Nutrient Balance in Aerobic Biological Treatment of Tannery Wastewater

by

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Abstract

The effect of nutrient composition of tannery wastewater on aerobic biological treatment, particularly on the removal of ammonia nitrogen (NH_3-N) and total nitrogen (TN) was investigated based on the theory of nutrient balance. During the biological treatment of conventional tannery wastewater, total organic carbon (TOC) and total phosphorus (TP) were almost exhausted. However, the removal of TN was unsatisfactory, suggesting that tannery wastewater contains excessive N source and insufficient C and P sources. When extra C and P sources were added together into the wastewater, the removals of NH_3-N and TN increased significantly. Under the optimal ratio of TOC:TN:TP (10:1:0.2), the removals of NH_3-N and TN were 100% and 80%, respectively, and the added C and P sources were almost consumed by activated sludge. This means that a good nutrient balance was achieved in this condition. Accordingly, when ammonium salts are replaced by organic acids and phosphates in the deliming and bating processes, it is reasonable to assume that the change of wastewater composition would favor the aerobic biological treatment of wastewater.

Introduction

Tannery wastewater commonly contains a large amount of ammonia nitrogen (NH_3-N) and total nitrogen (TN) due to the addition of ammonium salts in deliming and bating and the removal of non-collagenous proteins from raw hide/skin in beamhouse processes.[1] The end-of-pipe treatment is regarded as an effective approach to solving the serious impact of nitrogen. However, conventional secondary treatment (biological treatment) could not achieve satisfactory N removal efficiency. Therefore, a special N removal treatment, usually nitrification-denitrification, should be further performed.[2-4] On the other hand, the strategy of reducing N pollution at the origin, especially the use of non-ammonia deliming and bating technologies, has been recommended as a better solution. In our previous research, sodium hexametaphosphate, citric acid and sodium citrate have been successfully used in non-ammonia deliming and bating processes as substitutes for ammonium salts.[5, 6] With the use of these ammonia free chemicals, redundant P and C will be introduced into the wastewater although N is eliminated. It is known that the content of P in conventional tannery wastewater is extremely low due to the fact that nearly no P-containing chemicals are used. Therefore, we are deeply concerned with the introduction of P as it is also a restrictive nutrient in most freshwater systems that would cause eutrophication as the same as N.[7] In addition, citric acid and citrate contribute a great deal of total organic carbon (TOC) in wastewater, though they are reported to be easily biodegraded.[8] Anyway, the change of nutrient composition in wastewater will necessarily influence the aerobic biological treatment process.

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Aerobic biological treatment is a process that uses biodegradable organic matter in wastewater and oxygen to promote the growth of microorganisms, and hence removes the organic pollutants. Among a multitude of biological treatment processes, activated sludge process is regarded as the most classical method. This process involves activated sludge (a suspended biological floc composed of microorganisms) and oxygen in the adsorbing, oxidizing and removing organic pollutants in wastewater.[7, 9] In order to maintain the growth and reproduction of activated sludge, energy and C sources as well as several nutrients (mainly N and P sources) must be available in adequate amounts for microbial metabolism.[7] It has been reported that the nutrient balance is controlled by the mass ratio of C:N:P, generally around 100:5:1 for aerobic biological treatment, where N and P mean the contents of TN and total phosphorus (TP) in wastewater, respectively, and C commonly means COD or BOD in different literature.[10-14] It is worth noting that COD or BOD can be converted into TOC to represent the content of C[15-17] as a linear relationship can be established between TOC content and COD or BOD content for a given wastewater.[7] Furthermore, it is convenient to determine TOC and TN contents simultaneously by an instrument within 20 min. In this study, the effect of addition of C and P sources on aerobic biological treatment of tannery wastewater, especially the removal of NH_3-N and TN, was investigated. The optimal ratio of C:N:P in tannery wastewater, where the amount of C was characterized by TOC, was suggested. The results are also valuable for evaluating the effect of input change of nutrients caused by reformation of leather processing on biological treatability of tannery wastewater.

EXPERIMENTAL

Materials

Tannery wastewater and activated sludge were collected from Ruixing Leather Co., Ltd. (Haining, China). The wastewater was sampled from the primary clarifier, which was ready for biological treatment. The concentrations of TOC, NH_3-N, TN, TP as well as the pH of the raw wastewater were determined. The activated sludge was sampled from the aeration tank. The chemicals used for biological wastewater treatment and analysis of wastewater were of analytical grade.

