MEASURES TAKEN AGAINST WATER POLLUTION IN TANNERIES AND LEATHER FINISHING PLANTS

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ABSTRACT

This paper reviews the experience of several authors in the treatment of tannery effluents up to the present time. Special attention is paid to the mixing and equalization of tannery effluents, application of polycoagulants and thickening of the sludge.

INTRODUCTION

Tanneries and leather finishing plants need for production a considerable amount of water which leaves the manufacturing system as a highly polluted waste water. The most serious drawbacks of the tannery effluents are: their undesirable influence on the biological process in the recipient, undesirable taste and odour. Moreover, the tannery effluent may spread diseases or cause toxicity of the water.

Each tannery effluent is composed of several kinds of waste: soaks, limes, bates, pickles, chrome-, bleach- and fat-liquors, vegetable tan liquors, colouring baths and all kinds of wash waters.

All tanning operations are of the batch type and the effluents come on varied time schedules. All these factors make the purification of tannery wastes rather complicated. The main problem of purification of tannery effluents is the retention of suspended solids and the reduction of BOD before discharging the effluent into public waters.

In principle there are two ways of tannery waste purification: (1) with municipal wastes in the town's sewage works; (2) in a special purification plant.

The most important factors concerning the tannery effluent are[1]:

Volume—An increase in discharge results in a decrease in concentration. This is favourable when discharging effluents into the recipient. In the case of discharge into sewers and treatment in a municipal plant, the charges are based on the volume.

pH Value—The effluent discharged into the recipient or into the sewers should have a pH in the region 5–9.

Biological Oxygen Demand (*BOD*)—The upper BOD limit of the effluent discharged into the recipient should be less than 30 mg/l. The sewage works do not set limits but impose charges on the BOD removal.

Suspended Solids (*SS*)—Municipal treatment plants impose charges according to the amount of suspended solids. The highest load of suspended solids generally does not exceed 2000 mg/l. In the case of discharge into the recipient the suspended matters content should be less than 30 mg/l.

Soluble Solids—The effluent discharged into the sewers does not contain more than 5000 mg/l of soluble solids and 300 mg/l of sulphates.

Sulphides—Acidification of alkaline liquor with sulphides produces hydrogen sulphide. The effluent discharged into the municipal treatment plant generally does not contain more than 20 mg/l of sulphides (like hydrogen sulphide). The recipient should not contain more than traces.

Chromium—Chromium compounds are toxic to fish and have an undesirable influence on the biological oxidation process. They should not occur in the recipient. Sewage works impose heavy charges for concentration of trivalent chromium above 20 mg/l.

Fats and grease—The upper value of fats and grease in the effluent is 10 mg/l for discharge into the recipient and 100 mg/l for discharge into the sewers.

QUANTITY AND QUALITY OF THE EFFLUENT

There are great differences[2] in the waste waters discharged from the tannery. Kubelka[3] performed hydrologic measurements on the discharges during the day in one of the oldest Czechoslovak tanneries. The daily hydrograph is shown in *Figure 1*. The mean water requirement in a manufacturing process using both vegetable and chrome tanning in the ratio 1:1 was 54 l/kg of hides; it was 36 l/kg for vegetable tanning, and 72 l/kg for chrome tanning. The loss of water during the operation was covered by the water present in the rawstock. The greater part of effluents came from dehairing and tanning processes.

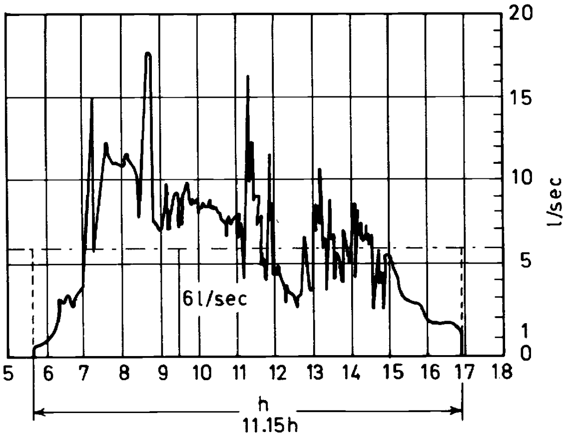

Figure 1. Hydrograph of the tannery effluent discharge.

