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Components within waste-waters, their characteristics and environmental effects (ii)

Total Dissolved Solids (TDS)

The total dissolved solids content is a measure of the total materials held in solution. These solids are determined by filtering the effluent, then simply evaporating a known volume to dryness and weighing the residue. These products can be from all stages of wet processing, but those that readily biodegrade may be removed by comprehensive effluent treatment. Components that might remain are organic materials that are either persistent or take a long time to biodegrade, and inorganic salts.

However, the main components of TDS are inorganic salts, and are viewed as mainly sodium chloride and sodium sulfate:

CHLORIDE CONTENT (Cl)

Chloride as sodium chloride is introduced into tannery effluents from the large quantities of common salt used in hide and skin preservation, from the pickling process, and residual from the manufacture of auxiliary products. As sodium chloride is very soluble and stable, it is unchanged by effluent treatment and remains in the environment. Considerable quantities of salt are produced by industry, and levels can rapidly rise to the maximum acceptable for potable water. Increasing salinity in ground water, especially in areas of high industrial population, is now becoming a serious environmental problem.

Inhibition of growth is experienced with plants, bacteria and fish in surface waters, and at high levels can lead to breakdown of cell structure. Chloride presence can also be inhibitory to biological effluent treatment.

If the water is used for irrigation, the salt content increases at surface level due to evaporation and crop yields fall. When flushed from the soil by rainfall, sodium chloride re-enters the eco-system and may

enter the ground water. Salt is unaffected by conventional treatment, and can only be concentrated in solution by membrane filtration. Dry salt recovery is only possible by evaporation, and this option is not feasible. Only if discharges are into tidal/marine environments are high salt contents acceptable.

The level of salt as chloride under acid conditions can be determined by titrating a known volume of effluent with silver nitrate solution using potassium chromate as an indicator. Under neutral or alkaline conditions, an excessive addition of silver nitrate is offered to the sample. This is then determined by back titration with potassium thiocyanate using ferric alum as the indicator.

SULFATE COMPONENT (SO₄)

Sulfates are a component of tannery effluent, having been introduced either by the use of sulfuric acid, or through using products with a high sodium sulfate content. Many chemical products contain sodium sulfate as a by-product of their manufacture, for example, chrome tanning powders and many synthetic retanning agents. The treatment of sulfide by aeration represents an additional source.

High levels of sulfate can be lowered by calcium-containing compounds to form calcium sulfate as this has a low level of solubility; however, complete removal from solution is not viable. Generally, the sulfate remains, or is broken down by anaerobic bacteria to produce hydrogen sulfide and odour. This process occurs very rapidly in effluent treatment plants and sewage systems where the conversion results in corrosion of metal parts and gradual erosion of concrete unless sulfate resistant.

However, it is possible within effluent treatment to flush hydrogen sulfide from solution, then, following entrapment

within a bacterial filter and with limited oxygen availability, to recover sulfur. In addition, when present in grey waters used for land irrigation, sulfates can be reduced to sulfur within the soil, thus providing crop nutrient. Nevertheless, where levels are high there is the risk of the concentration building up within ground waters.

Sulfate analysis is performed by adding barium chloride solution to a filtered sample of effluent. The sulfates are precipitated as barium sulfate and filtration, drying and calculation can determine the sulfate level.

Sulfide content

The sulfide content of a tannery effluent results from the use of sodium sulfide and sodium hydrosulfide, and the breakdown of hair in the unhairing process. There are many problems associated with this material:

- Under alkaline conditions sulfides largely remain in solution. When the pH of the effluent falls below 9.5, hydrogen sulfide is evolved, and the lower the pH the greater the rate of evolution. Characterised by its smell of rotten eggs, a severe odour problem is created.
- This gas is as toxic as hydrogen cyanide and even low level exposure will cause headaches and nausea, and there is a danger of attack to the surface of the eye. Many deaths are recorded from sulfide build up in sewage systems.
- Hydrogen sulfide gas is fairly soluble, and can be removed using wet alkaline scrubbing techniques. However, when dissolved by water droplets resulting from condensation, weak acids are formed with resultant corrosion. This typically weakens metal roofing, girders and metal building supports. In sewers



Panel 5

The toxicity of effluent components

The toxicity of effluent components following dilution in surface waters is a complex subject and there is a shortage of specific data. This is due to the wide variety of aquatic life, the nature of individual components, and their degradation rate both in suspension and as part of sediment. It is not possible to be specific for complex and multiple components of effluent and the effects on fish, invertebrates, algae and daphnia can be quite different.