Procedures for Aerobic Biological Wastewater Treatment

The wastewater and the activated sludge were mixed in a 2000 mL measuring glass, where the ratio of wastewater and sludge was 2:1 (v/v). An aeration device was used for the biological wastewater treatment (Figure 1). The ambient temperature (25°C) was controlled by an air-conditioner. After aerobic biological treatment, the mixture of wastewater and sludge was sampled for mixed liquor suspended solids (MLSS) and sludge volume (SV) determinations. At the same time, the mixture was centrifuged at 5000 rpm for 10 min. Then the supernatant was used for the measurements of TOC, NH_3-N, TN and TP.

Figure 1. Aeration device for biological wastewater treatment

Analytical methods

TOC and TN were measured by using TOC/TN analyzer (LiquiTOC, Elementar, Germany). NH_3-N was determined by distillation and titration method.[18] TP was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Optima 8000, PerkinElmer, USA) with acid digestion pretreatment.[18] MLSS and SV were measured according to the standard methods for the examination of wastewater.[18]

Aerobic Biological Treatment with the Addition of C and P Sources

Four groups of aerobic biological treatment trials were performed according to the procedures above. Group 1 was control without addition of C and P sources. Glucose (900 mg/L, based on the content of C, similarly hereinafter) was added in group 2 as C source. Trisodium phosphate (24 mg/L, based on the content of P, similarly hereinafter) was added in group 3 as P source. C and P sources (900 mg/L of glucose and 24 mg/L of trisodium phosphate) were added in group 4. Samples were collected after 0, 12, 24, 48, 72 and 96 h of biological treatment, and analyses were carried out immediately.

Aerobic Biological Treatment with Different C/N Ratios

Six groups of aerobic biological treatment trials were performed according to the procedures above. Group 1 was control without addition of C and P sources. Different amounts of glucose were added in the other five groups as C source to ensure that the ratios of TOC to TN (C/N) in the wastewaters were approximately 5:1, 8:1, 10:1, 13:1 and 16:1 (w/w, similarly hereinafter), respectively. Simultaneously, an equal amount of trisodium phosphate (24 mg/L) was added in each of the five groups as P source so that the ratio of TN to TP (N/P) was 1:0.2. Samples were collected before and after biological treatment for 48 h, and analyses were performed as described above.

Aerobic Biological Treatment with Different N/P Ratios

Five groups of aerobic biological treatment trials were performed according to the procedures above. Group 1 was control without addition of C and P sources. An equal amount of glucose (900 mg/L) was added in each of the other four groups as C source so that the C/N ratio was 10:1. At the same time, different amounts of trisodium phosphate were added in the four groups as P source to ensure that the N/P ratios in the wastewaters were approximately 1:0.05, 1:0.1, 1:0.2 and 1:0.5, respectively. Samples were collected and analysed before and after biological treatment for 48 h.

Aerobic Biological Treatment using Different P Sources

Three groups of aerobic biological treatment trials were performed according to the procedures above. Glucose was used as the C source for each group. Trisodium phosphate (TSP, $Na_3PO_4 \cdot 12H_2O$), sodium dihydrogen phosphate (MSP, $NaH_2PO_4 \cdot 2H_2O$) and sodium hexametaphosphate (SHMP, $(NaPO_3)_6$) were used as the P source, respectively. The ratio of TOC:TN:TP (C:N:P) was set to be approx. 10:1:0.2. Samples were collected and analysed before and after biological treatment for 48 h.

RESULTS AND DISCUSSION

Characteristics of Raw Tannery Wastewater and Activated Sludge

Table I shows the characteristics of the tannery wastewater after primary treatment. The pH of the wastewater was 7.95, which was suitable for aerobic biological treatment. The content of NH_3-N in wastewater (61.5 mg/L) accounted for about 50% of TN (124.2 mg/L), and the other half should be mainly organic nitrogen. As chemicals containing P were seldom used in leather processing except a little phosphated fatliquor, the TP concentration in wastewater was only 1.2 mg/L. As a result, the original ratio of C:N:P in the wastewater was approx. 3:1:0.01. The activated sludge used for the experiment was present in the form of tawny floc with good settling properties. The pH of the sludge was 8.40.