The temperature of the effluent is very important with regard to the chemical reactions, biological life and sludge treatment. *Figure 2* shows the average monthly temperatures of the effluent and of the air during a year in the tannery mentioned above. The average effluent temperature did not fall below 10°C even when the air temperature was below 0°C.

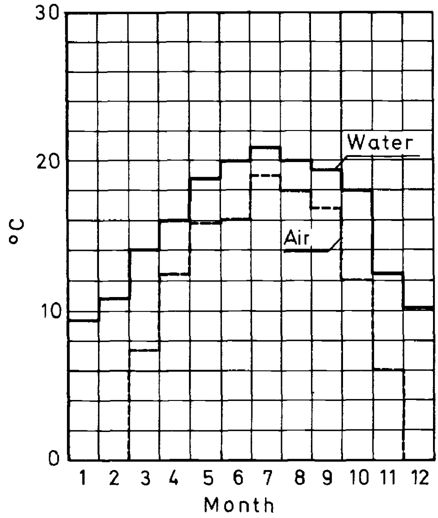

Figure 2. Monthly mean temperatures of air and effluent in a tannery.

According to the quality, tannery effluents may be divided into three main groups[4].

(a) Effluents from preparatory processes. They include soaks, limes, dehairing liquors, bates and pickles, deliming liquors, and all kinds of washings. Soaks are heavily charged with conservation means and organic matters. Limes are loaded with suspended matters, are strongly alkaline due to the excess of lime and contain the main amount of sulphide. Dehairing liquors contain sulphides as well and organic compounds in dissolved or colloidal form. Bates contain protoolytic enzymes and smaller concentrations of calcium salts. Pickles have a slightly acid reaction.

(b) Effluents from tanning processes. Two basic tanning processes are used at present in modern manufacture: chrome and vegetable tanning. Effluents from chrome tanning contain trivalent chromium compounds. Effluents from vegetable tanning are loaded with vegetable tanning materials, especially of the pyrogallol and catechol group· At present, these are replaced by synthetical materials.

(c) Effluents from final processes. This group is represented by the wastes from neutralization, dyeing and fat-liquoring. These effluents contain organic and inorganic acids, dyestuffs, chromium salts and fats.

The basic stages of hide processing are nearly the same in every manufacture. However, there is great variety in plant operation, and production possibilities. For this reason each tannery has an individual problem with effluent purification.

The major part of dissoved solids is sodium chloride, about 2000 mg/l. The colour of effluent from vegetable tanning is brown. Chrome tanning effluents are grey.

It is assumed that each kg of hides with a volume of 38 l of effluent produces about 50 g of BOD. 60 Per cent of this originates from the dehairing process.

The tannery effluents may contain the viruses of serious diseases. The spores of anthrax are particularly dangerous; they are resistant to usual disinfectants. Even a temperature of 100°C does not kill them completely. Sterilization of the tannery effluents would be very expensive and at present cannot be performed at reasonable costs. Therefore, it is preferable to prevent the spread of disease by disinfection of the raw hides.

METHODS OF TREATMENT

The character of tannery effluents shows that the methods of purification may be divided into two main groups[5–14]:

(1) Natural methods include the direct discharge of the effluent into the sea, estuaries, great rivers, etc. The effluents are only mechanically pretreated on screens and grids in order to get rid of coarse suspended matters, hair, etc.

In cases where large areas of land are available the tannery effluents may be used after the mechanical pretreatment for land irrigation or discharged into evaporation ponds.

However, all the above cases are now used only rarely.

(2) In most cases the tannery effluents are artifically treated in two steps[15,16]. The first step is a mechanical, eventually also chemical pretreatment, and the second step is the biological purification. The first step is generally performed during manufacture. For biological purification the effluent from the first step may be discharged to the municipal purification plant.