A measure of toxicity can be expressed as LD₅₀, representing the dose, which will kill 50% of a sample of a species. Not every species reacts to the same degree to a given exposure, and the type of response to an equal dose of a chemical may be very different. When values are given the species under test should be stated, and the time period taken for evaluation, normally 24 or 96 hours, or 14 days.

Environmental Quality Standards (EQS) are also used as a method of control for the protection of aquatic life, based on fate, behaviour and aquatic toxicity. Much of this information is drawn from research data covering a variety of sources and species to find the most sensitive. Considerable data is often available to form conclusions, but when data is scarce conclusions may include expert judgement. The EQS may be defined as the concentration of a substance, which must not be exceeded if a specific use of the aquatic environment is to be maintained.

Regarding metals that might be present in the tannery effluents - chromium, aluminium and perhaps zirconium, these are all classed as "high/moderate acute" and "chronic toxicity" to organisms and may accumulate. An acute effect may be defined as having a specific effect up to 96 hours on fish, and chronic effects may need a 21-day test period or even involve full life cycles including counting of eggs and their fertility.

The toxicity of many metals also varies according to pH temperature and water hardness. With reference to Cr(III), investigations have been performed on fish (unspecified) under conditions of exposure insufficient to cause severe toxicity, but sufficient to cause visual changes in behaviour. These dosages were at the level of 0.2 mg/l. It is understood, however, that daphnia has an even greater sensitivity, thus presenting a potential hazard to the fish food chain.

It should be noted that zinc and copper, although not used in processing leather, are described as high/acute and of chronic toxicity to aquatic life. These have maximum levels of 0.3 mg/l total

and 0.04 mg/l (dissolved) respectively as given in the Standards required by EC Fish Directive for salmon. Similar toxicity definitions apply to Cr(III) and it is stated that dosages of 0.2 mg/l caused behaviour change in fish (unspecified). In the absence of more specific data, loading in these orders might be considered as maximum permissible values for surface waters.

No limits are set for COD, as substances (and toxicity) cannot be specified. Other limits found in the Standards required for EC Fish Directives are presented in the table:

Suspended solids	<25 mg/l
BOD/5 days	<5 mg/l
Ammonia (as NH ₃)	<0.025 mg/l
Kjeldahl Nitrogen	<0.78 mg/l

It should be noted that there are no values for sulfides, although an excess will kill bacteria. The presence of sulfides will be included in the BOD analysis.

DIRECT TOXICITY ASSESSMENT

The use of chemical/biological methods of analysis with regard to toxicity limits of specific effluent components has been the basis for determining the limits for discharge into receiving waters. These techniques, however, cannot always account for:

- Unexpected toxic effects from the reaction of seemingly innocuous substances when mixed together.
- Some substances being toxic to aquatic life at levels too low for detection techniques to measure.

Techniques are under investigation in the USA and Europe that break away from the traditional approach. This involves taking samples of the effluent and testing the effect at various dilutions on organisms of increasing complexity, such as algae, daphnia, water fleas and fish that might be found in surface waters. Known as Direct Toxicity Assessment, this technique provides a means of testing the effects of complex discharges under near real conditions.

It is noted that where tannery discharges are directly into sewers, the municipality will hold the responsibility for final discharge. Where industrial waste-waters are directly received into surface waters, however, the industry may be directly affected, and investigations might lead to redefinition of limits at local and national levels.

major problems can result from corrosion of metal fittings, reinforcement and pipework.

- If discharged to surface water, there are toxicological dangers even at low concentrations. Sulfides can be oxidised into non-toxic compounds by certain bacteria in rivers, but this creates an oxygen demand and if excessive there is

damage to aquatic life.

Sulfide can be readily oxidised within effluent treatment using induced air, with manganese sulfate acting as a catalyst, to form mainly sodium sulfate. Alternatively they can be precipitated as ferrous sulfate.

There are several methods of determining sulfides. One of the most accurate relies on

the acidification of suitable quantities of effluent to generate hydrogen sulfide. This is flushed through the apparatus using nitrogen gas, trapped and converted into zinc sulfide, then assessed by iodine/thiosulfate titration. 

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