

Improved performance in combined nitrification/ denitrification of tannery waste

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By July 1984, industrial point sources in the U. S. will be required to meet effluent limitations consistent with the Environmental Protection Agency's (EPA) standards of "best available (treatment) technology economically achievable" (BAT). For the cattlehide tanning industry, substantial modification in both processing and effluent treatment practices will probably be required in order to meet BAT limitations.¹ Significantly, no treatment facility to date has demonstrated the capability of meeting the proposed requirements. A biological treatment system in use at a tannery in Winchester, N. H., however, is stated to hold great promise.^{2,13} The biological treatment system at this facility is a single sludge treatment system operated to provide both nitrification and denitrification. Such systems will be hereafter described as combined nitrification/denitrification or combined N/D systems.

Slow denitrification rates normally associated with combined systems can be improved by the use of staged denitrification.

At the Eastern Regional Research Center, U. S. Department of Agriculture, a combined N/D system is being evaluated. On the basis of studies conducted, we believe that proposed limitations for both chemical oxygen demand (COD) and total kjeldahl nitrogen (TKN) can be met. In addition, results show that the slow rate of denitrification normally associated with combined N/D systems can be improved by use of staged denitrification.³ The purpose of this paper is to describe results that demonstrate these findings.

THEORY

Extent of nitrogen removal. A combined N/D treatment system is shown in Figure 1. Apart from the internal staging, this system is the same configuration as that first suggested by Ludzack and Ettinger⁴ and the same as that comprising the first two stages of the Bardenpho process.^{5,6} In this system, the waste is nitrified

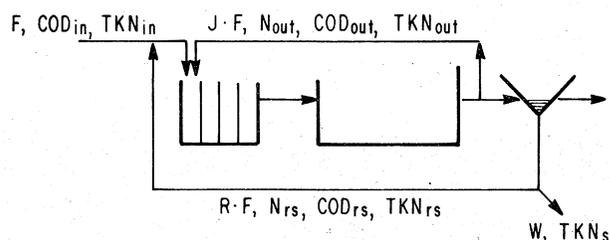


Figure 1—Schematic diagram for combined nitrification/denitrification.

in the aerobic zone and then is returned to the anoxic zone to be denitrified. The higher the rate at which the aerobic mixed liquor is returned to the anoxic zone, the greater the amount of nitrate that can be removed.

From this flow scheme, a mass balance equation can be developed relating the nitrate nitrogen in the effluent to the TKN of the influent and the ratio of the mixed liquor recycle rate to the feed rate.⁷ The nomenclature used is defined as follows:

F = Influent flow rate (1/h)

J = Ratio of the aerobic mixed liquor recycle rate to F (1/h:1/h)

R = Ratio of the sludge recycle rate to F (1/h:1/h)

W = Sludge wasting rate (1/h)

COD_{in} = Removable soluble COD in influent (mg/l)

COD_{out} = Removable soluble COD in aerobic mixed liquor recycle (mg/l)

COD_{rs} = Removable soluble COD in sludge recycle (mg/l)

TKN_{in} = Soluble TKN in influent (mg/l)

TKN_{out} = Soluble TKN in aerobic mixed liquor recycle (mg/l)

TKN_{rs} = Soluble TKN in sludge recycle (mg/l)

TKN_s = Total TKN in waste sludge stream (mg/l)

N_{out} = Nitrate in aerobic mixed liquor recycle (mg/l)

N_{rs} = Nitrate in sludge recycle (mg/l)

The following assumptions are made:

- The system is at steady state.
- No volatile suspended solids (VSS) enter the system in the feed or leave the system other than in the waste sludge. (Under these conditions the sludge wasting rate W is equal to the net sludge growth rate.)
- The composition of the clear liquid (non-sludge) fraction of the mixed liquor stream leaving the aerobic basin is the same as that of the mixed liquor and sludge recycle streams entering the anoxic basin at the front of the treatment system (that is, $COD_{rs} = COD_{out}$, $TKN_{rs} = TKN_{out}$ and $N_{rs} = N_{out}$).
- All of the nitrate entering the anoxic basin is converted to nitrogen gas and is lost from the system.