However, the biological methods may be applied in cases where the water does not contain toxic matter. The effect of biological treatment depends on several factors, e.g. pH, content of sulphide, chromium, vegetable and synthetic tannings, conductivity, etc. The BOD reduction by the activated sludge method is between 80–90 per cent while the chemical pretreatment reduces the BOD by 60 per cent. A combination of chemical pretreatment and the activated sludge method reduces the BOD content by 95 per cent[9,10,17].

Mechanical and chemical pretreatment

The tannery effluent is composed of several kinds of basic and acid wastes of various concentrations. For example, the first soaks are heavily loaded with sodium chloride and suspended organic matter, and have a high BOD value. Values of 3000 mg/l NaCl and 200 mg/l BOD are not uncommon. However, the volume of the effluents does not exceed 10–15 per cent of the total effluent[4,6].

The effluents from the limeyards and beamhouse contain inorganic and suspended matter, sulphide and colloidal protein and have high BOD values. They represent about 2–5 per cent of the discharge; it is possible to treat them chemically, immediately[18].

Kubelka[19] showed that the effluents of extreme pH form a relatively small part of the discharge (about 10 per cent). These effluents are represented by limes (about 1.6 l/kg of hides), colouring baths (about 3.1 l/kg), and chrome liquors (about 1.21/kg). All other effluents are more dilute. Therefore, it seems reasonable to segregate the most concentrated effluents and mix them together and to treat the rest of the effluents separately.

However, the most simple method of tannery effluent treatment is to combine all kinds of wastes in equalization and settling tanks. The basic and acid liquors with the soluble organic matter flocculate and the flocs are removed by settling.

Bianucci and De Stefani[7] comment on segregate treatment of chrome tanning effluents. Limes, pickles and dehairing liquors are mixed and coagulated by ferric chloride and hydrogen chloride (*Figure 3*). Chrome liquors are neutralized by sodium carbonate. After separate sedimentation all the effluents are mixed and discharged into the municipal purification plant.

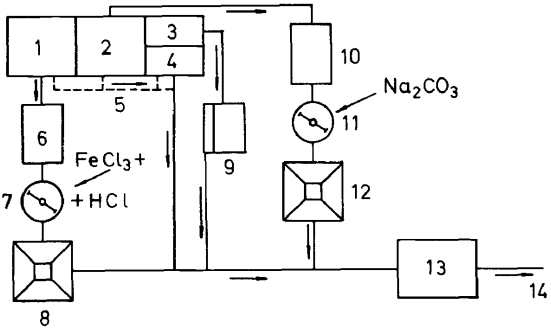

Figure 3. Scheme of a chrome tanning effluent system. 1, soaking, unhairing, deliming, pickling; 2, chrome tanning; 3, fatliqouring; 4, colouring; 5, wash waters; 6, storage tank; 7, reaction vessel; 8, sedimentation basin; 9, grease separator; 10, storage tank; 11, reaction vessel; 12, sedimentation basin; 13, storage tank; 14, to municipal treatment plant.

The tannery effluents contain a great amount of soluble or colloidal matter. When equalizing individual wastes this matter flocculates. If natural flocculation is not effective, it is helped by the addition of coagulants[23–25]. Good results have been achieved by the addition of milk of lime, ferrous, ferric[9] and alum salts[8, 10, 17, 25–28]. It has been found that alum sulphate is mostly suitable for vegetable tanning effluents. However, its dose rate is rather high—up to 1000 mg/l. From the economical point of view alum is often replaced by ferrous sulphate[29–32]. In recent years organic polycoagulants at low doses have been used with good results.

The settled sludge is voluminous and contains about 1–3 per cent of insoluble solids, of which about 50 per cent is of organic, and 50 per cent of inorganic character[33].

A substantial reduction in the concentration of chromium compounds is achieved when mixing the chrome waste with the beamhouse liquor. The chrome effluent after mixing with beamhouse liquors generally has a trivalent chromium content below 30 mg/l[1]. The precipitated chromium hydroxide is highly hydrated and the flocs settle down very slowly. Mixing with fresh lime slurry and addition of polycoagulant decreases the trivalent chromium content to 5–10 per cent.

Biological treatment

The method of biological treatment of tannery effluents was introduced in 1940[34]. The former practice consisted mainly of mixing acid and alkaline wastes followed by sedimentation or lagooning.

