TSS	2229	1470–3474	2239	1000–4740	2175	1365–2975
TVSS	-	-	1131	650–1540	-	-
TKN	358	112–640	214	208–220	265	195–325
Organic-N	223	102–347	119	84–159	120	76–172
NH_3-N	135	48–245	95	56–136	145	65–185
Total P	-	-	8.6	3.4–22.3	72	4.2–10.5
Total Cr	115.6	58–213	168	84–236	65	45–92
S^{2-}	51	17–110	52	10–121	50	26–82
Alkalinity	1350	797–1818	665	259–1132	490	345–725
Chloride	10300	6370–12800	7601	6150–9060	-	-
pH	8.1	6.4–9.98	8.4	6.41–10.1	8.3	7.35–9.74

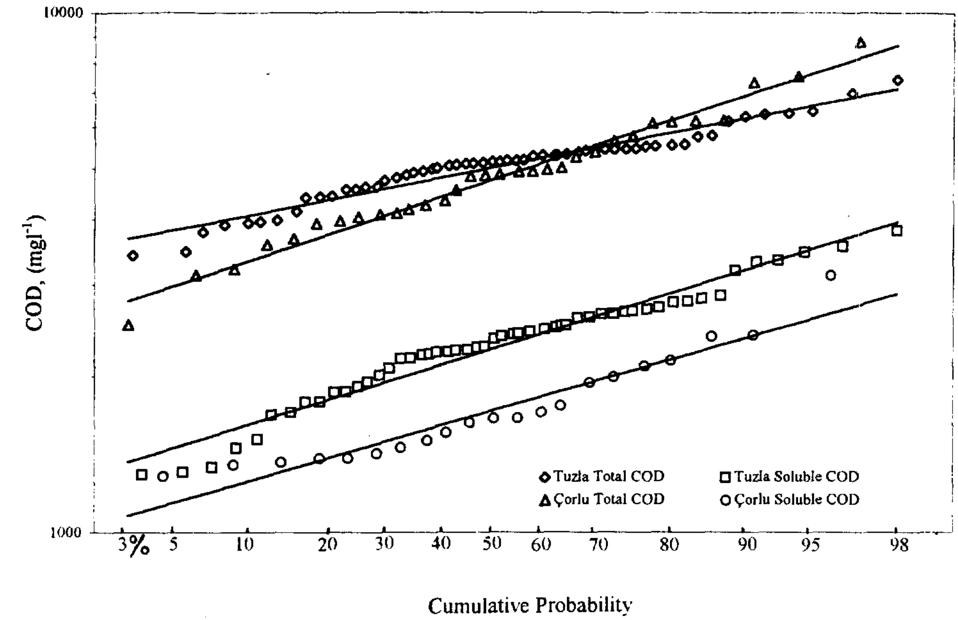

Figure 1. Statistical COD distribution of COD components.

The results yield a value of 5600 mg l^{-1} for the 70 percentile level which may be adopted as a design value. A similar strong fit is not depicted for the soluble COD portion. Other significant pollution parameters include a sulphide concentration of around 50 mg l^{-1}, total Cr^{+3} and nitrogen (TKN) concentrations varying in the range of 65-165 mg l^{-1} and 214-358 mg l^{-1} respectively. The effluents were also characterized by a high alkalinity content with a resulting average pH value of above 8.0 and choride concentrations of around 10000 mg l^{-1}, due to the chemicals used in the leather processing.

Table 2. Relationships between major parameters

Parameters	District I (Tuzla)	District II (Çorlu)	District III (Biga)	Domestic (Orhon et al.,1996)
Soluble COD/COD	0.46	0.36	0.44	0.35
BOD_5/COD	0.35	–	–	0.47
VSS/SS	–	0.48	–	0.7
Particulate COD/VSS	–	2.8	–	1.35
Cr/VSS (%)	5.1	7.5	3.0	0.006
NH_3/TKN	0.35	0.44	0.55	0.8
COD/N	14	23	18	9.2
COD/P	–	575	–	57
COD/N/P	–	150/6.5/0.2	–	–

