



Anaerobic digestion of tannery sludge: Lowering salinity to reduce sludge volume

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An investigation was performed to minimise the volume of tannery sludges by bio-degradation. To overcome the inhibiting effects caused by inorganic solubles used in leather manufacture, a novel technique was employed to reduce the salts content of these sludges. The investigation proved a success, and achieved a significant reduction in the volume of the sludge.

In a partnership between UNIDO and Zimbabwe's Bata Shoe Company, the 18-month research programme was conducted under the technical supervision of consultant Johan Barnard, Envirotan Water from South Africa. Bata (Zimbabwe) supported the effort with hardware and day-to-day manpower while UNIDO funded the consultant expertise under the ongoing project "Assistance in Tannery Pollution Control" (US/ZIM/98/069).

Solid waste treatment and its disposal is the single most expensive part of tannery waste management, and sludge disposal has become a major problem due to stricter disposal legislation and control. It is well known that bacteria decompose organic matter under anaerobic conditions as generally applied in the sewerage treatment industry. The volume of domestic solid waste is typically reduced by at least 60%, while the quality of the waste is improved, allowing less restrictive disposal routes. The process generates a significant volume of biogas (*a mixture of methane and carbon dioxide*), which can be used as a relatively clean energy source.

Anaerobic treatment of tannery sludge has been researched by others, but due to malodorous hydrogen sulfide gas generation and the generally poor efficiency of solids decomposition the process has not become viable for the tanning industry. It is believed that the poor efficiency is mainly due to the inhibiting effects of the high concentration of various inorganic salts present in the wastewater.

The research concept

It is possible to achieve a reduction in the salt concentration of a sludge by sludge dewatering, followed by re-hydration with pure water before digestion. The volume of water used is small if compared with the overall water usage. The majority (>90%) of the soluble inorganic salts can be removed during the dewatering step.

The total solids content of mixed tannery effluent is typically

around 15,000 mg/l. Of this, at least 10,000 mg/l (10g/l) represents inorganic dissolved salts, while the balance is made up of 4,000 mg/l suspended organic solids and 1,000 mg/l dissolved organic solids. Anaerobic digestion is capable of dissolving and digesting the biodegradable organic solids fraction.

With the suspended solids (SS) content of the mixed tannery effluent around 4,000mg/l, one kilogramme of SS is associated with 250 litres of water. After chemical precipitation of the solids and dewatering, the water volume left per kilogramme of solids is 4 litres at 25% solids content.

Before anaerobic digestion the sludge is re-hydrated back to around 5% solids by adding 16 litres of fresh water per kilogramme of solids. At this solids content it is possible to pump and mix the sludge inside the digester, which allows more efficient digestion.

This technique reduces the salt load by a factor of 250/4 i.e. from 10,000 mg/l as inorganic dissolved solids to 160 mg/l. This assures that the concentration of salts is reduced below the maximum allowable level for efficient methanogenic anaerobic digestion.

The volume of re-hydration water may be reduced if cleaner production technologies are introduced during tanning processes. The specific reduction of sodium, chloride and sulfate ions may be achieved by using salt-free hides, carbon dioxide de-liming, pickle liquor recycle and high exhaustion chrome tanning. Bata was using some of these techniques at the time of the trials. ►



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The Pilot Study

The sludge digestion pilot plant consists of a pre-mix tank coupled to a digester. Mixing within the system was managed using a re-circulating pump, and the temperature controlled to 35°C.

Sludge was fed on a daily basis and control variables including pH, volatile fatty acids (VFA), alkalinity and gassing rate were monitored. These parameters helped to determine the solids loading potential of the system.

Due to the sensitive nature of the methane forming bacteria to variations in pH, a maximum VFA to alkalinity ratio of 30% was set to maintain an optimal pH range of pH 7.0 to 7.8. Control of pH outside the stipulated range was achieved via additions of either bicarbonate ($pH < 7.0$) or phosphoric acid ($pH > 7.8$) to the system.

The system was operated on a daily feed and bleed basis. Although the clear supernatant liquor extracted from the digester contained mainly dissolved solids, the solids build-up in the digester was surprisingly low during the loading phase. The space load rate of the system ranged between 1 to 5 kilogrammes of dry solids per cubic metre digester volume per day.