Nowadays the purification of tannery effluents is normally completed by the biological treatment process following the mechanical–chemical pretreatment. Biological purification is a result of the combined agencies of animal and plant life in which bacteria play the major role.

The principal aerobic methods of treatment are: trickling filtration[35] and the activated sludge process[36–38].

Since the total alkalinity used in the tannery is greater than the total acidity, the mixed effluent is usually alkaline. The excess of alkalinity should be neutralized to prevent interference with biological purification processes.

High pH values may be decreased by carbonation of the lime liquors with the flue gas[37]. *Figure 4* shows a scheme of an installation of this type[27].

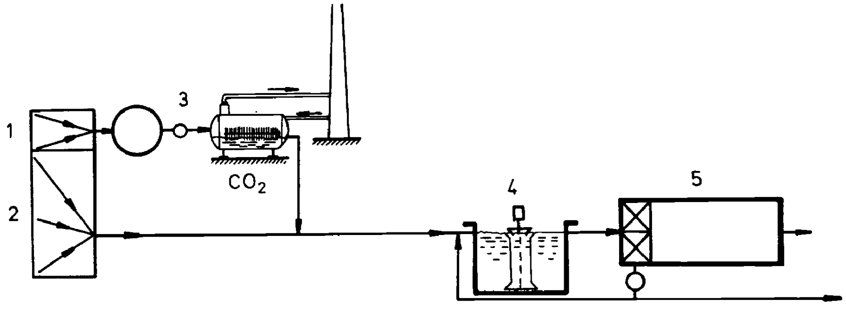

Figure 4. Scheme of the application of flue gas in biological treatment. 1, alkaline effluents; 2, wash waters; 3, flue gas; 4, aeration tank; 5, sedimentation basin.

The lime liquors are carbonated by means of flue gas and mixed with the rest of the effluent. The alkalinity is reduced and the effluent is treated in the aeration tank and the sedimentation tank. Moreover, the presence of carbon dioxide contributes to the removal of fats and grease[34].

Several tanneries discharge the pretreated effluent to the sewers. In this case the problem of treatment results in the treatment of tannery effluent mixed with domestic sewage by the municipal sewage works[4, 5, 39–41]. The mixing of tannery effluent with a certain amount of sanitary sewage has been found essential; however, the ratio varies with the nature and concentration of the wastes[42–48]. In the study of this process under different conditions several investigators have reported various periods of aeration for satisfactory reduction of dissolved organic matter. For example, Sastry *et al.*[49] commented that 48 hours aeration reduced the four hours oxygen demand value of a mixture consisting of 16 per cent of neutralized tannery waste and 84 per cent of domestic sewage by 82 per cent. The reduction was only 50 per cent if the tannery waste was not neutralized.

Tharabaj *et al.*[50] studied an activated sludge process on diluted vegetable effluent at a solids concentration of 2000–4000 mg/l. The best BOD reduction was after 24 hours from 1000 mg/l to 34 mg/l.

Jánský and Ludvík[40, 41] investigated the application of the activated sludge method to a mixture of industrial waste water having the character of a tannery effluent with domestic sewage.

The tannery effluent was diluted two or three times by wastes from paper, glue and textile industries. The ratio between the vegetable and chrome production was 1:1. The composition of the mechanically pretreated mixed effluent is shown in *Table 1*. Satisfactory results were achieved when the proportion of tannery effluent to domestic sewage was 2:1. Up to 90 per cent of BOD has been removed with a detention period of nine hours and a loading of 0.8–1.0 kg BOD per m^3 per day. The investigators commented on the rapid growth of fibre organisms during the pilot plant runs with activated sludge treatment. This was due to the specific nutrition condition caused by tannery wastes in the phase of sorption and synthesis of the biological organic matter.

