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Abstract

The EPA has identified extended aeration as a method "appropriate" for the biological treatment of tannery wastes. In this paper a conventional extended aeration (nitrification) system is contrasted with an extended aeration system designed for combined nitrification and denitrification (N/D) now under development at the Eastern Regional Research Center for secondary treatment of cattlehide tannery wastes. Parallel laboratory scale treatment studies were conducted, with each system held at 18-22°C and a sludge residence time of 20 days. Pretreated unhairing effluent was used as the model waste. Results indicate that in order to meet EPA proposed best available technology (BAT) limitations for chemical oxygen demand (COD) with either system, it is likely that a physical-chemical pretreatment of the unhairing effluent and other streams will be required.

The combined N/D system demonstrated the capacity to handle a nearly 40 percent greater COD loading rate than the conventional system, while producing the same degree of waste removal in terms of COD and TKN (total Kjeldahl nitrogen).

Introduction

Between July 1984 and July 1987 industrial point sources in the United States will be required to meet effluent limitations consistent with the EPA's standards of "best available (treatment) technology economically achievable" (BAT). For the leather tanning and finishing industry, substantial modification in both processing and effluent treatment practices will likely be required to meet BAT limitations (1). We believe that the best prospects for effective treatment of these effluents lie in: 1) physical-chemical pretreatment of segregated high-load waste streams, followed by 2) the pooling and biological treatment of the chrome-free streams not suitable for reuse. Accordingly, we have invested our research effort in such areas as physical-chemical treatment of sulfide unhairing waste, recycling and reuse of non-chrome streams, and biological secondary treatment for nitrogen

removal and control (2-5). Our research in biological treatment is reported here.

No treatment system to date has demonstrated the capability of meeting the proposed EPA requirements. However, biological extended aeration systems such as the Carrousel treatment system, in use at the A. C. Lawrence Shearling Tannery in Winchester, NH, appear to hold great promise (6,7)*. In general, such systems produce relatively little sludge and are capable of substantially reducing the COD, BOD_5, suspended solids, TKN, and ammonia (NH_3) from the wastewater. Two such systems have been the focus of our research — one designed for nitrification and one designed for both nitrification and denitrification.

In biological nitrification, an environment is created within the treatment system conducive to the growth of organisms capable of oxidizing ammonia to nitrate. Typical conditions include elevated oxygen tension and pH, moderate alkalinity, low sludge wasting rate and low COD loading rate (Table I). The first three conditions are necessary for optimal growth of nitrifiers. Alkalinity is also required to offset acidity produced in the oxidation of ammonia to nitrate (approximately 7 mg $CaCO_3$/mg NH_3) and to ensure proper sludge settling characteristics. The low sludge wasting rate is necessary to retain the slow growing nitrifier. A low COD loading rate is required to match this low wasting rate.

TABLE I

TYPICAL CONDITIONS FOR EXTENDED AERATION

Parameter	Range
Oxygen tension	>2.0 mg/l
pH	7.5 - 8.5
Residual alkalinity	50 - 100 mg/l (as $CaCO_3$)
Sludge wasting rate	3 - 10% per day of basin sludge inventory (reciprocal of sludge residence time × 100)
COD loading rate (Food-to-mass ratio)	0.05 - 0.10 Kg BOD_5/Kg MLVSS[a]·day or 0.15 - 0.30 Kg COD/Kg MLVSS·day

[a] MLVSS is defined as basin Mixed Liquor Volatile Suspended Solids.

Unfortunately, biological nitrification is not without drawbacks. It imposes a high demand for oxygen in addition to the low COD loading rate and the low sludge wasting rate. With tannery waste, for example, oxidizing ammonia to nitrate can increase the total oxygen consumption by over 40 percent. Further, converting ammonia to nitrate is simply trading one objectionable compound for another. Untreated tannery waste containing 200 ppm of TKN will yield approximately 140 ppm of nitrate nitrogen ($NO_3 - N$) in the nitrified effluent. Based on

a potential health hazard to infants, the EPA has suggested a quality criterion for domestic water supply of 10 ppm $NO_3 - N$. A limit of 90 ppm $NO_3 - N$ appears advisable for warm-water fish. The potential therefore exists that the tanner choosing nitrification today may tomorrow be faced with unanticipated nitrate limitations of either local, state, or federal origin. In fact, the Stanley report (which served as a basis for the 1974 EPA effluent limitations development document) did propose such limitations (8, 9). For this reason, alternatives to conventional nitrification must be considered.