Granting these assumptions, the reduction in influent TKN can be expressed as

$$TKN_{in} - TKN_{out} = (1 + R + J)N_{out} + TKN_s \cdot W/F \quad (1)$$

and the concentration of nitrate in the mixed liquor leaving the aerobic basin can be expressed as

$$N_{out} = [(TKN_{in} - TKN_{out}) - TKN_s \cdot W/F] / (1 + R + J) \quad (2)$$

If a first approximation of N_{out} is all that is required, further simplification can be made. Typically in this study TKN_{out} was 5 mg/l or less. In addition, an average 11 to 14% of the influent TKN was lost in the wasted sludge. If these factors are incorporated into Equation 2 as well as the typical design sludge recycle ratio of $R = 1$, effluent nitrate can be expressed as

$$N_{out} = (0.875 TKN_{in} - 5) / (2 + J) \quad (3)$$

By use of Equation 3, curves of effluent nitrate and total nitrogen removal were constructed for a hypothetical feed containing TKN at 200 mg/l (Figure 2). The total nitrogen curve indicates that above a mixed liquor recycle ratio of 4 or 5, an incremental increase in J offers little in terms of an incremental improvement in the percent of nitrogen removed. In part because of

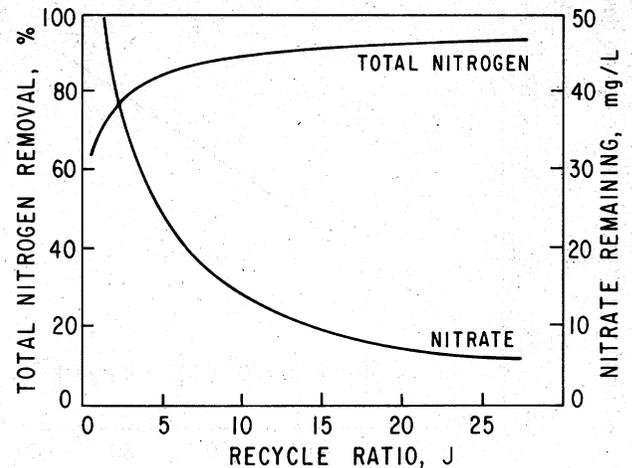


Figure 2—Effluent nitrate and total nitrogen removed after combined nitrification/denitrification. Nitrate values are calculated by use of Equation 3 for an influent containing TKN at 200 mg/l.

this factor, Barnard,⁵ in his work on municipal waste, chose to use a recycle ratio of 4 and then followed the recycle system with a second anoxic basin wherein the remainder of the nitrate was removed through endogenous respiration.

With a high TKN wastewater, this approach is far less attractive because of the excessively large reactor volume required for endogenous respiration. As a consequence, with a high TKN wastewater, use of a higher mixed liquor recycle ratio seems desirable. The balance between recycle and endogenous respiration must, of course, ultimately rest on economic considerations.

Rate of nitrate removal. In a recent study at ERRC,³ it was shown (Figure 3) that the rate of nitrate utilization (removal) per unit mass of biomass can be expressed in the linear form

$$-(1/x)(dN/dt) = KCOD_r + m \quad (4)$$

where

(dN/dt) = rate of nitrate utilization (mg/l·h)

COD_r = soluble removable COD (mg/l)

K = lumped rate constant (1/mg vss·h)

x = concentration of biomass (mg/l)

m = maintenance nitrate utilization rate (mg N/mg vss·h)