Table 1. Composition of the mixed effluent

Total solids	2000–3000 mg/l
Volatiles	50–60 per cent
pH	7.5–12.0
Alkalinity	up to 23 mval/l
Sulphide	up to 10 mg/l S^{2-}
Chrome	up to 2 mg/l Cr^{3+}
Tannins	up to 100 mg/l
Oxidisability	150–400 mg/l O_2
BOD	200–800 mg/l
Carbon	200–300 mg/l
Total nitrogen	30–100 mg/l
Total phosphorous	20–50 mg/l
C:N:P	10:2.5:1.3

Green[34] performed experiments on a trickling filter filled with coke; he treated synthetic effluent containing about 300 mg/l BOD. When the trickling filter worked well, this value was reduced to about 30 mg/l. Green focused his attention on constituents influencing biological processes. In the case of dosage up to 120 mg/l H_2S the sulphide was completely recovered as sulphate; with higher dosages (440 mg/l) the reduction was up to 70 per cent.

Green also investigated the influence of trivalent chromium in concentrations up to 100 mg/l Cr^{3+}. Chromium was detected in the effluent from the filter after several days. Its elimination before the biological purification process is necessary, and at most tanneries this is achieved by flocculation with alkaline effluents in equalization tanks.

The complete vertical technological scheme of a plant treating tannery effluent combined with domestic sewage is shown in *Figure 5*. The effluent flows through mechanical screen, grit chamber, sedimentation and equalization tanks, aeration tank, final clarifier. The settled sludge is transported into the sludge thickener and from it to the sludge drying bed.

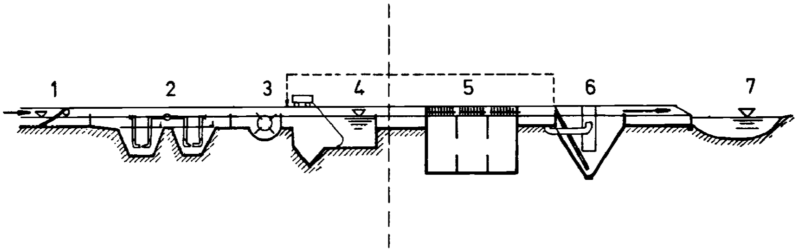

Figure 5. Complete scheme of a tannery effluent treatment plant. 1, coarse screen; 2, grit chamber; 3, fine screen; 4, mixing and equalization tank; 5, aeration tank; 6, final settling tank; 7, receiving stream.

Gates and Shun Dar Lin[51] performed pilot plant studies on the anaerobic treatment of tannery effluents[52–54]. With an effluent having a BOD of approximately 800 mg/l they obtained an effluent having a BOD of 100 mg/l. The anaerobic process showed no capacity to remove colour from the effluent. The value of 100 mg/l is high for discharge into the recipient but acceptable for treatment in a municipal treatment plant·

SPECIAL PROBLEMS

Mixing and equalization tanks

Mixing of acid and alkaline tannery effluents assists flocculation and produces flocs settling in the sedimentation basin. Therefore, great attention should be paid to the theory of mixing.

Perfect mixing[55] in a sedimentation basin is based on the equation of material balance

$$Vc_u = Vc_0 + Q\int_0^t (c_i - c_u)\,\mathrm{d}t \qquad (1)$$

in which V is the volume of the basin,

c_i, c_u are the inlet and outlet concentrations,
c_0 is the initial concentration in the basin,
Q is the discharge,
t is the time period.

According to the condition for perfect mixing, the concentrations in the basin and at the outlet, c_u, are equal. Let us assume the most simple case:

the volume of the basin, V, is constant (i.e. the discharge, Q, is constant) and the inlet concentration, c_i, is constant. Equation (1) may be differentiated and rearranged as:

$$\frac{dc_u}{c_i - c_u} = \frac{dt}{T} \tag{2}$$

in which $T = V/Q$ is the mean retention period.

The solution of Equation (2) gives

$$c_u = (c_i - c_0)(1 - e^{-t/T}) + c_0. \tag{3}$$

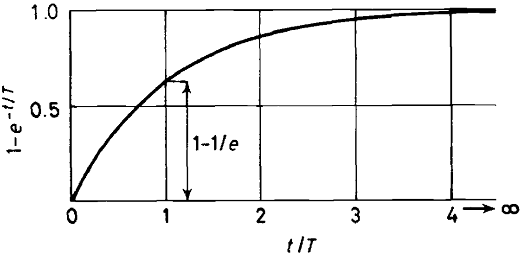

Figure 6. Graph of the $1 - e^{-t/T}$ function for perfect mixing.