We have investigated a combined nitrification/denitrification (N/D) system as an alternative to conventional nitrification (4, 5). The system is best described by considering the integrated nitrification and denitrification functions as separate unit operations (Figure 1). Generally, nitrification is accomplished either in a constant stirred ("complete mixed") reactor basin, or in an oxidation ditch. The

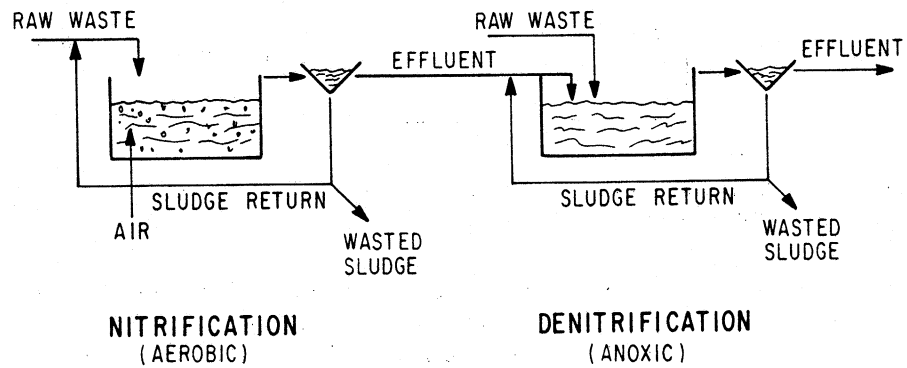

FIGURE 1. — Biological nitrification and denitrification.

composition of the basin-mixed liquor is relatively homogeneous, and the composition of the non-sludge fraction is virtually identical to that of the clarified effluent. The basin-mixed liquor is therefore high in nitrate and low in soluble TKN, BOD_5, and COD. In denitrification, high nitrate effluent (or mixed liquor) is fed to an anoxic basin along with raw waste. Here, the incoming COD (and BOD_5) is metabolized with nitrate (rather than oxygen) serving as the source of oxidant. In the process the nitrate is reduced to nitrogen gas.

The combined N/D treatment system under study at ERRC is shown in Figure 2a. By using a nitrogen mass balance and assuming that all recycled nitrate is removed in the anoxic zone, an equation can be developed relating the amount of nitrate in the effluent to the TKN in the influent, and the ratio of the mixed liquor recycle rate to the feed rate (5). Based on such an approach, curves of effluent nitrate and total nitrogen removal (TKN plus $NO_3 - N$) can be constructed for a hypothetical tannery waste containing 200 mg/l TKN (Figure 3).

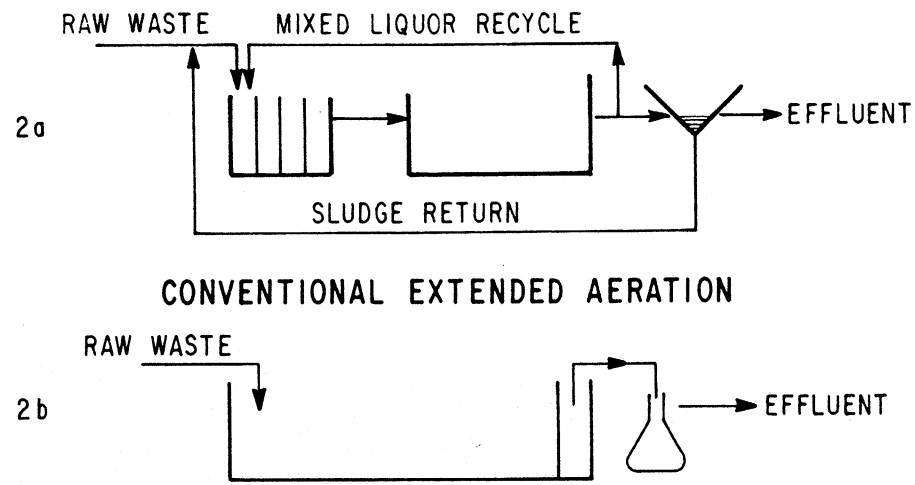

FIGURE 2. – Treatment systems under study: a, combined nitrification/denitrification; b, conventional extended aeration.