Experimental data were further evaluated as shown in Table 2, to obtain useful relationships between major parameters. The table also includes similar relationships previously derived for Istanbul domestic sewage (Orhon *et al.,* 1997): The soluble COD fraction, assessed by means of filtration through glass fiber filters with an effective pore size of 1.3 μm was found to vary between 36-46% of the total COD. The BOD_5/COD ratio was only 0.35, a very low level compared to domestic sewage; It should be noted that BOD appears to be a very poor parameter for tannery effluents since it can only reflect a small and unknown fraction of the organic content and also, it is very susceptible to strong inhibitors inherently present in these effluents. The

VSS/SS ratio calculated only for district 2 was 0.48, much lower than that of domestic sewage, due to a large spectrum of fibres and particulates escaping leather processing. The COD equivalent of VSS was unusually high, as 2.8 mg COD/mg VSS, indicating that a significant portion of the organic particulate matter was small enough to pass through 1.3 µm filters and be accounted for as soluble COD. The chromium content of the dry solids was measured to vary between 3-7.5%. The data in Table 2 also show that tannery effluents are rich in nitrogen and especally organic nitrogen, but very poor in phosphorus.

Effect of homogenization and plain settling on wastewater quality

Experimental data were collected for two years, from the treatment plant at the Istanbul Organized Leather Tanning Industrial District (district 1), and presented in Table 3. The plant was designed and contructed for three segregated wastewater streams and involved homogenization, plain settling and activated sluge treatment for combined wastewaters, together with additional chemical precipitation for the chromium line and chemical oxidation for the sulphide line. As flow segregation could not be achieved, plain settling and biological treatment are presently applied to the combined wastewaters (Orhon *et al.*, 1995).

Table 3. Effect of homogenization and plant settling on wastewater quality

Parameters	Raw wastewater	Homogenization outlet	Primary clarifier effluent
Total COD	5094	4506	2216
Soluble COD	2336	1345	1187
BOD_5	1760	1402	958
SS	2229	2988	794
VSS	-	-	506
TKN	358	367	226
Org N	223	209	62
NH_3-N	135	158	164
Total P	-	-	5.1
Total Cr	116	132	41
(Cr^{+3})	51	47	27
Sulphur (S^{--})			

Homogenization. This is a compulsory pretreatment step for leather processing which consists of a sequence of batch processes, each generating a wastewater totally different from the others. Consequently, homogenization provides a reliable estimate of what may be effectively regarded as leather processing effluent for the following treatment units, although its character may be somewhat different than that of the incoming stream, due to biological reactions taking place within the tank. In fact, homogenization often functions as a non-recycle biological reactor and provides sizeable COD removal which is overlooked in design, requiring aditional aeration together with mixing. This argument is supported by the data presented in Table 3, which shows a total COD removal of 11% . It should be noted that total COD is not a good parameter for homogenization which also receives a COD and SS input from the thickener supernatant. This input, very easily detectable from the SS concentration increase in the homogenization, impairs performance calculations based on total COD. A better index of organic matter degradation is provided by the change in soluble COD indicating a removal of 19% , also cofirmed by a BOD_5 removal of 20% . The dilution effect possibly induced by the thickener supernatant return should be taken into account when evaluating these apparent removal rates. A similar action is also observed with respect to organic nitrogen forms which appear to be reduced by 10% through hydrolysis and conversion into ammonia.

Plain settling. This pretreatment step provides useful information about the size distribution of pollutants, by defining settleable portions of significant wastewater components. As shown in Table 3, plain settling ensures a suspended solids removal of 73% with a corresponding COD and chromium removal of 51% and 64% respectively. With this step, the soluble COD undergoes a total reduction of 49% from raw wastewater to settled effluent. A similar reduction of around 45% is also observed for BOD_5 and sulphur, and 37% for TKN. Plain settling appears to improve the VSS/SS ratio to 0.63, with an effluent fixed solids concentration of 288 mg l^{-1}. This is an important parameter, because it indicates a potential inert solids accumulation of around 2000 mg l^{-1} in the subsequent biological reactor for a hydraulic retention time and sludge age of 2 days and 15 days respectively, values commonly adopted for the design of such systems. Finally, the Cr/SS ratio at the clarifier outlet is again 5.1%, identical to the previously determined ratio for raw wastewater.