Effect of Addition of C and P Sources on Aerobic Biological Treatment

In order to investigate the effect of addition of C and P sources on aerobic biological treatment, four groups of treatment trials were conducted. The results are shown in Figure 2. For the group with the addition of both C and P sources, the rates of NH_3-N and TN removal increased significantly compared with the other groups (Figure 2(a) and 2(b)). NH_3-N was exhausted after treatment for 24 h. TN concentration dropped to the minimum with the removal reaching more than 80% after treatment for 48 h. At the same time, most of the C source added was consumed (Figure 2(c)). The residual carbon should be non-biodegradable matter. In addition, Figure 2(d) shows that the concentration of TP in the C and P added wastewater decreased to 2 mg/L after treatment for 12 h and then remained stable. It should be noted that the determined initial concentration of TP in the wastewater was approx. 7 mg/L, although the offer of P was 24 mg/L. This may be due to the adsorption of phosphate on activated sludge. Actually this part of phosphate was also available for microorganisms. All the results above indicated that assimilation of microorganisms to was predominant in the initial 48 h, and C, N and P sources were used as nutrients for the microbial cell synthesis and growth. This could also be demonstrated by the increases of MLSS and SV, as shown in Figure 3. By contrast, the groups with the addition of single C source or P source as well as control resulted in poorer removals of NH_3-N and TN. During the treatment, the concentration of TN in wastewater decreased from 120 mg/L to 90 mg/L in the initial 48 h, and then slightly increased probably due to the autolysis and endogenous respiration of activated sludge. Moreover, TOC and TP in control group were almost exhausted at the end of biological treatment. These facts demonstrated that lack of C source and/or P source limited the consumption of N source by the activated sludge. Conventional tannery wastewater was rich in N source and lack of C and P sources in terms of the nutrient balance of activated sludge (see Table I and control group in Figure 2). Therefore, the strategies that can reduce N impact and supplement appropriate amounts of C and P in leather processing could be suggested in order to meet the nutrient requirement of aerobic biological wastewater treatment.

Effect of C/N Ratio on Aerobic Biological Treatment

Based on the results of the previous section, the duration of aerobic biological treatment was set to be 48 h for the following experiments. Six groups of aerobic biological treatment trials were carried out using different C/N ratios and equal N/P ratio (1:0.2). The effect of C/N ratio on wastewater treatment is shown in Figure 4 and Table II. The removal of NH_3-N reached 100% for all the groups with the addition of C and P sources, and the removal of TN in these groups was much higher than control (Figure 4). When the C/N ratio was

TABLE I
Characteristics of the tannery wastewater after primary treatment.