In the example shown, a minimum recycle ratio of 15:1 would be required to reduce nitrate to a suggested water supply level (i.e., 10 mg/l).

The concept of combining nitrification with denitrification is now new (6, 7, 11, 12). Unfortunately, in currently available systems, the rates of biooxidation and nitrate removal are so slow that excessive basin volume and low COD loading rates are required. The purpose of this paper is to demonstrate that, with the combined N/D system under development, these rates can be increased; in fact, the COD loading rate is substantially superior to that of conventional nitrification considered alone.

Experimental Influent

At ERRC we have developed a physical-chemical (P/C) pretreatment for lime-sulfide unhairing effluent – the most concentrated of the effluent streams (2). This P/C-treated effluent was the substrate in all of our biological treatment studies. Table II shows both the approximate composition of unhairing waste received from Ocean Leather Co. (Newark, N.J.) and the effluent from our P/C pretreatment. In pretreatment, about 80 percent of the TKN and COD was removed, and 95 percent of the sulfide was recovered. The rest of the sulfide was oxidized with hydrogen peroxide. If P/C pretreatment is used in a comprehensive system of tannery waste management, the influent to biological treatment is

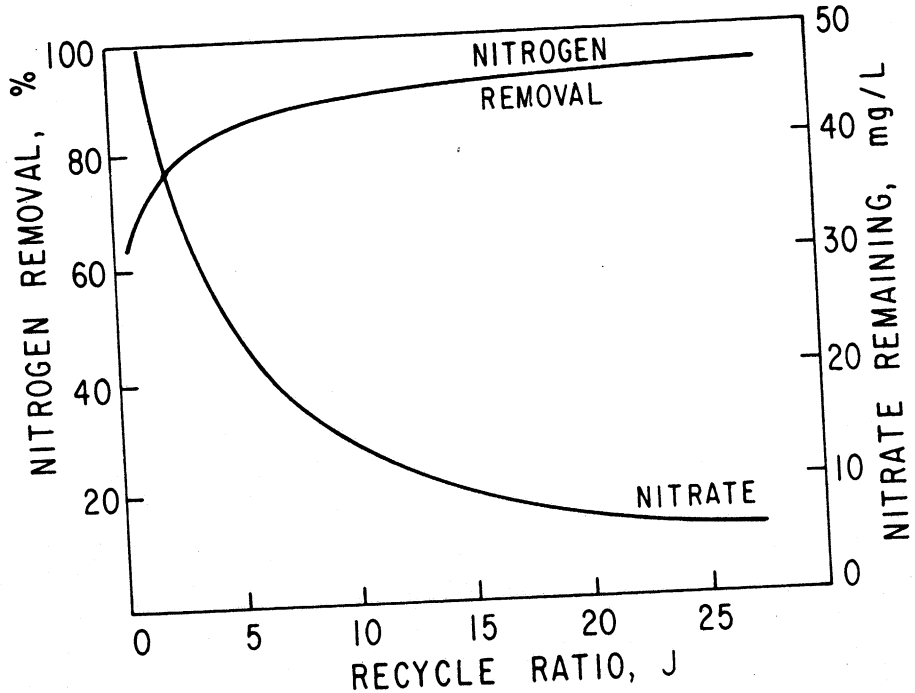

FIGURE 3. – Effluent nitrate and total nitrogen removal in combined N/D.

likely to contain up to 200 mg/l of TKN. P/C-treated effluent was therefore diluted to this concentration with tap water in all experiments.

