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Perspectives on Biological Treatment of Tannery Effluent

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Abstract

Leather processing is an important economic activity around the world and uncontrolled release of tannery effluents to natural water bodies causes environmental degradation and increases health risks to human beings. The treatment of tannery effluent is a complex technological challenge because of the presence of high concentrations of organic and inorganic pollutants of both conservative and non conservative nature. In this review paper information relevant to tannery effluents and its prospective on biological treatment processes and other recent potential biological processes are discussed. Emphasis is laid on the removal of organic matter (COD/BOD), NH_4-N and sulphide/sulphate from tannery effluent. Though the aerobic process is efficient in treating tannery effluent, it requires an extended aeration time at low organic loading rates and thereby increasing the overall treatment cost. Anaerobic process is not effective because of sulphide inhibition problems. Sulphide inhibition control is essential for successful anaerobic treatment of tannery effluent. Sequencing Batch Reactor (SBR) and membrane reactor technologies are found to be effective for removal of organic matter and ammonia, but they are having very high operational cost. A recent development is the employment of alternate electron acceptor/donor already present in tannery effluent for simultaneous removals of COD/BOD, NH_4-N and sulphide/sulphate with possibility of elemental sulphur recovery at higher organic loading rates. The recent development shows possibility of high rate treatment of tannery effluent in an alternate and an effective way suitable to both developing and developed countries.

Keywords: Tannery effluent; Biological treatment; Sulphate; Sulphide; Sulphidogenesis; Anoxic ammonia removal

Introduction

Leather processing is an important economic activity in many developing and developed countries. It has been estimated that the annual production of leather in the entire world is approximately 1.67 billion m^2, with an estimated trade value of US$ 70 billion. South Asia meets approximately 20% of world's needs [1]. Since most of the developing countries are using the traditional leather processing, the characteristics of effluent are similar. Tanneries in India are categorized as small (approximately 80 %), medium (approximately 15%) and large-scale [2]. These tanneries are mainly located in the states of Tamilnadu, Karnataka, Andhra Pradesh, Rajasthan, Punjab, Utter Pradesh and West Bengal [3]. The tannery effluent produced from traditional or conventional leather processing contains a high concentration of organics (COD/BOD), Suspended Solids (S.S) and inorganics like NH_4-N, SO_4^{2-} /S^{2-}, Cr(III) and Chlorides [4-6]. Uncontrolled release of tannery effluents to natural water bodies causes environmental degradation and increases health risks to human beings [7]. The environmental degradation caused is depletion of dissolved oxygen in streams/rivers, eutrophication of water bodies, toxicity to fishes and other aquatic flora and fauna [8,9]. Moreover, local inhabitants are suffering from water borne diseases associated with water pollution, e.g., gastroenteritis, hyperchloremic acidosis, hypertension, arteriosclerosis, cardiac arrest, retinal toxicity, hepatic fibrosis, hepatocellularcancer, diabetes, sperm damage, feto-maternal death, and impaired neurobehavioral functions [10]. Hence, appropriate treatment of effluent is required prior to its discharge into the environment [5]. For complete treatment of tannery effluent; primary, secondary and tertiary treatments are necessary. Primary treatment removes S.S, Chromium, Oil and Grease. Secondary treatment is normally employed for removal of pollutants using biological processes by oxidative-reductive processes. Tertiary treatment is required when color, refractory organic compounds and salts are to be removed and generally expensive physic-chemical treatments techniques are employed. As per the very recent directive of Central Pollution Control Board (CPCB), New Delhi, India, tanneries are required to meet zero liquid discharge (ZLD) norms because of the potential threat to environment and human beings by the discharge of tannery effluents. This directive has prompted tanneries to adopt advanced treatment techniques after secondary treatment to make the treated water re-usable in the tanneries.

In this review paper information relevant to tannery effluents and its prospective biological treatment processes and other recent potential biological processes are discussed. Emphasis is laid on the removal of organic matter (COD/BOD), NH_4-N and sulphides/sulphates. Finally, a recent development by employing alternate electron acceptors/donors already present in tannery effluent for simultaneous removal of COD/BOD, NH_4-N and sulphides/sulphates with possibility of sulphur recovery is included. The recent development shows possibility of high rate treatment of tannery effluent in an alternate and an effective way.

Pollution potential of tanneries

In the leather tanning process, a series of chemical treatments are performed by applying a large number of chemicals such as surfactants, acids, dyes, natural or synthetic tanning agents, sulfonated oils, and salts to transform animal skin into an unalterable and imputrescible product. Considering the large amounts of chemicals applied, and the low biodegradability of these chemicals, tannery effluent treatment is a complex technological problem [11].

