

Back to Basics: Environmental - Part 3 of 10

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

The main areas of focus for the monitoring and control of treated tannery effluent are, volume, the oxygen demand, suspended solids, total dissolved solids, sulfide, chrome as Cr and pH. However, there are many components in effluent and, if found in excess in relation to the local environment, then accordingly they are taken into closer account.

The detail given in the following sections addresses these major components in general, and their effects on the environment. Where appropriate, an overview of the techniques used to determine the levels of these elements is also given to provide insight into their nature.

The oxygen demand

Many components in effluents are broken down by bacterial action. Oxygen is required both for the survival of these bacteria (aerobic bacteria) and for the breakdown of the components. This breakdown can occur quite rapidly or may take a very long time according to the effluent composition.

If an effluent creates a high oxygen demand and is discharged directly into surface water then the sensitive balance maintained in the water is overloaded. Oxygen is stripped from the water causing oxygen-dependent micro-organisms, plants, fish and the river or lake to die. An environment where bacteria which are non oxygen-dependent (anaerobic) then becomes established creating toxic conditions in the waterway.

A healthy river can tolerate low levels of oxygen demanding substances, but the load created by tanneries is very high, so the effluent requires treatment before discharge.

Although primary effluent treatment, using chemical means and physical separation will reduce this demand, a secondary biological stage is required. Known as activated sludge treatment, the process uses bacteria to digest many soluble effluent components. This process requires high levels of oxygen being introduced into the effluent by blowing in large volumes of air. The plant has high capital and operational costs, and demands high levels of energy.

If the process works ideally, then water and carbon dioxide are produced in large volumes, but the process depends upon the growth of bacteria. As these die they form a biological sludge that has to be treated and ultimately disposed of. This sludge has a high water content and is often quite difficult to dewater, adding considerably to the treatment costs.

To assess the impact of an effluent on either discharge to surface waters or to set a value on the costs of treatment, the oxygen demand needs determining and this can be achieved in two different ways.

BIOCHEMICAL OXYGEN DEMAND (BOD₅DAY)

The technique for measuring the Biochemical Oxygen Demand (BOD) can be difficult to accurately manage. Essentially, the shaken effluent sample is allowed to stand for one hour so that all settled solids are excluded from the analysis. The liquor (supernatant) above the precipitate is drawn off and used in the analysis. A suitable volume of this sample is diluted in water, pH adjusted, and seeded with bacteria (often-settled sewage effluent). The samples are then incubated for five days in the dark at 20°C +/-1°C. The bacteria use oxygen dissolved in the water as the organic matter in the sample

is broken down. The remaining oxygen is determined either by an oxygen meter or by analysis. By comparison with effluent-free blank samples, the level of oxygen demanded by the effluent can be calculated.

This analysis, generally termed BOD₅, is widely used to assess the environmental demands of a waste-water. There are various weaknesses with this method of detection; the bacterial cultures can vary and the analysis is sensitive. If the most stringent care is not taken in preparation and analysis the results can be misleading.

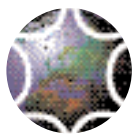
It should also be remembered that, although this is a measure of the oxygen requirements of bacteria under controlled conditions, many effluent components take longer than five days to break down. Some chemicals will only be partially broken down, while others may not be significantly affected. Typically, vegetable tanning wastes have a long breakdown period, often quoted up to 20 days. These longer digestion periods can apply to a variety of the chemicals used in manufacturing leathers, including certain retanning agents, some synthetic fatliquors and dyes.

This longer breakdown period spreads the environmental impact to a greater area, as the waste-water components are carried greater distances before breakdown.

CHEMICAL OXYGEN DEMAND (COD)

This method measures the oxygen required to totally oxidise the effluent sample. It sets a value on the materials that would normally be digested in the BOD₅ analysis, the longer term biodegradable products, as well as that are not affected by bacterial activity.

The method is very aggressive. A suitable volume of effluent is boiled with a powerful oxidising agent (potassium

**Panel 4****The disposal of used chrome tanned leather goods**

As 85-90% of leathers are chrome tanned, these leathers in themselves create a problem. Chrome compounds are safe in tanning, and chrome containing solid waste and sludges are manageable. However, leather goods are dispersed by the end of a useful life. They will not biodegrade, and simple incineration can convert some of the chrome into the dichromate form. Although these leathers can be ashed safely under controlled conditions, the logistics of collection and cost of treatment must ultimately be addressed.

dichromate) and sulfuric acid. As the effluent components oxidise they remove oxygen from the potassium dichromate and this removal is determined by titration.