TABLE II

APPROXIMATE COMPOSITION OF LIME-SULFIDE UNHAIRING EFFLUENT
(Except for pH, in mg/l)

	Unhairing effluent	Physical-chemical pretreated unhairing effluent
BOD_5	14,000	2,000
COD	31,600	4,700
Sulfide (as $S^=$)	2,000	<1
TKN (as N)	3,000	420
Ammonia (as N)	200	60
Nitrite (as N)	–	<1
Nitrate (as N)	–	<1
Phosphate (as P)	–	<5
Alkalinity (as $CaCO_3$)	18,000	250
pH	12	4

Experiments were conducted to contrast two extended aeration biological treatment systems—conventional nitrification and combined N/D—in the laboratory-scale treatment systems shown schematically in Figures 2a and 2b. P/C-treated effluent was found too low in pH and alkalinity and the COD-to-phosphorus ratio (COD:P) was too high to allow for efficient biological treatment. In extended aeration over 500 mg/l of alkalinity was consumed in oxidizing influent TKN to nitrate (approximately half of that was required for combined N/D). Phosphorus was required to replace that lost (as calcium phosphate) during pretreatment. For these reasons, diluted P/C-treated effluent was first neutralized with sodium hydroxide, then sufficient sodium bicarbonate and potassium phosphate were added to yield about 650 mg/l alkalinity (measured as calcium carbonate) and a COD:P ratio of 150.

The conventional extended aeration system consisted of a 5.5-liter constant stirred aeration basin with 0.25-liter quiescent zone (no mixing and no aeration). In the quiescent zone, sludge solids precipitated out of the mixed liquor and reentered the aeration basin via an opening in the partition separating these sections. Thus the quiescent zone served as an effluent clarifier. Effluent was continuously obtained from the clarification zone by use of a siphon tube connected to an external overflow device (i.e., 250-ml side arm bottle). The nominal feed rate was 0.1 l/hr. The aeration basin was sparged with air (1 to 1.5 liters/min per liter of basin volume) to provide both sufficient oxygen and good mixing. A minimum oxygen tension of 2.0 mg/l of oxygen was maintained at all times.

The combined N/D system consisted of a four-stage anoxic basin 5 liters in volume, followed by two aerobic basins of 11 liters each. The nominal feed rate was 0.75 l/hr. The aeration zone, with the exception of a final 2.2-liter stage, was sparged with air at 1 to 1.5 l/min per liter of basin volume. The final aerobic stage was sparged with both air and nitrogen to limit the effluent dissolved oxygen tension to about 1.0 mg/l and thereby reduce the amount of oxygen recycled to the anoxic zone. In full-scale treatment, oxygen tension is reduced prior to mixed liquor return only through microbial respiration. The anoxic zone was covered and sparged at 1 to 1.5 l/l•min with nitrogen to exclude oxygen and insure good mixing. The clarifier was a 9-liter Plexiglas cylinder with V-notch overflow weirs. The cylinder rested on a magnetic stirring table used to agitate the settled solids 2 to 4 seconds every minute. The mixed liquor recycle ratio was operated at 15:1.

Restated, the objective of this study was to demonstrate that in combined N/D substantially more waste can be treated (per unit mass of activated sludge or per unit volume of basin) than in the conventional extended aeration. Because on a laboratory scale an unrealistically wide range of sludge concentrations can be carried within the treatment basin, a volumetric load handling comparison is in-

valid. In such instances, one of the best measures for comparing capacity is the so-called food-to-mass (F/M) ratio.

$$F/M = (\text{kg COD applied/day})/(\text{kg MLVSS})$$

where MLVSS = treatment basin mixed liquor volatile suspended solids.

Under laboratory conditions, this ratio was determined by feeding a treatment basin at a constant application rate while wasting daily a constant percentage of the activated sludge in the treatment basin [sludge residence time is defined as (fraction of sludge inventory wasted per day)$^{-1}$]. The inventory of sludge in the treatment basin is allowed to rise or fall to reach its own equilibrium with the waste application rate.

In both extended aeration systems, an aerobic sludge residence time of 20 days was maintained by wasting 5 percent of the aerobic basin sludge inventory each day. All experiments were conducted at 18-22°C.