The tannery and waste water plant

At the time of the investigation, the Bata tannery (location: Gweru, Zimbabwe) processed around 500 salt cured hides to the finished state for footwear leather per day. This generated around 300 kilolitre of wastewater per day, comprising a stream of high pH sulfide containing liquors and a second stream of low pH and general liquors.

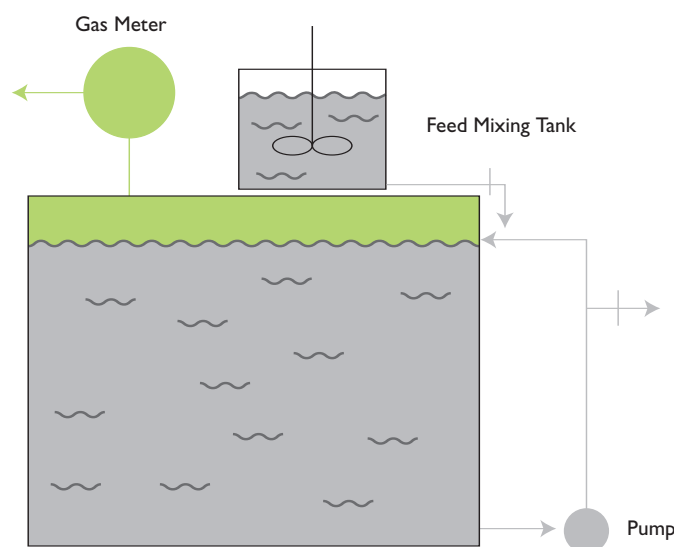
The first stream was aerated in a sulfide oxidation basin until the sulfide concentration dropped below 10 mg/l. The two streams then mixed in a mixing tank, where lime and alum were added manually until flocculation was achieved. The mixed liquor was then transferred to two parallel clarifiers for sludge precipitation, and the settled sludge transferred to sand drying beds.

The clarified liquors were pumped to two large, biologically active, evaporation ponds, located some four kilometres from the factory. Due to the relatively low organic concentration of the effluent, these ponds were capable of breaking down the organic pollution load, without the presence of malodour present in typically overloaded ponds. It is significant to note that the ponds also sustained a viable population of *Spirulina Algae*, which attracted a large variety of aquatic bird species.

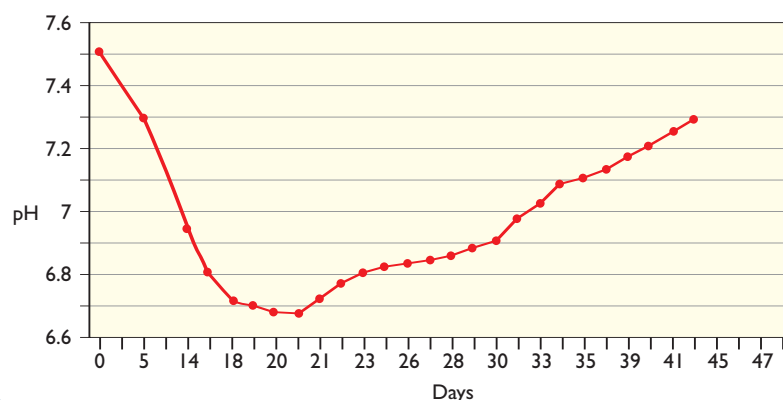
Due to the high exhaustion chrome tanning process, chrome was not precipitated separately, which enhanced the alum flocculation process, and the quantity of chrome present in the effluent was substantially lower than normal. The average COD of the clarified liquor was around 1,000 mg/l., partly due to efficient primary treatment and the use of cleaner production technologies, notably lime liquor recycle and CO₂ deliming.

The settled sludge with about 3% solids content (around 675 kg as dry mass) was transferred to the sludge drying beds. After seven days of dewatering and drying the sludge achieved a solids concentration of around 25%, being equivalent to 2,700 kg of wet spadable sludge.