In this equation, $KCOD_r$ and m are, respectively, the growth related and nongrowth related rates of nitrate utilization. If a simple stoichiometric relationship is assumed between the rates at which COD_r and nitrate are utilized then

$$-(Y/x)(dCOD_r/dt) = -(1/x)(dN/dt) \quad (5)$$

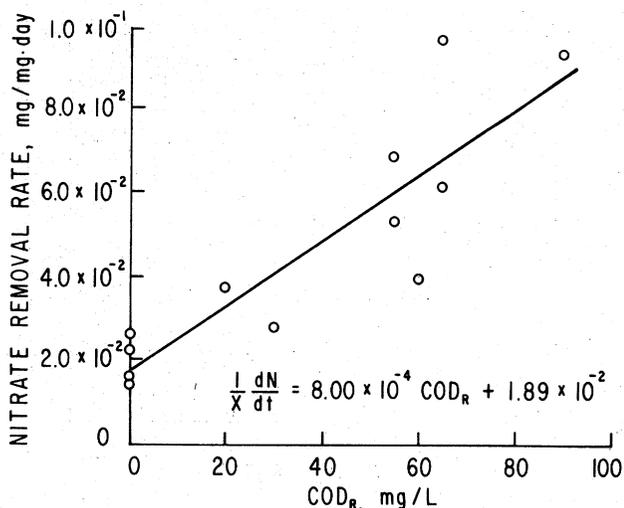


Figure 3—Nitrate removal rate, $(1/x)(dN/dt)$, in combined nitrification/denitrification as a function of soluble removable COD. Solids residence time was 20 days.

where

$$(dCOD_r/dt) = \text{rate of } COD_r \text{ utilization (mg/l}\cdot\text{h)}$$

$$Y = \text{stoichiometric coefficient (mg N/mg } COD_r)$$

If adsorption of COD_r by biomass can be neglected, the rate of disappearance of COD_r will be equal to the rate of utilization of COD_r ($dCOD_r/dt$). Under these circumstances, it can be shown that in a plug flow reactor basin with a constant biomass concentration and influent removable COD (COD_0)

$$COD_r = -m/K + (COD_0 + m/K) \exp(-Kx\tau/Y) \quad (6)$$

and

$$-(1/x)(dN/dt) = (KCOD_0 + m) \exp(-Kx\tau/Y) \quad (7)$$

for $COD_r > 0$

where

$$\tau = \text{hydraulic residence time (h)}$$

In the treatment of tannery effluent, however, adsorption cannot be neglected.³ Thus Equation 7 as derived is not quantitatively valid. Nonetheless, this equation provides a useful qualitative description of nitrate removal through systems of a plug flow type. In particular, this equation can be used to depict the reaction kinetic behavior of the series of complete mix reaction basins comprising the anoxic zone in Figure 1.

With Equations 6 and 7, the superiority of a plug flow basin over complete mix basin can be shown. In both plug flow and complete mix regimes, the rate of nitrate utilization at any point in the basin is proportional to the COD_r in the immediate environment

(Equation 4). In a complete mix basin, this COD_r is the amount of removable COD that remains un-utilized at the conclusion of the nitrate removal process. Typically, this residual COD_r is low, and in accordance with Equation 4, the nitrate removal rate will be low as well.

In a plug flow basin, COD_r will be COD_0 at the inlet of the treatment basin ($\tau = 0$) and will fall exponentially with increasing hydraulic residence time. In the region of rapidly falling COD (that is, low τ), COD_r and nitrate removal rate will be considerably higher than that found in a complete mix basin. It is this early advantage that enables a plug flow basin to outperform a complete mix basin of equal size.

In the context of the combined N/D system shown in Figure 1, the influent COD concentration (COD_0) is the composite of the three streams entering the anoxic zone. That is

$$COD_0 = (COD_{in} + JCOD_{out} + RCOD_{rs}) / (1 + J + R) \quad (8)$$

With this added information, important interrelationships between wastewater COD (COD_{in}) and mixed liquor recycle ratio (J) can be deduced.