pH	TOC (mg/L)	NH_3-N (mg/L)	TN (mg/L)	TP (mg/L)
7.95	413.7	61.5	124.2	1.20

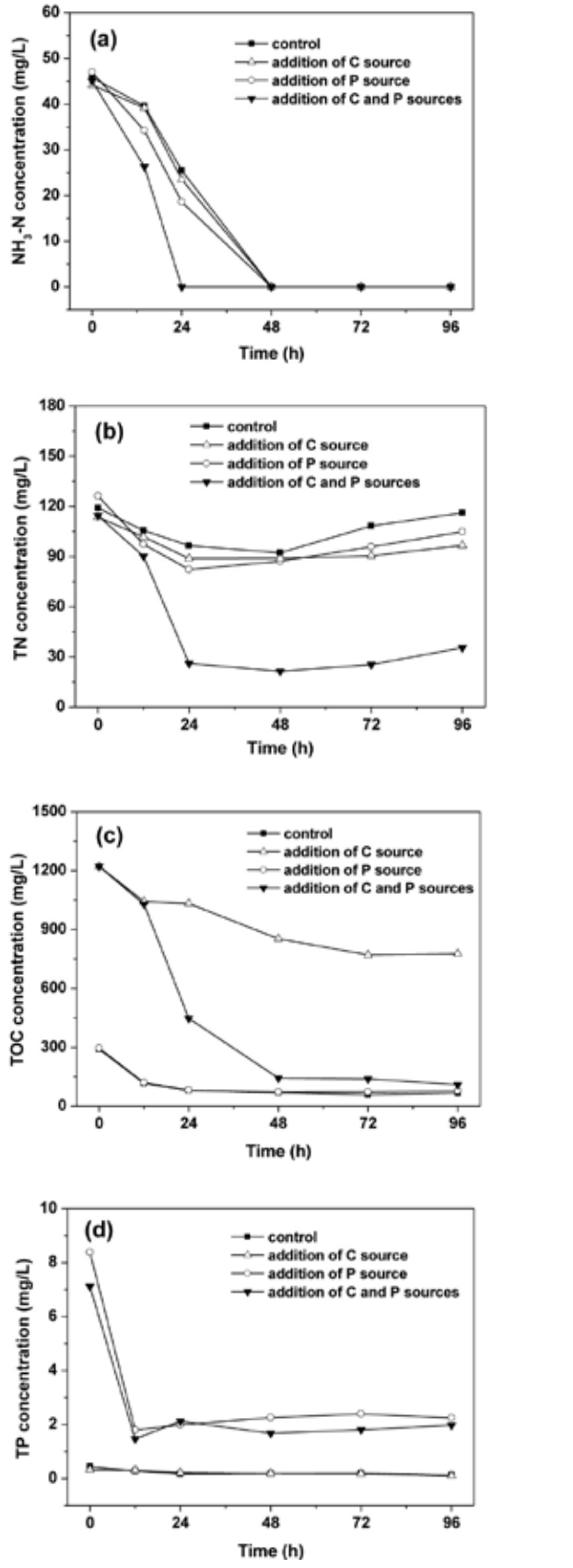

Figure 2. Effect of addition of C and P sources on aerobic biological wastewater treatment: (a) NH_3-N; (b) TN; (c) TOC; (d) TP.

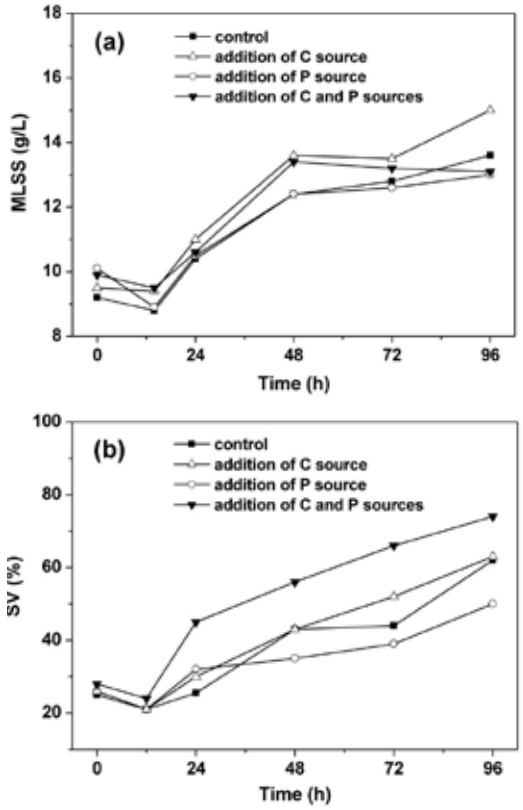

Figure 3. Effect of addition of C and P sources on activated sludge properties: (a) MLSS; (b) SV.

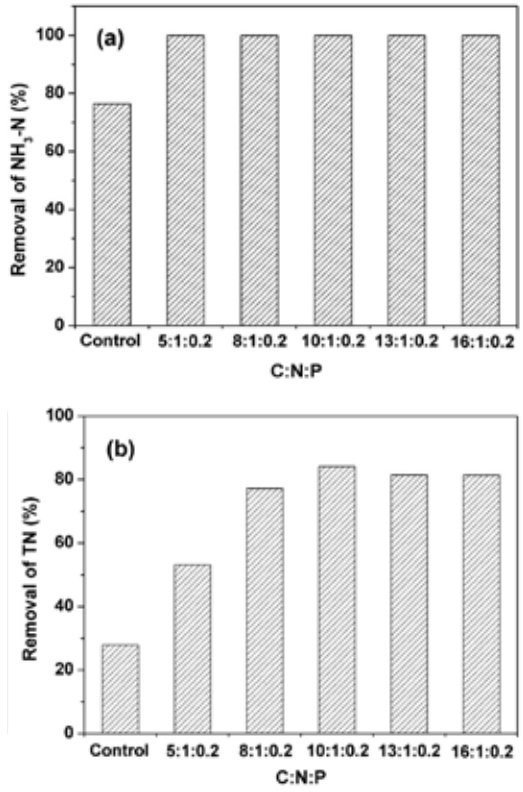

Figure 4. Effect of C/N ratio on aerobic biological wastewater treatment: (a) NH_3-N; (b) TN.