Methods of Analysis

Analyses for chemical oxygen demand were by the EPA dichromate method (Storet No. 00335, c.v. for analysis equaled 1.3 percent) (13). Analyses for nitrate nitrogen were by the EPA cadmium reduction method (Storet No. 00630, c.v. for analysis equaled 3.0 percent). Analyses for total Kjeldahl nitrogen were by the AOAC micro-Kjeldahl method (No. 42.014, c.v. for analysis equaled 5.2 percent) (14).

Results and Discussion

Potential advantages of combined N/D over conventional extended aeration include a superiority in COD loading, reduced aeration/mixing horsepower, and reduced sludge production. In addition, by virtue of differences in aerobic and anoxic metabolism, improved effluent quality is also possible. Each of these potentialities is addressed in the paragraphs below. Data presented (Figure 4 and Table III) summarize the results of over six months of continuous laboratory operations. While these results are based on research conducted at 18-22°C, in northern climates where low winter temperatures (<10°C) are encountered, stable nitrification of tannery waste has yet to be demonstrated.

Loading Rate — Food-To-Mass Ratio

Food-to-mass ratios are shown in Figure 4. As presented, the average F/M for the conventional extended aeration system at 18-22°C was 0.32 kg COD/kg MLVSS·day or approximately 0.1 kg BOD_5/kg MLVSS·day (i.e., 0.3 kg BOD_5/kg COD for tannery waste). This result compares favorably with the

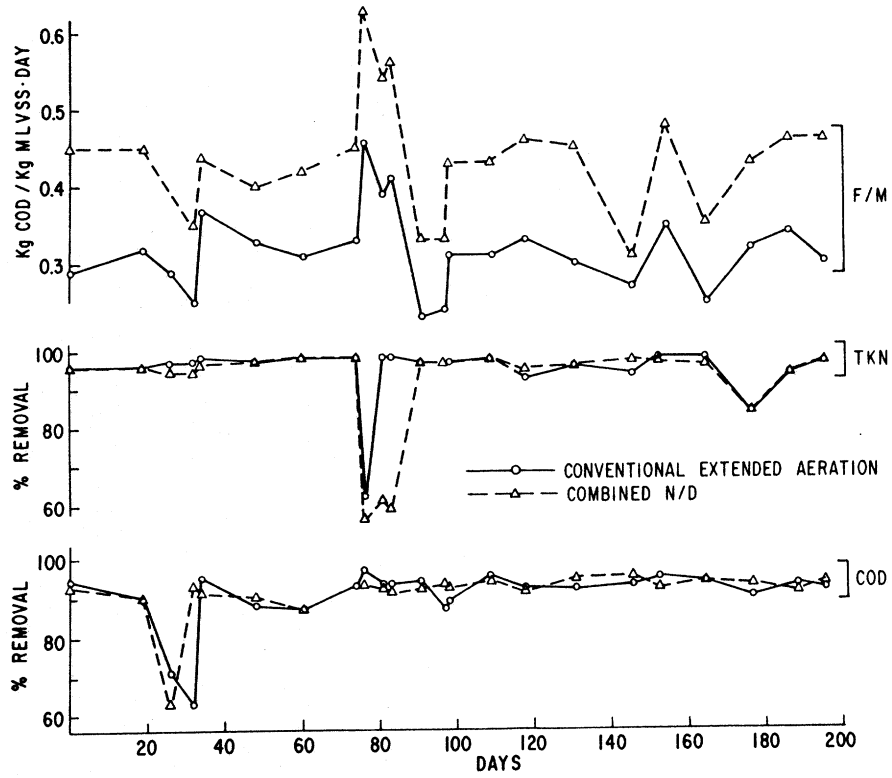

FIGURE 4. – Comparison of combined N/D with conventional extended aeration.

TABLE III

ADDITIONAL RESULTS

	Combined N/D	Conventional extended aeration
Oxygen tension, mg/l	2-3 (in aerobic zone)	2-3
Effluent pH	7.5-7.8	7.5-7.8
Alkalinity consumed as $CaCO_3$ (influent minus effluent)	200-300	550-700
Effluent TKN, mg/l	<10	<10
Effluent nitrate, mg/l	10-20	130-160
Effluent COD, mg/l	200-500	200-500

typical design range for full-scale operation of 0.05 to 0.10 kg BOD_5/kg MLVSS·day for year-round temperature operations. The average F/M ratio for the combined N/D system, on the other hand, was 0.45 kg COD/kg MLVSS·day – 38 percent greater than that obtained with the conventional system. In the simultaneous comparison of F/M over the 6-month period for the two systems (Table IV), the F/M for combined N/D was significantly greater ($p < 0.05$).