The amount of wastewater and the pollution generated during each major operation involved in a typical leather tanning process are presented in Table 1 [4,12]. The combined volume of tannery effluent

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produced in the conventional tanning process varies from 34 to 56 m^3/T (ton) of raw hide processed. This is comparable to that produced in Indian tanneries i.e., 35-40 m^3/T of raw hide processed [13]. Table 2 presents the Indian and the international scenarios of characteristics of combined tannery effluents [1,5,6,11,12,14-17]. The characteristics of Indian tannery effluent are comparable with that produced elsewhere except in case of high TDS value. The high TDS value in Indian tannery effluent is due to addition of common salt as the major preservative for raw hides. However, the characteristic values shown in Table 2 shows that the techniques of treatment of tannery effluent employed by one country can be adopted in another country.

Overview of tannery effluent treatment

Three stages of treatment are usually required in order to meet the stringent discharge norms applicable in many countries for safe disposal of tannery effluent to the environment. They are primary, secondary and tertiary stage treatments. Such three stages of treatment are required because of the complex characteristics of tannery effluent. Primary treatment involves screening, equalization, chemical treatment and primary sedimentation. It is mainly employed to remove suspended solids, chromium, oil and grease, and sulphides in some cases. However, an appreciable amount of COD (50- 65%) and TKN (40-50%) are also removed in the primary treatment [12].

Secondary treatment usually involves a biological process for removal of non conservative type organic matter (COD/BOD), Sulphides, and TKN/NH_4-N in some cases. Tertiary treatment is essential for removing refractory organic compounds imparting colour and inorganic salts and they are considered as conservative pollutants. The following sections describe tannery effluent treatment practiced in India and elsewhere.

Tannery effluent treatment in developing countries

Tanneries in developing countries like India, Bangladesh, Pakistan, Egypt, Srilanka etc. can be grouped into four major categories for effluent treatment and management [18]:

1. Large and medium scale tanneries with adequate land, finance and managerial capacity, with individual effluent treatment plants. There are nearly 200 individual tannery effluent treatment plants in India.
2. Tanneries located in clusters and do not have adequate land and financial/technical capability. Such units are usually provided with a Common Effluent Treatment Plant (CETP). There are 17 CETPs in India, out of which 13 are in Tamil Nadu, 2 in Uttar Pradesh, 1 in Bangalore and 1 in Jalandhar.
3. Cluster of tanneries in cities like Istanbul and Izmir in Turkey, Kolkata and Jalandhar in India, Colombo in Srilanka, and Cairo in Egypt etc. do not have adequate land even to set up a CETP. The only solution in such cases is to relocate and develop a separate industrial complex with CETP system. The newly established leather complex at Kolkata, India, with a CETP system to relocate all the 540 tanneries in Kolkata city is a typical example.
4. Scattered small-scale tanneries cannot set up individual effluent treatment plants. Such units should be relocated to one of the clusters with CETP system or should be closed down.

The basic process flow diagram followed in India for both individual and common effluent treatment systems, is shown in Figure 1 [5,14,19]. It can be seen from this process flow diagram that secondary stage treatment is carried out mainly for the removal of BOD/biodegradable COD and sulphides.

In certain cases, anaerobic process is replaced with aerobic process. A two stage aerobic treatment with an intermediate clarifier and the sludge recycling facility is usually adopted [14]. Though this approach gives a better effluent quality the cost of treatment is high.

Tannery effluent treatment in developed countries

The tannery effluent treatment in developed countries is usually carried out to a higher degree to meet the discharge standards for nitrogen also. This is because of stringent nitrogen standards are enforced in such countries. Primary treatment followed by the extended aeration process with nitrification and denitrification is practiced to obtain the required treated effluent quality. Such treatment is efficient in removal of high concentrations of suspended solids, Cr III, organic matter (COD/BOD), TKN/NH_4-N and sulphides [12]. Advanced integrated pond systems [20], Sequential Batch Reactor (SBR) technology [3,15,21-24] and MBR technology [25] are among the recently developed alternatives for the removal of both organic matter and nitrogen from tannery effluent.