TABLE II
Wastewater parameters before and after treatment using different C/N ratios.

C:N:P	TOC (mg/L)		TN (mg/L)		TP (mg/L)	
	0 h	48 h	0 h	48 h	0 h	48 h
Control	271.6	66.4	120.6	87.0	0.21	0.02
5:1:0.2	660.1	71.2	119.3	55.9	10.21	1.63
8:1:0.2	994.7	82.2	119.8	27.3	9.65	1.56
10:1:0.2	1198.5	102.8	118.0	18.7	9.88	1.24
13:1:0.2	1651.5	259.7	118.3	21.9	7.78	1.59
16:1:0.2	1979.2	645.5	112.3	20.8	8.29	1.73

5:1, it was found that the removal of TN was only 53% (Figure 4(b)), and the residual TOC in wastewater was nearly the same as control (Table II). This means that C source was insufficient using this C/N ratio, resulting in a large surplus of N source. The removal of TN increased to the peak of 84% in the C/N ratio of 10:1, and then showed no more enhancement with further increase in C/N ratio. Meanwhile, the residual TOC in wastewater kept rising (Table II), suggesting that the C source added was excessive in the C/N ratios of 13:1 and 16:1. In general, the optimal C/N ratio for aerobic biological treatment was 10:1.

Effect of N/P Ratio on Aerobic Biological Treatment

The investigation on the effect of N/P ratio on aerobic biological treatment was further performed based on the optimal C/N ratio of 10:1. Figure 5(a) shows that NH_3-N was exhausted after treatment for 48 h in all the experimental groups where both C and P sources were added, which was similar to the results shown in Figure 4(a). The removal of TN as well as the consumption of TOC was positively correlated with the offer of P (Figure 5(b) and Table III). When the N/P ratio was 1:0.2 or 1:0.5, the removal of TN achieved 80%, and the residual TOC was around 100 mg/L. However, the TP concentration in wastewater was as high as 5.74 mg/L in the N/P ratio of 1:0.5, indicating that P source was excessive in this condition. On the contrary, P source was inadequate for nutrient need of aerobic biological treatment in the N/P ratio of 1:0.1 or 1:0.05, which led to relatively low removals of TN and TOC. In consideration of nutrient balance of activated sludge, the optimal ratio of C:N:P was 10:1:0.2.

Effect of Different P Sources on Aerobic Biological Treatment

In order to investigate the effect of different P sources on aerobic biological treatment, three types of phosphates, i.e. TSP ($Na_3PO_4 \cdot 12H_2O$), MSP ($NaH_2PO_4 \cdot 2H_2O$) and SHMP ($(NaPO_3)_6$) were used as the P source for the treatment, respectively. The ratio of C:N:P was adjusted to 10:1:0.2 for all

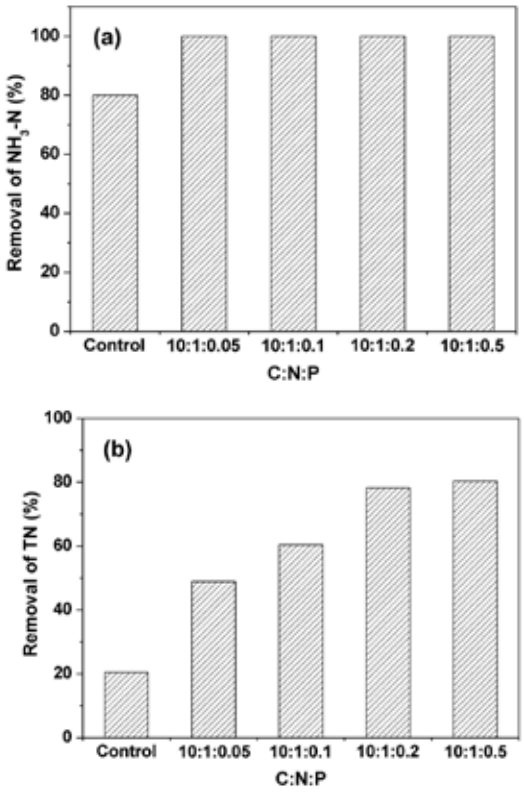

Figure 5. Effect of N/P ratio on aerobic biological wastewater treatment: (a) NH3-N; (b) TN.

