



Back to Basics: Environmental - Part 5 of 10

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

Nitrogen

Nitrogen is contained in several different components in tannery effluent and sometimes there is a need to differentiate between these sources.

TOTAL KJELDAHL NITROGEN (TKN)

Several components in tannery effluent contain nitrogen as part of their chemical structure. The most common sources are ammonia from ammonium salts used in deliming, and generated - together with urea and amines - from the hydrolysis of proteinaceous materials from liming/unhairing operations.

There are two direct problems:

1. Nitrogen is required for plant growth, but high levels made available from nitrogen-containing substances overstimulate this development. Water based plants and algae grow too rapidly, so waterways become clogged and the flow can become restricted. As these plants die, there is a disproportionately high amount of organic matter for breakdown. If this load exceeds the natural supply of oxygen from the river, then plants, fish and micro-organisms die and ultimately anaerobic conditions develop.
2. Nitrogen released from the hydrolysis of proteins and from the deliming process exists in the ammoniac form. This can be converted by bacteria to form water and nitrogen gas, which is released to the atmosphere. Both of these breakdown products are non toxic, but large quantities of oxygen are needed in the process. If this oxygen demand is greater than the natural level of supply

in a watercourse, then toxic anaerobic conditions rapidly develop.

These nitrogen-containing compounds can be broken down as an added component within biological effluent treatment. In this event the effluent is slowly circulated from the normal aerobic biological treatment, through an anaerobic stage and back to the aerobic, with the evolution of nitrogen gas. However, an additional oxygen demand is created, requiring an increase in plant size and energy costs. Calculations show that with a typical tannery effluent, around 40% of the oxygen requirements are taken up by removing the nitrogen component.

The nitrogen-containing compounds, except nitrate or nitrite, can be determined by the Kjeldahl method of analysis. In this technique, boiling with sulfuric acid to form ammonium compounds digests all the nitrogen-containing matter. In a second stage this ammonia is released by boiling with sodium hydroxide, then trapped in a boric acid solution. The level of ammonia released is determined by titration and the value as nitrogen calculated.

AMMONIUM CONTENT AS NITROGEN (N)

This is sometimes required in discharge limits and often confused with TKN. As ammonium compounds are a large part of the TKN, the problems associated with rapid plant growth and oxygen demand are the same. These compounds mostly result from the deliming, neutralisation and dyeing processes, with a comparatively small quantity produced from liming and unhairing. The analysis is similar to TKN but omits the initial digestion stage. The nitrogen component resulting from protein wastes is thus excluded.

Oils and grease

Natural oils and greases are released from within the skin structure during leather manufacture.

As greases and fatty precipitates float, they can form mats, which collect and bind other materials causing a potential blockage problem, especially within effluent treatment systems. If surface waters become contaminated with grease or thin layers of oil, the transfer of oxygen from the atmosphere will be reduced. If these fatty substances are in the form of an emulsion, being biodegradable they create a very high oxygen demand.

These components are determined by shaking the effluent sample with a suitable solvent and allowing the solvent to separate into a layer on top of the effluent. This solvent dissolves fatty matter and a quantity can be drawn off and evaporated to dryness. This leaves residual grease for weighing and calculation.

pH value

Acceptable limits for the discharge of waste-waters to both surface waters and sewers are found ranging from between pH 5.5 to 10.0. Although tighter limits are often set, there is always greater tolerance to the alkali side. This is because carbon dioxide from the atmosphere and from biological processes in healthy surface water systems tends to lower pHs very effectively to neutral conditions. If the pH of surface waters is moved too far either way from the pH range 6.5 - 7.5, then there is loss of more sensitive fish and plant life.

Municipal and common effluent treatment plants prefer discharges to be more on the alkali side as the corrosive effect on concrete is reduced. Metals tend



to remain insoluble and more inert, and any evolution of hydrogen sulfide is minimised. When biological treatment is carried out the pH is lowered to more neutral conditions by evolved carbon dioxide.