First, high COD_{in} will yield a high COD_0 and a high nitrate removal rate. It is therefore expected that the rate of nitrate removal with an industrial-strength waste should be greater than that with municipal waste. Second, in combined N/D little removable COD remains after aerobic treatment (that is, COD_{out} is small). Therefore, a large J will yield a low COD_0 and a low nitrate removal rate. This result is in good agreement with the findings that first stage Bardenpho denitrification of municipal waste ($J = 4$) proceeds at a moderate nitrate removal rate of 0.07 mg N/mg·d, whereas oxidation ditch type treatment ($J = 30$ to 50) achieves only an endogenous rate (for example, .02 mg N/mg·d).⁸

Finally, it can be deduced that moderate nitrate removal rates are obtainable with a variety of COD_{in} - J combinations—higher COD_{in} allowing the use of a larger J . In particular, it is reasoned that an industrial-strength waste such as tannery effluent should be able to support the use of a relatively high J and still maintain a nitrate removal rate in excess of 0.07 mg N/mg·d.

EXPERIMENTAL

Experimental influent. End-of-pipe tannery effluent is a composite of a series of highly complex processing effluents (Table 1). In our view, the best prospects for effective treatment of the composite effluent lie in: (1) the 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 recycle or reuse. We have, therefore, de-

Table 1—Chrome tannery effluent stream contributions.¹⁰

Effluent stream	Flow (%)	BOD (%)
Soaking	11.8	17.7
Unhairing	11.8	58.9
Liming	23.5	11.8
Bating	14.1	1.0
Chrome tanning	3.5	4.7
Retan, coloring, and fat liquoring	23.5	2.4
Finishing	11.8	3.5
Total	100.0	100.0

veloped a physical-chemical (P/C) pretreatment for lime-sulfide unhairing effluent—the most concentrated of the effluent streams.⁹ This P/C-treated effluent has served as the substrate in biological treatment studies.

Table 2 shows the proximate composition of unhairing waste received from a leather tannery in Newark, N. J., and the effluent from our P/C pretreatment. In pretreatment, about 80% of the TKN and COD was removed, and 95% of the sulfide was recovered. The rest of the sulfide was oxidized. If P/C pretreatment is used in a comprehensive system of tannery waste management, the influent to biological treatment is likely to contain approximately 200 mg/l for TKN. P/C-treated effluent was therefore diluted to this concentration with tap water in all experiments. P/C-treated effluent was found too low in pH and alkalinity, and too high in COD-to-phosphorus ratio (COD:P) to allow for efficient biological treatment. For this reason, diluted P/C-treated effluent was first neutralized with sodium hydroxide and then sufficient sodium bicarbonate and potassium phosphate were added to yield 600 mg/l alkalinity (measured as calcium bicarbonate) and a COD:P of 150.

Equipment and procedures. Experiments were designed primarily to demonstrate the use of a staged anoxic zone in the combined nitrification/denitrification of an industrial-strength waste. All of the experi-

Table 2—Proximate composition of lime-sulfide unhairing effluent.

	Unhairing effluent (mg/l)	Physical-chemical pretreated unhairing effluent (mg/l)
BOD ₅	14 000	2 000
COD	31 600	4 700
Sulfide (as S ²⁻)	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

ments were conducted in a laboratory scale system shown schematically in Figure 1. The system consisted of a four-stage anoxic basin 5 litres in volume, followed by two aerobic basins of 11 litres each. The two aerobic basins were considered to comprise a single aerobic zone. The hydraulic retention time was 36 hours, based on a nominal feed rate of 0.75 l/h. The aeration zone, with the exception of the final 2.2-litre stage, was sparged with air (1 to 1.5 l/min per litre of basin volume) to provide both sufficient oxygen and to insure complete mixing. The final aerobic stage was sparged with both air and nitrogen in order to limit an effluent dissolved oxygen content to about 1.0 mg/l and thereby reduce the amount of oxygen recycled to the anoxic zone. The anoxic zone was covered, sparged at 1 to 1.5 l/min with nitrogen in order to exclude oxygen, and again to insure complete mixing.

