Treatment of gelatine factory effluent†

JP Maree[1]*, CGB Cole[2], A Gerber[1], and JL Barnard[3]
[1]*Division of Water Technology, CSIR, PO Box 395, Pretoria 0001, South Africa*
[2]*Davis Gelatine Industries, PO Box 5019, West Krugersdorp 1742, South Africa*
[3]*Meiring and Barnard CC, PO Box 28734, Sunnyside 0132, South Africa*

Abstract

In the process of gelatine manufacture, bovine hide is soaked for several months in lime pits. The pit effluents are high in pH, COD and calcium content and constitute a major source of pollution. Because of the associated municipal levies for effluent discharge, there are prospects for the installation of an economic, on-site treatment facility.

Two process configurations were evaluated for treatment of the above effluent, namely anaerobic treatment and combined anaerobic-aerobic treatment. In the latter treated water was used to dilute the raw water by 58%. Calcium carbonate which precipitated during treatment, served as a medium on which bacterial growth could occur in the primary anaerobic stage. Ceramic Raschig rings were used as immobilisation medium in the aerobic biofilter and activated carbon in the secondary anaerobic stages.

Insoluble organic and solubilised and complex organic molecules were biodegraded to simpler molecules through hydrolytic reactions in the primary anaerobic stage. The produced molecules were further fermented to short-chain volatile acids, resulting in the pH of the water being reduced from 12,0 to 8,1, the COD reduced from 20 500 to 17 500 mg/ℓ and calcium reduced from 5 210 to 1 680 mg/ℓ (as $CaCO_3$) as a result of calcium carbonate crystallisation. Except for the initial period of the experiment (first 50 days) no methane production was achieved in the anaerobic reactor as a result of high concentrations of sulphide (1 200 mg/ℓ (as S)), ammonia (1 800 mg/ℓ (as N)) and propionic acid (1 000 mg/ℓ), and a pH of 7,9. In the aerobic and secondary anaerobic stage, organic acids were biodegraded to CO_2, resulting in a further COD reduction to 6 000 mg/ℓ and calcium reduction to 230 mg/ℓ (as $CaCO_3$). This study demonstrated that the effluent can effectively be neutralised via biological treatment, resulting in a 95% removal of the effluent calcium and a 74% reduction of the COD value.

Introduction

Gelatine is a heterogeneous mixture of water-soluble proteins derived from the collagen of animal hide or bone. It has a diversity of uses, for example, in food from wine fining to confectionary and in industry from matches to photography.

In South Africa the main source of gelatine is bovine hide and only the pieces not suitable for tanning are used. The "waste" hide available varies from green masks from local abattoirs through partly processed (dehaired) tannery waste (both wet and dry), to hide preserved by drying, salting, and also by treatment with sodium metabisulphite for short-term preservation.

The process used to convert insoluble hide collagen into water soluble gelatine is a process of protein hydrolysis and denaturation, and the first step is one of prolonged soaking in a dilute lime suspension in lime pits. The soaking results in swelling of the hide and a marked reduction in shrinkage temperature. This treatment permits the complete conversion of collagen to gelatine of good gelling properties. Another obvious effect of liming is the hydrolysis of asparagine and glutamine with the release of ammonia and the consequential drop in the isoelectric point of the collagen from 9 to 5. The effluent of the lime pits is referred to as pit liquor. After liming the conditioned hide is extensively washed and treated by soaking in dilute acid in order to reduce the inorganic contamination to low levels. The final denaturation of the collagen is achieved by gentle warming to produce a dilute solution of gelatine which is then filtered, concentrated, gelled, dried and milled to a powder. The process produces a large amount of effluent, approximately 300 m³/t, and hence both water and effluent disposal are major cost factors.