Figure 6 illustrates the shape of the function $(1 - e^{-t/T})$ depending on t/T. Let us analyze two limiting conditions:

$$\text{(a) } t = 0, \qquad c_u = c_0$$
$$\text{(b) } t \to \infty, \qquad c_u = c_i$$

$$\text{At } t/T = 1, 1 - e^{-t/T} = 1 - \frac{1}{e} = 0.632$$

i.e. in the time interval corresponding to the mean retention period, there is still a considerable amount of the initial water in the tank.

Figure 7 shows examples of mechanically agitated equalization tanks where the conditions of perfect mixing could be approximately accomplished. The mechanically agitated tank must be followed by a sedimentation device.

Several tanneries use vessels for the storage of effluents discharged during 24 hours. Perfect mixing in these storage tanks could equalize the content and provide an effluent of constant quality.

Another means for equalization of the tannery effluent is a horizontal sedimentation tank [56, 57] of constant cross-section having the distribution of inlet effluents on the front side and along the side walls (*Figure 8*). The discharge in the tank is not uniform.

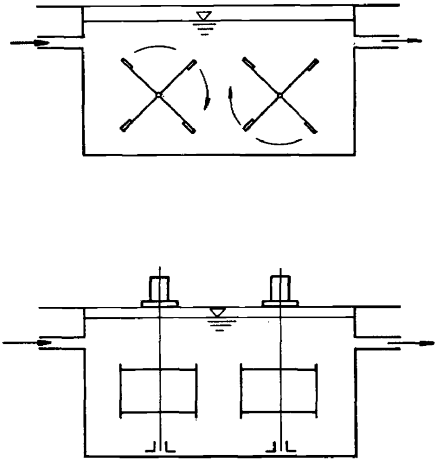

Figure 7. Types of mechanically agitated equalization tanks.

The volume, V, of the tank is computed from the relation

$$V = \frac{QT}{2},$$

in which Q is the total discharge,
T is the mean retention period.

The distribution of the inlets along the longitudinal axis of the tank follows the hyperbolic law. Hence the mean acceleration, a, of flow in the tank is constant:

$$a = \frac{v_0{}^2}{2l},$$

in which v_0 is the mean velocity at the end of the tank,
l is the length of the tank.

In practice the mean retention period $T \leqq 6$ hours provided good flocculation and also efficient sedimentation.

Polycoagulants

The total BOD produced in the tannery effluent is divided into all dispersion phases: suspended matters, colloids, and true solutions. A small dose of polycoagulant may substantially improve the removal of suspended and colloidal matters. BOD caused by dissolved and colloidal organic matters is rarely reduced.

The primary effect of polycoagulants is in the formation of heavier flocs settling at a higher rate[58]. The settling efficiency is improved, which is connected with the decrease of BOD.

Polycoagulants are divided into anionic, cationic and nonionic. The effect of polycoagulants depends on the electrical charges, molecular weight, and chain formation. The result of the polycoagulant action depends on

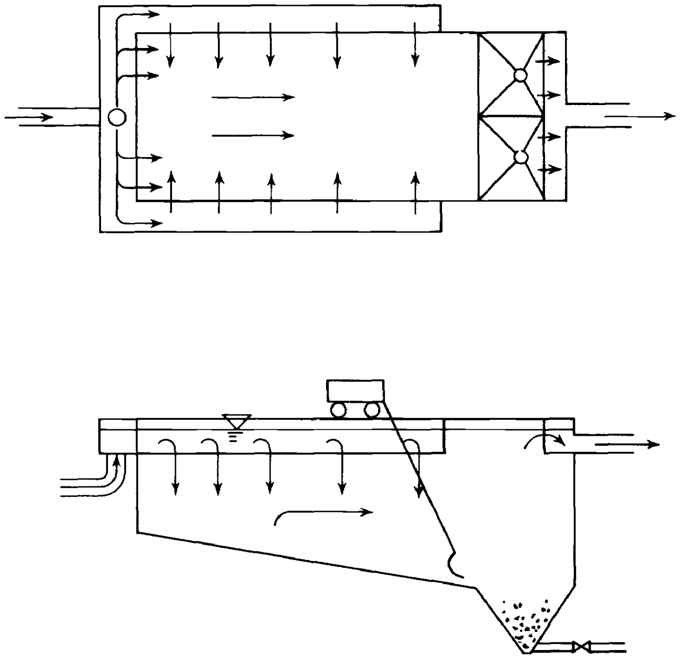

Figure 8. Horizontal equalization–sedimentation tank.