The clarifier was a 9-l polymethyl methacrylate cylinder with V-notch overflow weirs. The cylinder rested on a magnetic stirring table used to agitate the settled solids 2 to 4 seconds per minute. Excess solids were wasted from the last aerobic stage. The solids residence time was maintained at 20 days, based on the aerobic volume. The mixed liquor recycle ratio was operated at 15:1. All experiments were conducted at 18 to 20°C.

Methods of analysis. Analyses for chemical oxygen demand were performed by the EPA dichromate method.¹¹ Analyses for nitrate nitrogen were performed by the EPA cadmium reduction method.¹¹ Analyses for total Kjeldahl nitrogen were performed by the AOAC micro-Kjeldahl method.¹²

RESULTS

Degree of nitrate removal. The results of typical experiments are shown in Table 3. For clarity the experiments are listed in order of descending influent COD. (NOTE: CODs presented in this table are total soluble CODs). The seventh column of the table gives the nitrate concentration of the mixed liquor leaving the aerobic basin.

These values can be compared to values in the eighth column that were calculated by use of Equation 2 and the assumption that 12.5% of the influent TKN is lost to the waste sludge. As seen, the calculated values are consistently low.

This discrepancy is largely attributed to an overestimation of the amount of nitrate removed in the anoxic zone—each mg/l of nitrate leaving the anoxic zone increases the final effluent nitrate concentration roughly by the same amount.

In the data presented, the greatest difference between observed and calculated N_{out} values occurred in experiments with the lowest influent COD and the lowest nitrate removal rates. This finding is consistent with the removal rate model presented and suggests that, at these lower influent concentrations, insufficient COD was

Table 3—Combined nitrification/denitrification—summary of results.

	Feed rate l/h	TKN _{in} mg/l	TKN _{out} mg/l	Influent COD mg/l	Effluent COD mg/l	N _{out} observed mg/l	N _{out} calculated mg/l	Nitrate removal rate mg/mg·d
Run 1 J = 14.7 R = 1.0	0.71	209	4.0	1649	110	16.5	10.7	0.15
Run 2 J = 16.2 R = 0.84	0.70	240	<1.0	1627	72	15.2	11.6	0.17
Run 3 J = 15.2 R = 0.97	0.76	227	9.0	1462	136	12.8	11.0	0.16
Run 4 J = 13.1 R = 0.93	0.77	173	9.0	1413	75	12.8	9.5	0.16
Run 5 J = 15.0 R = 0.90	0.72	171	2.0	1248	84	26.0	8.7	0.13
Run 6 J = 14.4 R = 0.90	0.76	218	4.0	1039	102	22.4	11.5	0.14

provided to achieve the desired degree of nitrate removal.

The overall rates of nitrate removal in the anoxic zone are also shown in Table 3. In all cases the removal rates are substantially higher than the 2.93 mg/mg·h (0.07 mg/mg·d) rate suggested for design by EPA.⁸ From these data, however, it is not clear whether the high rates can be attributed to staging or simply to the high-influent COD.

More revealing are the typical stage-to-stage nitrate

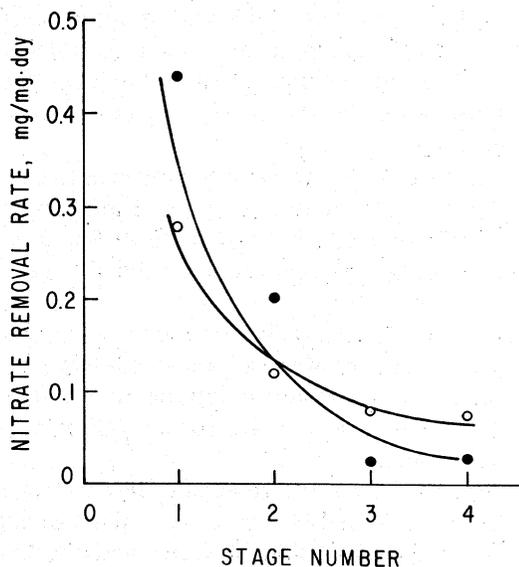


Figure 4—Nitrate removal rates across the four stages of the anoxic basin shown in Figure 1. Data are taken from the experimental runs 2 (●) and 6 (○) in Table 3.

removal rates shown in Figure 4. In the range of conditions studied, the nitrate removal rates were high in the first stage, dropped off markedly in the second stage and then leveled off in the third and last stages. These data are consistent with an exponential decay in reaction rate depicted in the rate model. The particularly high first stage nitrate removal rate demonstrates the positive effect of high-influent COD and the use of a staged anoxic basin in taking advantage of that initial driving force.