TABLE IV

ANALYSIS OF VARIANCE

Parameter		s.s.	df	m.s.	F[a]
Food-to-Mass Ratio	Total	0.3452	45		
	Treatment	0.1668	2	0.0834	20.*
	Error	0.1784	43	0.0415	
Percent TKN Removal	Total	5997.	45		
	Treatment	303.	2	151.5	1.14
	Error	5694.	43	132.4	
Percent COD Removal	Total	2227.	45		
	Treatment	8.	2	4.	<1
	Error	2219.	43	51.6	

[a] F(0.95, 2, 43) = 3.25.
* Significant.

This substantial increase in the amount of COD that can be treated per unit of biomass can be largely attributed to the use of staging in the anoxic zone. Previous results have shown that the amount of COD decreases as the basin-mixed liquor passes from stage to stage (i.e., COD decreases with increasing hydraulic residence time). Only in the aerobic zone – the final stage – is the waste of effluent quality. Because in the F/M range studied, the rate of biooxidation increases with COD, the COD profile created within the staged anoxic zone results in an overall high rate of biooxidation. Note also that the rapid oxidation of COD requires an equally rapid consumption of oxidizing agent. Thus, the use of a staged anoxic zone provides for the rapid removal of COD and of nitrate.

Aeration/Mixing Horsepower

In many conventional wastewater treatment systems, rotating impeller mixers are used to supply oxygen to the wastewater (aeration) and to keep the activated sludge in suspension (mixing). Typically, about 0.75 to 1.0 hp per 1000 ft^3 of basin volume is required for mixing; in this power range, rotating impellor mixers supply roughly 2 to 3 lb O_2/1000 ft^3. As a general rule, design for conventional extended aeration systems is most cost effective when the horsepower re-

quired for aeration is not allowed to exceed that required for mixing. For this reason, in a totally aerobic system, use of a staged front end to boost the rate of biooxidation (and consequently increase the local demand for oxygen) is of dubious economic advantage. However, because in the combined N/D under current study, nitrate-ladened mixed liquor provides the source of oxidant, the biooxidation rate can be raised without resorting to excessive aeration/mixing horsepower.

Sludge Production

Since the sludge resident time for the conventional system is maintained by wasting (discarding) one-twentieth of the sludge under aeration each day, an average of 0.16 kg MLVSS must be disposed of per kg of COD applied – (0.05 kg MLVSS wasted/kg MLVSS•day) (kg MLVSS•day/0.32 kg COD). Based on a similar calculation, in combined N/D an average of 0.11 kg MLVSS is wasted per kg of COD applied. This 28 percent drop in waste sludge solids produced is again attributed to the high rate of biooxidation achieved in the staged anoxic zone – the more COD burned, the less turned into sludge.

COD and TKN Removal

In combined N/D an average of 91 percent of the influent TKN was removed compared to 95 percent in the conventional extended aeration system. COD removal was 91 and 90 percent, respectively. In the simultaneous comparisons of TKN and COD over the 6-month period (Table IV), there was no significant difference between combined N/D and conventional extended aeration ($p < 0.05$). The lower overall TKN removal demonstrated by the combined N/D system is largely a consequence of the poor removal obtained during the period of highest COD loading. This suggests that the combined N/D system may be more susceptible to COD overloading (due to its quasi plug flow nature). If this proves to be the case, waste equalization and/or a higher mixed liquor recycle ratio may be advisable. Unfortunately, either solution would result in an increase in total basin volume which will partially offset the advantages in COD loading of the combined N/D system. The drop in F/M at about 30 days with a corresponding drop in COD removal is difficult to explain. If anything, a drop in COD removal would be expected to result from an overload (i.e., high F/M) rather than an underload.