Effect of chemical settling on wastewater quality

The effect of chemical settling was investigated on wastewater samples from the three districts, using lab-scale jar-test experiments; both alum and iron salts ($FeSO_4$, $FeCl_3$) were used as coagulants together with a suitable anionic polyelectrolyte. The pH was adjusted by appropriate addition of lime. The results obtained from samples from district 2 were compared with the performance of the full-scale treatment system in operation for the last 2 years; the treatment scheme includes equalization, chemical treatment with coagulation, flocculation and settling and activated sludge type of biological treatment. The use of iron salts was discontinued in the plant in favor of alum, because of the dark color generated by iron complexes of tannin-like materials present in the wastewater.

The mean values of the experimental data collected from lab-scale chemical settling tests, for more than a year, are given in Table 4. The results show that chemical treatment produces an effluent with a COD of around 1000-1100 mg l^{-1} regardless of the district investigated, and a suspended solids concentration of less than 200 mg l^{-1}. The COD results are also confirmed by the performance of the full-scale plant during the same period.

Table 4. Effect of chemical settling on wastewater quality

Parameters	District I (Tuzla)		District II (Çorlu)		District III (Biga)	
	Initial[1]	Treated	Initial[2]	Treated	Initial[3]	Treated
Total COD	5756	1050	4705	1108	4180	1120
Soluble COD	1170	-	1600	-	1495	-
SS	2640	248	2300	128	2070	205
TKN	363	208	-	-	250	175
Total Cr	42	< 0.5	167	1.9	65	0.35
Sulphide	78	24	42	10.6	68	16

[1]Homojenization outlet;lab-scale Primary effluent
[2] Homogenization outlet;full scale
[3] Raw wastewater;lab-scale

In the plant, performance was much better in terms of suspended solids associated with an average effluent concentration of lower than 100 mg l^{-1}. Chromium removal was almost complete within the pH range maintained (between 7.5-8.5). Settlement of particulate organic nitrogen was also observed resulting in a total TKN reduction of around 30-35%. As shown in Table 5 which illustrates selected test results, iron salts were operative in the range of 500-1000 mg l^{-1}, whereas alum was effective within a lower dose of 250-600 mg l^{-1}, with pollutant removal rates almost independent of the coagulants dosage applied and the pH maintained in the experiment.

COD fractionation of chemically treated wastewater

Tannery wastewaters require biological treatment to meet stringent effluent limitations. Optimal design of biological treatment systems relies on a thorough evaluation of the organic load. The total COD, although a convenient parameter, cannot be regarded as a valid index of the organic load, because it covers a large spectrum of organic compounds with different biodegradation characteristics as well as inert components of influent origin or generated during biological treatment as residual microbial products (Orhon *et al.*, 1989). Consequently wastewater characterization, to be a useful tool for process modelling, should involve COD fractionation, in addition to assessment of conventional polluting parameters. The commonly adopted approach today is to evaluate the total COD as the sum of two major components; *biodegradable COD* and *inert COD,* and to further subdivide biodegradable COD into *readily biodegradable COD* and *slowly biodegradable COD* (Henze, 1992).

In this study, COD fractionation was performed on samples from district 1 (Tuzla), previously subjected to chemical settling. Table 6 present results obtained from 5 different sets. In one of the sets, parallel experiments were run to compare the magnitude of significant COD fractions before and after chemical treatment. The readily biodegradable COD was measured in accordance with the method proposed by Ekama *et al.*, (1986).

