CHAPTER 26

THE TANNING INDUSTRY

CHARACTERISTICS OF THE WASTE WATER

The composition of the waste water from the tanning industry contains pollutants from the hides, products from their decomposition and chemicals and various spent solutions used for preparation of the hides and during the tanning process. The most highly polluted waste water comes from the liming and tanning operarations (Sierp, 1959).

The waste water coming from the preliminary soaking of hides contains such pollutants as fat, blood, hair, salts, solid particles, pieces of flesh, etc. The waste water has a dull grey colour with a perceptible odour of hydrogen sulphide. The lime wet effluents contains mainly calcium compounds, sodium and potassium sulphide, albuminous substances, residual hair, pieces of flesh and fat. This water is dirty green and has a putrid odour. The pH is above 9.0 and the amount of the suspended matter is as high as 2-4%.

As the washing proceeds the pH of the waste water changes from a high pH to about 7.0, and the amount of suspended matter decreases to below 0.2%.

Waste water from the pickling and chromium tanning processes contains traces of proteinous material, sodium chloride, mineral acids and trivalent chromium (Scholz, 1959). When this waste water is mixed with alkaline waste water precipitation of chromium hydroxide will take place. The waste water from the tanning has a pH below 4.0 and a low content of suspended solid.

Waste water from other tanning processes contains tannic compounds and other organic impurities. The colour of this waste water is dirty brown and the pH is below 5.0.

Waste water discharged from dyeing and oiling processes is black to dark brown in colour. It contains fat, mineral oils and dyes and has a high content of suspended matter.

As seen from this description it is hardly possible to define tannery waste water due to the great variability in composition.

An example of the analysis of waste water from the tanning industry is given in Table 26.1.

TABLE 26.1

Examples of waste water from the tanning industry

Component	From chromium tanning	Mixed waste water	After mechanical cleaning	After chemical precipitation with $Ca(OH)_2$
pH	9-12	8-9	8-9	10-11
Suspended particles (g/l)	0.5-2.5	1-2	0.1-0.4	0.1-0.2
Total dry matter (g/l)	7-8	3-5	2-3	1.0-2.5
BOD_5 (g/l)	0.5-0.8	0.5-1.0	0.3-0.5	0.2-0.4
COD (g/l)	0.5-1.0	0.5-1.2	0.4-0.8	0.2-0.5
Total nitrogen (mg/l)	150-350	100-200	40-100	30-60
Total P (mg/l)	50-200	10-40	10-30	1-5
Ammonium nitrogen (mg/l)	50-100	50-100	40-80	25-50
Sulphide (mg/l)	30-100	2-10	1-5	1-3
Chloride (g/l)	1-2	1-2	1-2	1-2
Sulphate (mg/l)	100-400	100-400	100-400	100-400
Chromium (mainly as Cr^{3+}) (mg/l)	20-100	0.1-2.0	traces	traces

Apart from the waste water from the production departments in tanneries, the total waste water includes the effluent from auxiliary departments such as those producing tanning extracts, and hair cleaning and glue manufacturing. The waste water from the washing and cleaning of hair is odourless, has a grey-green colour and contains calcium and sodium ions and a small amount of sodium sulphide. The water from the production of tanning extracts is relatively clean. It is slightly acidic due to the presence of organic tanning agents, but they are mostly present only in low concentrations.

Treatment methods

Recovery processes for certain components reduce their concentration in the waste water. The waste water from the deliming process can partially be used again for the removal of lime from the hides. Chromium(III)hydroxide is precipitated from the waste water and after separation in a settling tank is re-used.

The treatment of waste water from tanneries often comprises four stages (Yukio, 1969). In the first stage coarse suspended solids are removed using grids and screens. The grids have a spacing of 20-30 mm and the screens a mesh size of 0.5-5 mm. At least 40-60% of pieces of hide, flesh, fat and felted hair are removed by this mechanical treatment.

The second stage is the storage and gradual discharge of spent tanning liquor for further treatment.

These waste waters have the largest BOD_5 of all the water from the various processes, but because of the storage and uniform discharge of the effluent the treatment of the total waste water is not adversely affected by any disturbances occurring as a result of fluctuating discharge. The storage tank must of course have a capacity enough to store the maximum waste water output for at least 24 hours.

The third stage is flocculation of the pollutants. After mixing the combined waste water still has a high pH. Aluminium sulphate, iron(II)sulphate or lime are the most frequently used coagulants. After coagulation and sedimentation the pH is adjusted with carbon dioxide. The amount of coagulant used varies with the composition of the waste, but generally 400-1300 mg calcium oxide/l or 200-500 mg iron(II)sulphate or aluminium sulphate/l are used.

Other alternative coagulants (Scholz, 1967) have been recommended for the treatment of tannery waste water:

1. Hydrogen carbonate and iron(II)sulphate.
2. Iron(III)sulphate and iron(II)hydrogen carbonate.
3. Stack gas from boilers for neutralization.
4. Stack gas for neutralization of calcium containing waste materials.

In all four cases further treatment is required.

The last stage involves biological treatment either on trickling filters or in an activated sludge plant (Green, 1960). It is necessary, in spite of the pretreatment, to dilute the waste water with either river water or domestic sewage in the ratio 1:1 or 1:2 (Jung, 1959). However, Hunter et al. (1969) claim that a completely mixed activated sludge system is directly adaptable to the treatment of chromium tanning wastes either alone or in conjunction with municipal waste water. A BOD_5 removal of over 90% may be anticipated in the system with about 40% removal achieved in the primary clarifier. It seems that a high pH and significant chromium content do not have an adverse effect on the biological system. It is also remarkable that excellent chromium removal can be achieved by biological treatment.

If there is a high coliform content in the effluent it should be treated with chlorine doses of 20-30 mg/l.

Chemical oxidation is also used for treating tannery waste water (Shuttleworth, 1965).

Examination of the biological treatment process for a mixture of tanning waste water and municipal waste water in the ratio 2:1 gives the values of constants shown in Table 26.2.

TABLE 26.2

Coefficients for treatment of waste water from the tanning industry mixed with municipal waste water in the ratio 2:1

Coefficient +)	Unit	Value
k	l/mg/day	$3.7 \cdot 10^{-4}$
a	not stated	0.46
a_1	" "	0.75
b	day^{-1}	0
b_1	"	0.1
LF	-	0.2-0.4

+) see Chapter 11.

Tanning liquor can be re-used, but it is nececessary first to remove the dyestuffs from the spent liquour.

Several methods offer an attractive solution to this problem:

1. Adsorption on activated carbon.
2. Extraction with acetone.
3. Oxidation with sodium hypochlorite.
4. Flocculation with aluminium or calcium hydroxide.
5. Coagulation with organic polyelectrolytes such as polyacrylamide.
6. Ion exchange using an adsorption ion exchanger (see also chapter 24).

The latter three methods seem to be economically the most attractive.

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