Panel 1: Anaerobic Digester Pilot Plant



Panel 2: pH stabilisation at start-up Anaerobic digestion of tannery sludge



The pilot anaerobic digester plant

A plastic container with a 1,000-litre capacity was fitted with inlet and outlet pipe connections and used as a digester. A mixing tank of 50-litre capacity was connected for the feed, and a circulating pump with a capacity of 40-litres per minute was used to mix the system. A thermostat controlled the temperature through a direct electrical heating element mounted in a jacket inside the digester. A gas meter was fitted on the top of the digester. The general arrangement is shown in *Panel 1*.

The start-up phase

The unit was started by adding 10 kilogrammes (based on dry solids) of sludge to 1,000 litres of water. No further sludge was added to the unit, and it was allowed to stabilise. During a six-week start-up period a population of methane gas bacteria established itself. An initial drop in pH to 6.6, followed by a gradual increase back to 7.5 typifies this phase. This is illustrated in *Panel 2*.

It is important to note that the anaerobic digestion process is typified by two distinct biochemical phases:



Acid phase bacteria – have the ability to liquefy solids via enzymatic chemical action. The end product of this stage is volatile fatty acids (VFA), which mainly consist of acetic acid. Under ideal conditions the acid phase bacteria can reproduce quickly, and with high solids loading the pH will drop relatively fast.

Gas phase bacteria – reproduce very slowly, and, as they digest the VFAs cause a rise in pH. They do not generate gas at a pH below seven.

For this reason, it is important to feed the digester at a rate that satisfies both types of bacteria. Initially the digester is fed at a very low loading to allow the gas phase bacteria to grow without stress. As more gas phase bacteria is formed the loading rate may be increased.

The loading phase

After the six-week stabilisation period, routine feeding was started, at a digester space load rate (SLR) of 0.05-kg sludge per m³ per day. This rate was increased at a rate of 10% per day, for five days a week. A digester SLR of 5.5 kg was reached after 170 days on line, as shown in *Panel 3*.

The solids concentration inside the digester increased gradually over time. The total solids reduction over the period is calculated by expressing the solids added during the period to the total solids left at the end. The performance is shown in *Panel 4*.

This reduction of solids is relatively high compared with other findings (e.g. *domestic sludge at 60%*). This is ascribed to the relatively low inorganic content of the sludge feed due to the washing technique and the high biodegradability of the organic

solids. It is noted that at a later stage of the study BATA reported a solids reduction higher than 90%.

Control of the digester

The loading potential of the digester is a function of acid and gas bacteria being able to perform well together. Acid bacteria reproduce quickly, so consequently the VFA concentration will also rise quickly, and pH will drop. Gas bacteria reproduce slowly, but once a population is established, it will convert all the available VFA to gas and pH will rise.

Control of the process may be achieved by monitoring the digester pH. However, due to the buffering effect of bicarbonate in the digester, the change in pH due to overloading is only noticed after the buffering capacity of the unit has been exceeded. By this time a sudden drop in pH is noticed and gas phase bacteria are lost due to the low pH.

The system should be controlled between pH 7.0 and 7.6. The best way of controlling this is by measuring VFA and alkalinity daily and to adjust the feed load by keeping the VFA: Alkalinity ratio below 0.3. As it is not always possible to achieve this smoothly, external control of pH may be required.

If pH threatens to drop below pH 7.0, bicarbonate buffer may be added to the digester. If the pH rises beyond pH 7.6, it is possible to either increase the feed loading or to add an acid. Normally phosphoric acid is added, as the phosphorus (P) is required as a micronutrient for the bacteria. Tannery sludge does not normally contain enough P relative to the nitrogen (N) and carbon (C) concentrations. The ideal ratio between C : N : P for good anaerobic digestion should be about 100 : 16 : 1.

In addition, the daily gas production is an ideal indicator of the viability of the gas phase bacteria and the system.

It is noticeable that the VFA to alkalinity ratio increased beyond 30% towards the end of the run of 150 days. The pH was still higher than pH 7.0, but the system became vulnerable due to the low buffering capacity. This occurred at a SLR between 3 and 4 kg per m³ per day. From this it may be concluded that the system should not have been loaded higher than 4 kg / m³ / day, to avoid the danger of losing the gas phase bacteria.