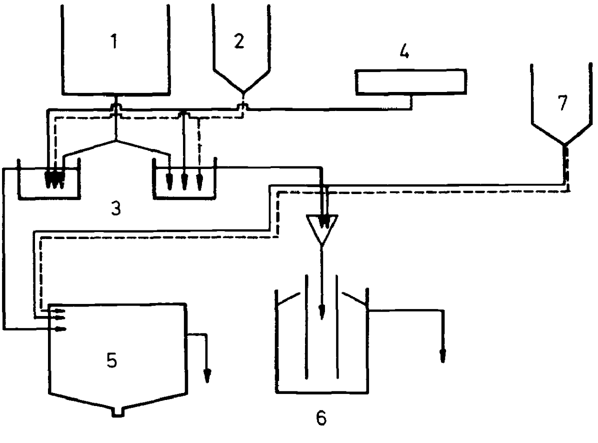

Figure 9. Scheme of a pilot plant for chemical treatment of tannery effluents. 1, effluent; 2, aluminium sulphate; 3, primary flocculation tanks; 4, air blower; 5, Emscher tank; 6, sludge blanket clarifier; 7, polycoagulant feed (Praestol).

the pH, temperature, effluent quality, degree of turbulence, retention period in the clarifier, etc.[59].

Most investigators reported that suspended particles in tannery effluent are positively charged. They are coagulated by anionic polycoagulants having numerous free electrical charges along the polymer chains.

Sproul *et al.* reported[60, 61] the application of Separan AP 30 with the following results: reduction of BOD by 50 per cent, SS by up to 99 per cent at the loading of the settling tank following the storage basin 14.0 m^3/m^2/day. The polycoagulant improved the thickening of the sediment[62].

Schwarz[63] performed tests with the anionic polycoagulant Praestol 2850. The effluent was chemically pretreated in the sludge blanket clarifier (*Figure 9*). At a dose rate of 200 mg/l of aluminium sulphate and 2–4 mg/l of Praestol the permanganate consumption decreased by 75 per cent. The raw effluent was mixed in the ratio 1 : 1 with domestic sewage.

The results achieved with the application of polycoagulants indicated that they may act as primary coagulants of tannery effluents, without pH adjustment.

SLUDGE DISPOSAL

In a well-operating purification plant with proper sedimentation[3] about 10 per cent of sludge is separated from the initial waste volume. This sludge contains up to 4 per cent of dry weight. The sludge volume should decrease to about 1–2 per cent of the initial volume of mixed waste water[3]. Modern methods give lower values.

The sludge is composed of the coarse material retained in the grid chamber and on the mechanical screens, chemically precipitated sludge from the equalization and sedimentation tanks, and biological sludge from the activation and final settling tanks. Fresh sludge has a low viscosity and may be easily transported in pipes.

The most simple and cheap method of tannery effluent sludge disposal is by thickening and air-drying it on prepared beds.

The theory of sludge thickening is based on the assumption of Kynch[64–66] that 'at any point in a dispersion the velocity of fall of a particle depends only on the local concentration of particles'.

Yoshica *et al.*[67] developed a graphical method for the determination of the minimum solids handling capacity, $G_{\min}$ (kg/m^2 h)

$$G_{\min} = \frac{w_x}{(1/c_x) - (1/c_k)} \tag{6}$$

in which c_x is the concentration of minimum solids flux between the inlet concentration, c_n, and concentration of the thickened sludge at the outlet, c_k,

w_x is the settling velocity at concentration c_x.