Chromium compounds

Metal compounds are not biodegradable and are viewed as remaining long term in the environment, or being accumulative. For this reason they receive close attention. There are two forms of chrome associated with the tanning industry, and their properties are often confused.

CHROME (III) - trivalent chrome

Chromium compounds are produced as waste from the chrome tanning process, as part of retanning systems and by displacement from leathers by retanning and dyeing processes.

This chrome is discharged from processes in the soluble form but when it is mixed with other tannery waste-waters from other processes, especially if proteins are present, there is a very rapid reaction. Fast-settling precipitates are formed, mainly protein-chrome, which add to the sludge generation.

However, very fine semi-colloidal solids are also formed, and these have been made very stable by the chrome - in effect the protein has been partially tanned. This makes this component more resistant to biological breakdown, and the biological treatment process is inhibited.

If these colloids pass into the wider environment, such as a river, they break down slowly creating a precipitate of chromium hydroxide, which will remain long term in the eco-system.

When chrome enters a treatment system, the sludges become contaminated. This in turn restricts the methods of disposal.

There are several methods of determination, but the first stage usually comprises boiling a known volume of sample with concentrated nitric acid to ensure complete solution of the chrome. After suitable dilution, the chromium level is determined by atomic absorption. Iodine/thiosulfate titrations are sometimes used where high levels of chrome are expected, but this technique is not accurate at low concentrations.

CHROME (VI) - hexavalent chrome

Hexavalent chrome is not found in tannery effluent. Although this product

Panel 6

Sampling techniques

The composition of an effluent sample is very dependent upon the sampling technique. This can affect the apparent performance of a tannery against set limits. There are two main methods that are used:

1. Composite: samples taken over a 24-hour period and mixed together.
2. Spot samples: a single sample is taken for analysis.

Ideally, an automatic sampler should take composite samples, with 24 samples taken at one-hourly intervals and mixed before analysis. If charges are made, then these are normally based on these values.

Where spot samples are taken, there are usually allowances for variation in effluent strength, often allowing a 50% increase in strength although this may not apply to all components.

The position of the sampling head is important. If it is too low, then there is the possibility of sludge being drawn into the sampler. This is also an important point when spot samples are taken as these are often manual. The sampling point should always be the same to reduce variables.

It is noted that when an authority takes samples the tannery should hold a duplicate sample. The sample should be shaken before the duplicate is poured, and the sample bottle should be clean, fully filled, airtight and kept under cold conditions. It is not unknown for samples to be incorrectly identified, or mistakes to be made in analysis. Duplication always gives a visual check against the original, and the chance for a second analysis if there are reasons for doubt.

was used within the first chrome tanning systems around 100 years ago, it was reduced within the process to form a tanning agent. Forms of chromium sulfate soon replaced this early technique, and chromium tanning compounds are now used in the trivalent state.

Although Cr(VI) does not comprise part of tannery effluent, for the record, for industries where Cr(VI) is used in operations, dichromates are toxic to fish life. There is easy penetration of cell wall, absorption being mainly through the gills, and it is accumulative. Analysis is specialised, being based on colorimetric analysis at 55 nm.

Other metals

Other metals which might be discharged from tanneries and where limits to discharge may be set include aluminium and zirconium.

These metals have different toxicity according to the chemical species, also by the presence of other organic matter, complexing agents and the pH of the water. In particular, aluminium appears to inhibit the growth of green algae and crustaceans are sensitive to low concentrations.

Cadmium, which might occasionally be found in some pigments, if subsequently solubilised under acid conditions, is considered highly toxic. It is accumulative and has a chronic effect on a wide range of organisms. If it becomes a component of potable water it can cause bone embrittlement.

Solvents

Potential sources of solvents are degreasing and finishing operations. However, solvent degreasing systems have been largely replaced by water-based degreasing techniques, and the availability of new finishing products has very significantly reduced solvent use in finishing. Nevertheless, solvents in effluents discharged to surface waters can form a microfilm on the surface of the waters, inhibiting uptake of oxygen. The breakdown of solvents is variable. Some inhibit bacterial activity and remain in the eco-system for long periods of time. Analysis is highly specialised. ●

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