If it is assumed that a composite of tannery effluents (after P/C-pretreatment of the unhairing stream) can be biologically treated with equal facility, it is projected that with either system over 98 percent of the TKN and about 95 percent of the COD can be removed from tannery waste. Although it is difficult to translate EPA effluent limitations into required percents of removal, we calculate that BAT limitations for chrome tannery and finishing operations will require removal of approximately 96 percent of the influent TKN and 98 percent of the

influent COD (1, 9). Thus, P/C-pretreatment of unhairing waste, followed by biological treatment of the composite effluent, apparently will fall marginally short of meeting BAT in terms of COD. The COD results obtained, therefore, indicate that, although it should be possible to meet the proposed BAT limitations, it is likely that a P/C pretreatment of more than the unhairing stream (e.g., primary settling of combined effluent streams) will be required.

Conclusions

Based on continuous laboratory scale studies at moderate temperature, the combined N/D system under development at ERRC possesses a superiority in COD load handling ability (compared to conventional extended aeration) that may well translate to substantial savings in treatment costs. The combined N/D system handled an average of 0.45 kg COD/kg MLVSS•day, or 38 percent greater than conventional extended aeration, while producing substantially the same degree of waste removal both in terms of COD and TKN. The potentially greater sensitivity of the combined N/D system to COD overloading may require design precautions that partially offset this advantage. In order for either treatment system to meet proposed EPA effluent limitations, it is likely that a P/C treatment of the unhairing effluent stream and other streams will be required.

Acknowledgments

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References

1. Environmental Protection Agency. "Leather Tanning and Finishing Point Source Category Effluent Limitations Guidelines, Pretreatment Standards and New Source Performance Standards." *Federal Register,* **44,** 128 (July 2, 1979).
2. Komanowsky, M., Sinnamon, H. I., and Aceto, N. C. "Physiochemical process for recovery of by-products from lime-sulfide unhairing waste." Presented at the 74th Annual Meeting American Leather Chemists Assoc., Lake Placid, N.Y., June 18-22, 1978.
3. Komanowsky, M. "Recovery of by-products from tannery waste waters." Presented at the 10th Engineering Foundation Conference on Environmental Engineering in the Food Industry, Asilomar Conference Grounds, Pacific Grove, Calif., Feb. 24-29, 1980.

4. Panzer, C. C. "Design for nitrogen removal from tannery unhairing waste." *Proc. 34th Ind. Waste Conf.,* Purdue University, Lafayette, IN, pp. 394-402 (1980).
5. Panzer, C. C., Komanowsky, M., and Senske, G. E. "Improved performance in combined nitrification/denitrification." *Proc. 35th Ind. Waste Conf.,* Purdue University, Lafayette, IN, pp. 105-113 (1981).
6. Refling, D. R., and Barber, L. K. "Advanced wastewater treatment of a tannery effluent." Presented at the 7th Water and Wastewater Equipment Manufacturers Ind. Pollution Conf., Philadelphia, PA., June 5-7, 1979.
7. Zemaitis, W. L., and Barber, L. K. "Three years of operation and performance of the first United States Carrousel." *Proc. 12th Mid-Atlantic Ind. Waste Conf.,* Bucknell U., Lewisberg, PA., pp. 128-131 (1980).
8. Stanley Consultants. Development document for effluent limitation guidelines and standards of performance for the leather tanning and finishing industry — draft document, June 1973.
9. Environmental Protection Agency. "Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Leather Tannery and Finishing Point Source Category." EPA 440/1-74-016-a. Washington, D.C., 1974.
10. Barnard, J. L. *J. Water Pollution Control (South Africa),* **72,** 705 (1973).
11. Ludzack, F. J., and Ettinger, M. B. *J. Water Pollution Control Fed.,* **34,** 920 (1962).
12. Environmental Protection Agency. "Process Design Manual for Nitrogen Control." EPA Technology Transfer, Washington, D.C., 1975.
13. Environmental Protection Agency. "Manual of Methods for Chemical Analysis of Water and Wastes." U.S. EPA Technology Transfer, Washington, D.C., 1974.
14. Association of Official Analytical Chemists. "Methods of Analysis." 11th edition AOAC, Washington, D.C., 1970.

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