Because of the large volume of water involved it is unlikely that it would be economical for Davis Gelatine to undertake its own final effluent treatment. However, it is fortunate that pit liquor constitutes a relatively small volume (96 m³/d) of highly contaminated water at 20 000 to 25 000 mg/ℓ COD, which is responsible for some 20% of the total effluent contamination. Hence, treatment of this volume may well prove to be economical at today's high municipal disposal charges.

The aim of this study was to evaluate, from a technical point of view, the following two process configurations for the removal of chemical oxygen demand (COD) and calcium, and neutralisation of the water:

- anaerobic treatment and
- anaerobic-aerobic-anaerobic treatment.

Materials and methods

Feedstock

For the purpose of these experiments, which were spread over more than twelve months, 25 ℓ of a composite pit liquor from the factory was made up from time to time. Samples were taken from several pits that had come to the end of their liming time and these samples were blended to produce a composite sample representative of a day's effluent. This composite liquor was stored under refrigeration until used. It was envisaged that pit liquor for treatment would receive a preliminary settling process, hence, no effort was made to mix the pit contents before dipping a jug into the pit liquor to draw the required sample, i.e. the samples were intentionally taken in such a manner as to be relatively free from suspended lime, hair and other insoluble matter.

Anaerobic treatment

Two identical bench-scale systems were set up and operated in parallel. Each system consisted of a peristaltic feed pump, a 20 ℓ glass bottle as reactor vessel, a gas pump for mixing purposes and a gas meter. Both digesters were immersed in a temperature con-

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*To whom all correspondence should be addressed.
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trolled water bath, maintained at 37°C by means of a thermostat/mixer. The outlet of each reactor vessel was set at such a level as to provide a minimum working volume of 10 ℓ. The reactor was not completely filled with liquid to allow space for foam formation which resulted from subsequent biogas recirculation. Continuously-stirred feedstock was introduced into the reactors by means of a peristaltic pump, at a target rate of 2 ℓ/d. Liquid was withdrawn from the reactors once every 24 h, when an amount equal to the volume of feedstock introduced during the preceding full day was removed and utilised for analytical and other purposes. As a result, the average hydraulic retention time of the liquid in the reactors was 5 d. The solid fraction of the withdrawn sample was separated from the liquid phase by centrifugation and returned to the reactor. Thorough agitation of the reactor contents was achieved by forced circulation of biogas from the digester head-space through open tubes extending to the bottom of each vessel. Excess biogas escaped from the system via totalising gas meters installed in the exhaust line.

The digesters were inoculated with waste anaerobic sludge, derived from a full-scale glucose-starch waste processing plant, and fed with unaltered glucose-starch effluent for the first ten days. Thereafter, this feedstock was gradually replaced with pit liquor from Davis Gelatine, Krugersdorp, until 100% pit liquor was fed from day 35. The pit liquor was supplemented with 10 mg/ℓ orthophosphate (as P) to eliminate a deficiency of this macro-nutrient.

Anaerobic-aerobic-anaerobic treatment

The process comprised primary anaerobic, aerobic and secondary anaerobic stages (Fig. 1). The primary anaerobic and secondary anaerobic stages consisted of 1 ℓ columnar reactors. Two-thirds of the primary anaerobic reactor was filled with sludge from an anaerobic digester at a sewage treatment plant. The level of the solids in this reactor was controlled by sludge withdrawal every 60 d. The aerobic stage consisted of a downflow filter, packed with ceramic Raschig rings, which acted as an inert fixed bed on which an aerobic bacterial population could grow, and a settling tank for sludge recycling. A dosage of 200 mg/ℓ phosphate (as P) was introduced to the filter to eliminate a phosphate shortage. Air was pumped into the bottom of the aerobic filter as oxygen source. A total of 16 mℓ/d water evaporated as a result of aeration as indicated by the difference in the rates of inflow and outflow. The secondary anaerobic reactor was filled to a level of two-thirds with granular activated carbon. The reactors were inoculated with activated sludge from a laboratory activated sludge plant. Feedstock consisted of pit liquor which was kept at 4°C.