This method is often favoured as it provides results in hours as opposed to days. It is more reliable and cost effective, as it is easier to manage larger numbers of samples.

These results are always higher than the BOD₅ results. As a rule of thumb the ratio between COD:BOD in untreated effluent samples varies between 2:1 and 3:1, and can rise to 100:1 for treated effluents. These ratios are dependent upon the chemicals used in the different leather making processes and their rate of biodegradability.

It should be noted that both of these techniques are based on settled effluent, not filtered. The semi-colloidal material that forms part of the suspended solids is also included in the BOD and COD determinations. Normally 1 mg/l suspended solids will generate a COD increase of approximately 1.4 mg/l.

Solids

There are several different classes of solids found in tannery effluent.

GROSS SOLIDS

These solids are larger than a sampling machine can handle and are therefore not measured. Their presence is, however, obvious and fully recognised due to the dangers that they present.

These solids are often large pieces of leather cuttings, trimmings and gross shavings, fleshing residues, solid hair

debris and frequently broken down paper from bags. The largest pieces can be removed by coarse bar screens set in the waste-water flow, then screening at 0.5-2.0mm, and settlement.

Major problems can develop with these materials if they settle in pipe work as they provide a source of blockage. The problem can become very serious when effluents have to be pumped, as often the blockages occur in inaccessible pipe work. The costs of replacing a burned out motor or broken rotors are high.

If discharged into gullies, ditches or water-courses the debris rapidly accumulates causing blockage and stagnation.

SUSPENDED SOLIDS (SS)

The suspended solids component of an effluent is the quantity of insoluble matter contained in the waste-water. These insoluble materials cause a variety of problems when they are discharged from a site, and essentially are made up of solids with two different characteristics.

Settleable solids

This is material which can be seen in suspension when an effluent sample is shaken, but settles out when the sample is allowed to stand. The majority of these solids settle out within 5 to 10 minutes, although some settling of fine solids can still be taking place after one hour.

These solids are produced from all stages of leather making and comprise of fine leather particles, residues from various chemical discharges and products from different waste liquors reacting together. A very large quantity is generated from beamhouse processes.

If the waste-waters are for treatment as provided by sewage works or common effluent treatment, the main problems are due to the considerable volume of sludge formed in primary treatment as the solids settle out. Sludge often contains up to 97% water, creating huge quantities of 'light' sludge. However, viscous sludge contains water at around 93%, and can easily cause blockages in sumps, sludge pumps and pipe work. All of this sludge has to be removed, transported, dewatered, dried and deposited causing high demands on plant, equipment and resources.

If the discharge is into surface water, then the flow rate will strongly influence how far the material carries before it settles out on the bed of the stream or river. Even a thin layer of settled sludge

can form a blanket that cuts off oxygen from that area of the river or lakebed. The plant and aquatic life die, creating foul conditions.

Semi-colloidal solids

These are very fine solids that for practical purposes will not settle out from an effluent sample, even after standing for a considerable time. They can, however, be filtered from solution and, therefore, together with the more readily settleable solids, form the suspended solids of an effluent as measured analytically.

The majority of these solids are protein residues from the beamhouse operations - mainly liming processes - but high quantities are also produced from poor uptake in vegetable tanning processes. Other sources are from retanning areas, but, they can be removed by coagulation and settling.

These solids will not directly cause sludge problem, but they can break down in the long term. This is by bacterial digestion producing solids, which will eventually settle, while also creating a high oxygen requirement.

THE DETERMINATION OF SOLIDS**Outline determination of suspended solids**

Gravimetric suspended solids analysis measures both settleable and semi-colloidal solids and the technique is simple. A known volume of the effluent is taken and filtered through a filter paper, which is then dried and reweighed. The difference between this weight and that of the original paper is the weight of the dry solid material contained in the sample.

Outline determination of settleable solids

The suspended solids analysis is the most common method used to assess insoluble matter, but occasionally the settleable solids content is required. This measures the solids component with the fast settling rate. This can be determined by allowing the shaken sample to settle and filtering a known volume of the semi-colloidal matter remaining in suspension. After drying and weighing, the quantity of semi-colloidal matter can be calculated. The difference between the suspended solids and this figure is the level of settleable solids. ●

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