Table 5. Selected results of lab-scale chemical settling experiments

Set	Coagulant	Dosage (mgl^{-1})	pH	COD (mgl^{-1}) Initial	COD (mgl^{-1}) Final	Total Chromium (Cr^{+3}) (mgl^{-1}) Initial	Total Chromium (Cr^{+3}) (mgl^{-1}) Final
	Alum+poli	300+2	8.0	6144	1315	198	4.6
1	Alum+poli	300+2	7.5		1325		5.5
	Alum+poli	450+2	7.5		1162		4.0
	Alum+poli	600+2	7.5		1085		4.5
	Alum+poli	400+2	8.5	4183	947	133	1.54
2	Alum+poli	500+2	8.5		983		1.21
	Alum+poli	1000+2	9.0		1221		1.4
	$FeCl_3$+poli	500+2	8.2	4980	1525	135	< 0.5
3	$FeCl_3$+poli	750+2	8.1		1215		< 0.5
	$FeCl_3$+poli	1000+2	8.1		1137		< 0.5
	$FeCl_3$+poli	750+2	7.2	4650	1215	125	< 0.5
4	$FeCl_3$+poli	750+2	8.1		1215		< 0.5
	$FeCl_3$+poli	750+2	9.2		1195		< 0.5

Table 6. COD Fractionation of chemically treated wastewater

Run No	Total COD,C_{T1} mgl^{-1}	Readily Biod. COD,S_{S1} mgl^{-1}	Inert COD,S_{I1} mgl^{-1}	Slowly Biod. COD,X_{S1} mgl^{-1}	S_{S1}/C_{T1}	S_{I1}/C_{T1}	X_{S1}/C_{T1}
1	775	271	120	384	0.35	0.155	0.495
2	775	270	120	385	0.35	0.155	0.495
3a	1080	388	200	492	0.36	0.185	0.455
3b	2750*	400	200	2150	0.18	0.09	0.73
4	1160	570	290	360	0.44	0.25	0.31
5	1200	448	190	562	0.37	0.16	0.47
Avg	1000	377	184	439	0.37	0.18	0.45

* homogenization outlet

The inert COD fraction was assessed using the procedure defined by Germirli *et al.*, (1991). All tests were carried out on soluble fractions as they involved chemically settled samples. The experimental results indicate that around 20% of the total COD is expected to be resistant to biological degradation; of the remaining portion 35% is determined as readily biodegradable COD, leaving 45% as slowly biodegradable COD. As the COD content of the chemical settling effluent was ascertained to be around 1000-1100 mg l^{-1}, the outlet of the secondary clarifier is likely to contain a soluble residual COD of more than 200 mg l^{-1}, if microbial products are also accounted for. It is interesting to note that the same results were obtained as expected, for the readily biodegradable and inert COD fractions of the same sample before and after chemical settling (set 3), providing excellent support for the reliability of the experimental methodology; the results also show that chemical settling removes 73% of what would be slowly biodegradable COD.

CONCLUSIONS

On the basis of the experimental findings, the conclusions of this study may be expressed as follows:

Organized industrial districts need to be considered as a new subcategory for the leather industry. They provide a better and consistent picture of effluent quality. The wastewater generated is strong, with an average COD content of 5000 mg l^{-1} and a VSS content of 2200 mg l^{-1}.

Homogenization, an indispensable pretreatment step for leather processing effluents, acts as a non-recycle biological reactor and provides significant removal of soluble COD, a fact that should be considered for evaluating related aeration requirements during subsequent biological treatment.

Settleable fractions of major polluting parameters are such that plain settling constitutes poor pretreatment potential settled effluent is still a strong waste with around 2000 mg l^{-1} COD, 800 mg l^{-1} suspended solids and 40-50 mg l^{-1} chromium. A problem that is usually overlooked appears to be the fixed solids content of the settled wastewater with a chromium fraction of around 5%, constituting a significant burden on the following biological step. The fixed solids in the primary effluent is likely to result in a concentration of 2000 mg l^{-1} in the aeration tank, for the sludge ages typically adopted for tannery wastewater treatment.

Chemical settling generates an ideal effluent with a COD of around 1000 mg l^{-1} and practically no suspended solids and chromium. COD fractionation shows that only 20% of the total COD is biodegradable, an observation which merits serious consideration when defining effluent standards.

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