Peristaltic pumps were used for recirculation purposes and a cylinder pump was used for feeding raw water to the primary anaerobic stage. The various flow rates are indicated in Fig. 1. The only exception occurred when the recycle stream was set at zero for a period of three weeks in order to determine its effect on the performance of the process.

Analytical

Total fatty acids (TFA), COD, total phosphate, sulphate, sulphide, calcium and alkalinity were determined manually according to Standard Methods (1985). Orthophosphate, nitrate/nitrite, ammonia and chloride were determined by means of an auto-analyser and metals such as magnesium, sodium and potassium with atomic absorption spectrophotometry. Fatty acids (acetate, propionate, lactate, butyrate, i-valerate and caproic acid)

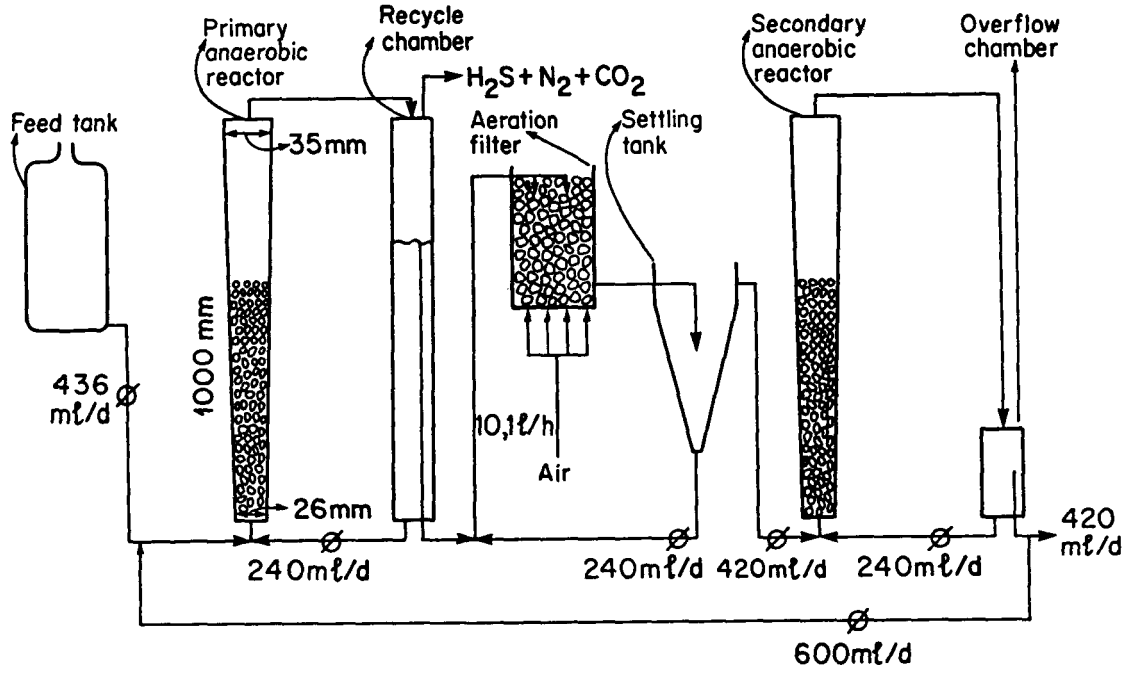

Figure 1
Schematic diagram of three-stage laboratory-scale plant used for biological treatment of gelatine factory effluent

were determined periodically, using a high performance liquid chromatograph equipped with a biorad fast acid column and an ultraviolet detector at 214 nm. The volume of the biogas produced in the anaerobic reactor was measured with a totalising gas meter.

Results and discussion

Anaerobic treatment

Results relating to the performance of the digesters are summarised in Table 1. Individual parameter values pertaining to the two reactors matched almost perfectly and hence no distinction is made between them in the discussion.