the groups. Table IV shows that the removals of TOC, TN and TP in the group using TSP as P source were higher than those in the other two groups. This may be due to the fact that TSP was dissolved in the wastewater as orthophosphate, which could be directly available to the activated sludge.[19] SHMP, as a type of polyphosphate, should be firstly converted into orthophosphate and then utilized by activated sludge, which probably resulted in slower removal of TOC and TN.[19] But in fact, the addition of SHMP as P source is still effective to remove the pollutants in the tannery wastewater.

TABLE III
Wastewater parameters before and after treatment using different N/P ratios.

C:N:P	TOC (mg/L)		TN (mg/L)		TP (mg/L)	
	0 h	48 h	0 h	48 h	0 h	48 h
Control	234.2	64.3	116.6	92.8	0.15	0.06
10:1:0.05	1126.3	428.4	113.3	57.9	1.33	0.40
10:1:0.1	1195.6	239.9	110.6	43.8	3.42	2.41
10:1:0.2	1150.1	116.7	116.6	25.4	5.85	1.42
10:1:0.5	1150.1	100.8	117.1	23.1	15.19	5.74

TABLE IV
Wastewater parameters before and after treatment using different P sources.

P source	TOC (mg/L)		NH_3-N (mg/L)		TN (mg/L)		TP (mg/L)	
	0 h	48 h	0 h	48 h	0 h	48 h	0 h	48 h
$Na_3PO_4 \cdot 12H_2O$	1099.6	89.2	43.4	0	116.1	27.5	10.30	1.46
$NaH_2PO_4 \cdot 2H_2O$	1145.7	195.7	43.4	0	115.8	55.0	14.97	3.88
$(NaPO_3)_6$	1151.7	187.7	43.8	0	118.7	54.4	10.80	4.54

Discussion on the Nutrient Balance in Aerobic Biological Treatment

In the view of nutrient balance in aerobic biological treatment, C and P sources in conventional tannery wastewater are insufficient to some extent, whereas N source is excessive due to the use of ammonium salts in deliming and bating as well as the removal of non-collagenous proteins from the raw hide/skin. In our previous research, SHMP, citric acid and sodium citrate have been successfully applied in non-ammonia deliming and bating processes as substitutes for ammonium salts.[5,6] The reformation of technologies is inevitable to change the nutrient composition of tannery wastewater. The contents of C and P sources in wastewater would increase, while the content of N source would decrease significantly, which makes the modified ratio of C:N:P closer to the requirement of nutrient balance in comparison with the original ratio. Therefore, it can be inferred that aerobic biological treatment of the wastewater produced from the non-ammonia process should be easier than that of conventional tannery wastewater, and the difficulty of nitrogen removal will be alleviated greatly.

In addition, although the wastewater and the activated sludge used in this study were collected from a typical tannery, the optimized ratio of C:N:P (10:1:0.2) for the aerobic biological treatment may not be perfectly suitable for other tanneries in consideration of the differences in leather processing, wastewater composition and activated sludge. However, the exploration of the biological wastewater treatment in terms of nutrient balance is still instructive. Besides the reformation of leather processing mentioned above, a comprehensive treatment of tannery wastewater together with other industrial wastewaters rich in C and P (such as pulp and paper mill wastewater, organic chemical industry wastewater) may be an effective solution where the complementary nutrients supplied by these wastewaters could meet the requirement of nutrient balance, and thus favor the aerobic biological treatment. As industrial parks have begun to spring up in China, the comprehensive treatment of wastewaters from different industries becomes more possible.

CONCLUSIONS

Conventional tannery wastewater is commonly rich in N, but lacks C and P in terms of nutrient balance, which limits the aerobic biological treatment of the wastewater by activated sludge. The addition of C and P sources in wastewater, especially in the C:N:P ratio of 10:1:0.2, was shown to remarkably improve the removal of NH_3-N and TN. These results infer that the strategies of reducing N input and appropriately introducing C and P in leather processing would be favorable for the construction of nutrient balance in wastewater and the increase in efficiency of biological wastewater treatment.

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