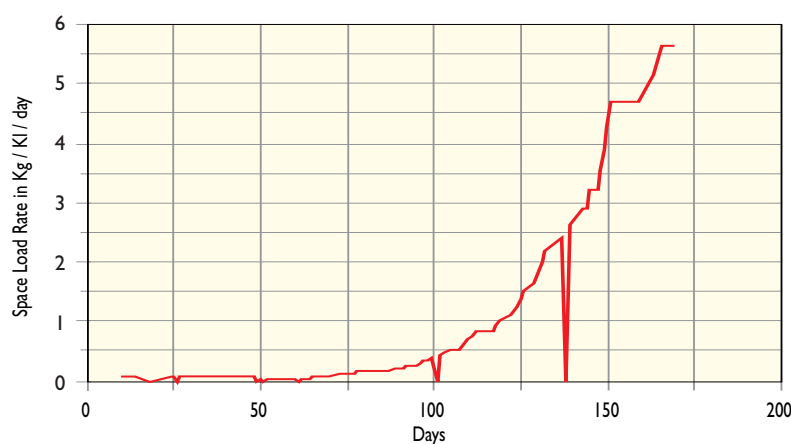
Temperature effects

It is well known that anaerobic bacteria work optimally at a temperature ranging between 34 and 38°C. The efficiency of the system reduces dramatically at lower temperatures. In this study the ambient temperature of the digester contents ranged between 15 and 25°C, so it was necessary to heat the digester contents to achieve an effective digester space load rate.

The heating of systems requires costly energy input, and use of temperature control depends on the efficiency of biogas production from the digester. Ideally the process should have a positive energy balance.

This is typically achieved when the biodegradable COD fraction of the feed exceeds 5000 mg/l. At 3 to 5% solids, tannery sludge typically exceeds this COD limit by far, but the gas production within this study did not reach an economically viable level. This may have been due to the large temperature variation, as the temperature control did not work well. The temperature varied between 42 and 18°C, and this variation did not allow the gas phase bacteria to perform ➤

Panel 3: Digester space load rate
Anaerobic digestion of tannery sludge



Panel 4: Percentage reduction of washed sludge

Total solids added over 170 days	=	93 kg
Total solids left inside digester	=	16 kg
Then solids reduction is	=	77 kg
Percentage reduction	=	77 / 93
	=	82.8%



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optimally. Also, temperatures above 40°C can cause permanent failure of the gas phase bacteria and must be prevented at all cost.

Inhibiting chemicals

Chemicals in tannery sludge that may inhibit the process are sodium, calcium, ammonia, chloride, sulfate, heavy metals, and bactericides. As shown in the section entitled "The research concept", the salts were reduced below the critical inhibiting level of 3000 mg/l by the sludge washing technique. Laboratory studies also ruled out the possible effect of trivalent chromium as used by tanners. At the pH range of anaerobic digestion, the Cr(III) is not in solution and addition of higher Cr(III) concentrations did not inhibit the gassing potential of the system. The effects of bactericides were not tested, but according to literature some of the additives to degreasing chemicals may have a preserving effect up to 100 days. Glutaraldehyde also has a bactericide effect, and will tend to be precipitated with sludge during wastewater treatment.

Gassing studies

After the installation of a gas meter, the sludge loading of the unit was reduced back to one kilogramme per 1,000 litres per day. This loading was maintained until reasonably steady gas measurements were made between days 290 to 320. The load

was increased to two kilogrammes per m³ per day at day-320. The gassing rate of the system doubled after the sludge feed was doubled. The conversion rate of gas volume per kilogramme of dry solids feed, reached 150 litres per kilogramme.

This is considerably lower than approximately 600 l/kg/day as expected of highly biodegradable organic solids, although an improved control of temperature may be significant.

Findings from the investigation

- Good sludge digestion was obtained after washing sludges to reduce the inorganic solubles (*salts*) content.
- During the main part of the research period the solids reduction of tannery sludge averaged about 83%. Later Bata stated reductions to 96%.
- It was found that good handling skills—especially temperature control—are of utmost importance to achieve positive process performance.
- Bio-gas production of 150 litres per kilogramme dry solids was achieved and could probably have been increased with improved temperature control.

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