Initial period

The performance of the digesters was excellent during the first 50 d of the experiment as indicated by a 95% COD removal, 83% sulphide removal, 95% calcium removal and pH reduction. Thereafter the COD value increased to 17 500 mg/ℓ, almost equal to the value of the influent. Thus, when 100% lime pit liquor was dosed, COD was removed efficiently only for a period of 50 d with anaerobic treatment.

The performance achieved during the initial period (until day 50) can be related to the following biological reactions in the anaerobic reactors:

- Hydrolysis
- Acidogenesis
- Hydrogenogenesis
- Methanogenesis

TABLE 1
COMPOSITION OF LIME PIT LIQUOR BEFORE AND AFTER ANAEROBIC TREATMENT

Parameter	Units	Untreated	Treated Day 50	Treated Day 120
COD (filtered) (as O_2)	mg/ℓ	20 545	1 000	17 500
COD (unfiltered) (as O_2)	mg/ℓ	23 423	-	-
Volatile fatty acids	mg/ℓ	-	1 000	7 000
Acetate	mg/ℓ	-	-	3 900
Propionate	mg/ℓ	-	-	1 000
Lactate	mg/ℓ	-	-	70
Butyrate	mg/ℓ	-	-	700
i-Valerate	mg/ℓ	-	-	900
Valerate	mg/ℓ	-	-	60
Caproic acid	mg/ℓ	-	-	50
Gas production	ℓ/d	-	6,0	0,0
Total phosphate (as P)	mg/ℓ	2,7	-	-
Sulphide (as S)	mg/ℓ	1 192	200	1 200
Nitrate (as N)	mg/ℓ	<0,2	-	-
Ammonia (as N)	mg/ℓ	235	700	1 800
Kjeldahl nitrogen (as N)	mg/ℓ	1 238	-	-
Sodium (as Na)	mg/ℓ	3 900	3 900	3 900
Potassium (as K)	mg/ℓ	186	200	200
Calcium (as $CaCO_3$)	mg/ℓ	4 665	250	250
Magnesium (as Mg)	mg/ℓ	38	20	20
Sulphate (as SO_4)	mg/ℓ	209	-	-
Alkalinity (as $CaCO_3$)	mg/ℓ	5 334	4 000	7 000
pH		12,0	7,8	7,8

- not determined

End period

Subsequent to day 50, the effluent soluble (filtered) COD levels gradually rose towards influent levels (Table 1, day 120). the reduced COD removal could be ascribed to the following conditions in the anaerobic reactor:

pH: Smith and Hungate (1958) showed that the optimum growth for one species of methanogenic bacteria found in digesters takes place in the pH range 6,5 to 7,7. This range is below the pH value of 7,8 that was measured in the reactor (Table 1).

Ammonia: Free ammonia is more toxic than the ammonium ion, NH_4^+ (McCarty, 1964a, 1964b, 1964c, 1964d; Kugelman and Chin, 1971). If the concentration of free ammonia exceeds 150 mg/ℓ (as N), severe toxicity will result, whereas the ammonium ion concentrations must be greater than 3 000 mg/ℓ (as N) to have the same effect. The dissolved free ammonia at pH 7,8 is estimated to be about 5,0% of the total ammoniacal species present at 35°C. Thus, the estimated free ammonia concentration at the conclusion of the test ranged from about 75 to 100 mg/ℓ (as N). These levels are considered well into the toxic range and the conclusion could be drawn that the digester failure could be ascribed at least partially to excessive build-up of free ammonia, which in turn is associated with the relatively high pH of the digester content.