The minimum surface, F, of the thickener is

$$F = \frac{Q_n c_n}{G_{\min}},$$

in which Q_n is the discharge of the inlet into the thickener.

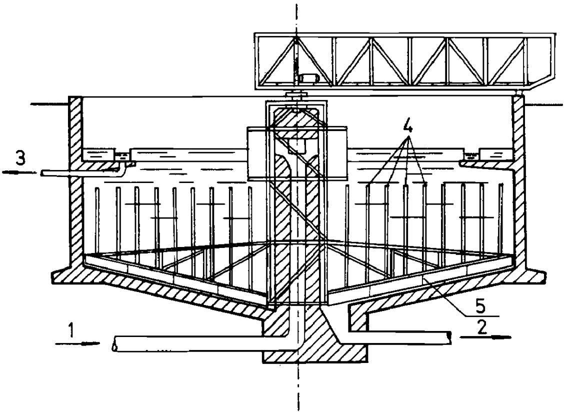

Figure 10. Flow-through thickener. 1, effluent; 2, outlet of thickened sludge; 3, outlet of decanted water; 4, stirring rods; 5, moving rakes.

The scheme of a continuous operating thickener is shown in *Figure 10.* This tank is provided with a stirring device. The sludge sedimentation is accelerated by the stirring at slow speeds. Jánský[68] reported the thickening of the mixed sludge from 2.5–6 per cent and the load of the thickener up to 5 kg/m^2 h.

The thickened sludge at a concentration of about 6 per cent is discharged to air-drying beds[69, 70]. The initial depth of the sludge depends on the desired parameters of the dried sludge and may reach 60 cm. A substantial part of the water from the thickening sludge (about 50 per cent) evaporates and the rest infiltrates through the layers of sand and gravel. The minimum

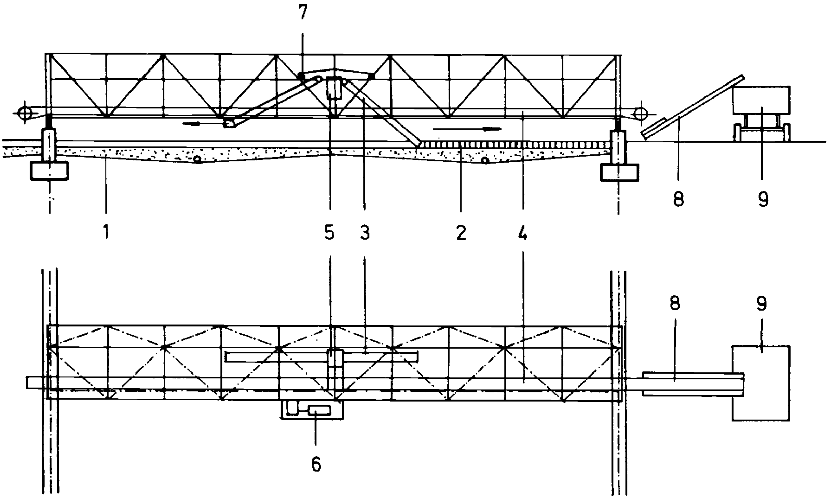

Figure 11. Air-drying bed with mechanical remover. 1, filter layer; 2, dewatered sludge; 3, removing device; 4, belt elevator; 5, remover drive, 6, bridge drive; 7, remover crane; 8, belt elevator; 9, lorry.

concentration of dried sludge for further transport is 20 per cent of dry weight. The period for air-drying is 14–21 days[3] in summer and up to 70 days in winter and in wet weather. The need of space is less than 0.1 m^2 for 1 kg of hides. The depth of the dewatered sludged on the sludge drying bed is generally about 20 cm. It is removed mechanically (*Figure 11*).

The digestion of sludge from tannery effluents is hindered[45,46] by the presence of toxic matters, especially sulphide and chromium. However, several authors commented[71] on the good digestion of mixed sludge from domestic and tannery effluents. Noack *et al.*[72] found in mixed wastes of domestic and tannery effluents in the 1:1 ratio 512 l/kg of gas per kg of organic matter, and in the case of a 1 (domestic):2 (tannery) ratio 460 l/kg of organic matter after 20 days of digestion.

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