COD and TKN removal. 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 (EPA Subpart A) will require removal of approximately 96% of the influent TKN and 98% of the influent COD.^{1,13} In combined N/D an average of over 97% of the TKN and 93% of the COD was consistently removed from the experimental influent. Based on the results obtained here, we project that if combined N/D is coupled with physical-chemical pretreatment of the unhairing stream, up to 98% TKN and 96% of the COD can be removed from chrome tanning waste. Therefore, with this combination of treatments, EPA proposed TKN requirements can be met but the COD requirements cannot. Further, the results indicate that although it should be possible to meet the proposed BAT limitations for COD, P/C pretreatment of more than the unhairing stream will probably be required.

The relatively high degree of COD removal achieved through combined N/D was an encouraging but unexpected result. On the basis of prior studies of simple activated sludge and nitrification carried out continu-

ously for over a year, it was concluded that on average no more than 90% of the influent soluble COD could be removed through biological means. The additional 3% removal achieved here suggests that through the use of moderate recycle combined N/D, effluent COD can be reduced by over 30% of that obtained in the simpler systems studied. Side-by-side comparison of treatment systems are planned to confirm these results.

Implication in larger scale. It is clear from the results that the strong point of the staged anoxic basin is the particularly high rate (and degree) of nitrate removal achieved in the first stage in response to the large concentration of COD_r available there. To take full advantage of this COD_r for nitrate removal, it is important to minimize the amount of oxygen available. In the laboratory system, the presence of oxygen in the anoxic basin was reduced first by limiting the rate of aeration in the last aerobic stage and second by sparging the anoxic zone with a large volume of nitrogen gas. This approach would hardly be practical on commercial scale. An alternative is to provide a means to allow the endogenous activity of the sludge to reduce the oxygen concentration of the mixed liquor to near zero before recirculation to the anoxic zone. In one such scheme, a staged anoxic zone could be followed by an oxidation ditch sized to provide a sufficient aerobic volume for nitrification plus an additional increment of volume sufficient to allow the residual oxygen to be utilized prior to reaeration. The aerobic mixed liquor would be drawn from the point of lowest oxygen concentration and recycled to the anoxic zone.

In a potentially less expensive but less versatile scheme, the staged anoxic basin could be replaced by a narrow anoxic channel that is added to the oxidation ditch. At the point of lowest oxygen concentration, the aerobic mixed liquor flowing around the ditch would be split, and a portion would flow through the anoxic channel. Wastewater and recycled sludge would be fed to the system at the inlet to the anoxic channel. Because the entire flow pattern (anoxic and aerobic horizontal flow velocities) would likely be powered by the oxidation ditch aerators, the recycle ratio (J) may be difficult to control.

CONCLUSIONS

In combined N/D, over 97% of the TKN and 93% of the soluble COD can be removed from P/C-treated lime-sulfide unhairing effluent. Nitrate formed in the process can be removed at a high rate because of both the high influent COD concentration and the use of a staged anoxic zone. The amount of nitrate removed through combined N/D is dependent on the aerobic mixed liquor recycle ratio. For chrome tanning and finishing operations to meet proposed EPA BAT limitations, it is likely that P/C pretreatment of the unhairing effluent stream and other streams will be required.

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Authors. Curtis C. Panzer, Michael Komanowsky, and Gerald E. Senske are chemical engineers, Eastern Regional Research Center, U. S. Department of Agriculture, Philadelphia, Pa.

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