Volatile fatty acids: Table 1 shows that volatile fatty acids gradually accumulated in the digester and eventually reached concentrations of approximately 6 300 mg/ℓ (as acetic acid). The fatty acids consisted of 3 900 mg/ℓ acetate, 1 000 mg/ℓ propionate, 700 mg/ℓ butyrate and lesser amounts of lactate (70 mg/ℓ), valerate (60 mg/ℓ), iso-valerate (90 mg/ℓ) and caproate (50 mg/ℓ). Neither acetic nor butyric acids have any significant toxic effects upon hydrogen-utilising methanogenic bacterial at concentrations of up to 10 000 mg/ℓ (Hobson and Shaw, 1976). Propionic acid, on the other hand, exhibits partial toxicity to methanogenic bacteria at a concentration of 1 000 mg/ℓ at neutral pH (Hobson and Shaw, 1976). As this concentration of propionic acid was present in the water, it could be considered as one of the agents in the reactor which was at least partially responsible for toxicity.

Sulphide. The increase in the sulphide concentration from 200 to 1 200 mg/ℓ from day 50 to day 120, could be ascribed to the fact that it was not efficiently stripped from the water. The failure of the reactor could also be ascribed to this condition, more than to any other single factor. This problem was exacerbated by the relatively high pH of the reaction mixture.

The ionisation of H_2S, yielding the potentially toxic species HS^- and $S^=$, not only increases with rising pH but the stripping of H_2S from the medium as a result of gas recirculation comes to a virtual standstill under these conditions.

General

It can be concluded that the anaerobic stage alone is not sufficient for the treatment of gelatine factory effluent because the activity of the methanogenic bacteria is inhibited by some or all of the above-mentioned factors. Therefore, it was decided also to evaluate the configuration, anaerobic-aerobic-anaerobic, for the treatment of gelatine factory effluent.

TABLE 2
CHEMICAL COMPOSITION OF UNTREATED AND ANAEROBIC-AEROBIC-ANAEROBIC TREATED WATER

Parameter	Untreated	Untreated/ recycle combined stream	Treated		
			Primary anaerobic	Aerobic	Secondary anaerobic
COD (as O_2)	23 016	13 166	13 019	6 012	6 000
Calcium (as $CaCO_3$)	5 210	2 321	1 680	367	230
Alkalinity (as $CaCO_3$)	6 527	4 336	6 547	3 873	2 750
Sulphate (as SO_4)	1 496	902	647	712	473
Ammonia (as N)	190	315	585	350	405
pH	11,1		7,9	7,7	8,1

All units expressed in mg/ℓ

Anaerobic-aerobic-anaerobic treatment

Results relating to the performance of anaerobic-aerobic-anaerobic treatment (Table 2) were collected over a period of 11 months. The three-stage configuration achieved 74% COD and 96% calcium removal, while the pH was also neutralised to pH 8,1.

Primary anaerobic stage

The data for the primary anaerobic reactor in Table 2 compare well with those in Table 1 (day 120 when steady-state conditions were achieved) based on anaerobic treatment only. Little COD removal was obtained in the primary anaerobic reactor (reduced from 13 166 to 13 019 mg/ℓ O_2) which indicates that organic compounds were converted to fatty acids but not to methane. The reduction in calcium was ascribed to CO_2 production from hydrogenesis reactions. The neutralisation of the pH from 11,1 to 7,9 could be explained by the presence of acidogenesis and hydrogenesis reactions. Sulphate was also reduced in this stage (from 902 to 647 mg/ℓ).

Aerobic stage

In the aerobic stage, COD was reduced in the diluted stream from 13 019 to 6 012 mg/ℓ (Table 2). This can be ascribed to fermentation of fatty acids to CO_2.

The decrease in calcium and alkalinity could be explained by calcium carbonate crystallisation:

$$Ca^{2+} + CO_3^{=} \rightarrow CaCO_3 \quad [1]$$

The ammonia content decreased from 585 to 350 mg/ℓ in the aerobic stage. This could be ascribed to nitrification:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad [2]$$

Secondary anaerobic treatment

The secondary anaerobic reactor had little effect on the quality of the treated water as indicated in Table 2. Its major benefit was that sulphate was reduced from 712 to 473 mg/ℓ. It is therefore concluded that the secondary anaerobic stage is not essential for the treatment of gelatine factory effluent.

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