Appraisal of biological treatment of tannery effluent

In Ref. [26] studied the biokinetics and toxicity assay of primary treated tannery effluents using batch reactor. Their results showed that primary treated tannery effluent is not toxic to microorganisms. Also, they concluded that a Food to Microorganism (F/M) value of 0.09 and a Hydraulic Retention Time (HRT) more than 24 hours are required for meeting the effluent BOD discharge standard of 30 mg/L applicable in India. The half-velocity constant (Ks) was in the range of 245 to 312 mg/L as BOD. A relatively higher value of Ks for tannery wastewater as compared to that for domestic wastewater indicates that substrate removal is slower and hence, longer retention time is required for complete biodegradation of tannery wastewater. These results suggest that the extended aeration system is the most appropriate activated sludge treatment method for tannery wastewater. Ref. [27] studied the performance of a bench scale, continuous flow activated-sludge reactor for treating the primary treated effluent from a chrome-tanning industry, at temperatures varying between 12 and 34 °C. They found that optimum temperature for BOD removal was between 26 and 34

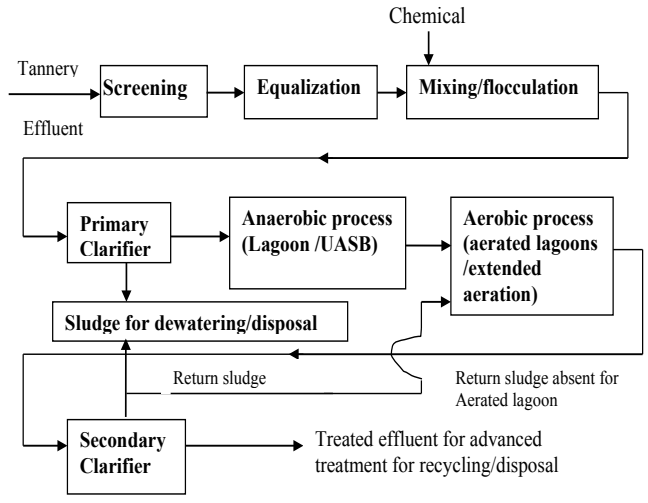

Figure 1: Process flow diagram for a typical tannery effluent treatment system in India.

Operation/Process	WW Flow (m^3/T)	Pollution load (kg/T of raw hides processed) if conventional technology is employed								
		S.S	COD	BOD	Cr	S^{2-}	NH_3-N	TKN	Cl^-	SO_4^{2-}
Soaking	7-9	11-17	22-33	7-11	-	-	0.1-0.2	1-2	85-113	1-2
Liming	9-15	53-97	79-122	28-45	-	3.9-8.7	0.4-0.5	6-8	5-15	1-2
Deliming/Bating	7-11	8-12	13-20	5-9	-	0.1-0.3	2.6-3.9	3-5	2-4	10-26
Tanning	3-5	5-10	7-11	2-4	2-5	-	0.6-0.9	0.6-0.9	40-60	30-55
Post Tanning	7-13	6-11	24-40	8-15	1-2	-	0.3-0.5	1-2	5-10	10-25
Finishing	1-3	0-2	0-5	0-2	-	-	-	-	-	-
Total	34-56	83-149	145-231	50-86	3 -7	4-9	4-6	12-18	137-202	52-110

Table 1: Summary of pollution loads in effluents contributed by individual operations of leather tanning. SS- Suspended Solids; COD- Chemical Oxygen Demand; BOD-Biochemical Oxygen Demand; Cr- Chromium; S^2-Total aqueous sulphides; NH_3-N- Ammonia as Nitrogen; TKN- Total Kjeldhal Nitrogen; Cl–Chloride; SO_4^{2-}-Sulphate; T- Ton; WW- Wastewater (Source: European Commission [12]).

S No	Characteristics	India	International*
1	pH	7-8.5	7-7.5
2	Suspended Solids	2000-3000	1844-3311
3	COD	3000 -6000	3222-5133
4	$BOD_5$20°C	1200 -2700	1111-1911
5	Sulphate COD/Sulphate ratio	1000-3000/2-3	1156-2444/2.1 – 2.8
6	Sulphides	25-220	88-200
7	TKN	250-400	267-400
8	NH_4-N	100-300	89-300
9	Chromium(III)	60-75	67-156
10	Chloride	6000-9500	3044-5700
11	TDS	10000-21000	8000-13899

*Calculated based on average effluent quantity of 45 m^3/T of raw hide (Adapted from: European Commission).

Table 2: Characteristics of combined tannery effluent, all values are in mg/L except COD/Suphate ratio and pH.

°C and showed that primary treated effluent is amenable to biological treatment, with a BOD removal efficiency ranging from 84 to 92%. Their kinetic study also yielded a higher half velocity constant (113-142 mg/L), indicating that activated sludge treatment of tannery effluent requires more time for the treatment. Ref. [28] demonstrated Biological pretreatment of tannery wastewater using a full-scale hydrolysis acidification system in a cold region. The average BOD/COD of the tannery wastewater was improved from 0.38 to 0.56, and the pH decreased from 8.4 to 7.6 after the hydrolysis acidification treatment. The results showed that hydrolysis acidification could improve the biodegradability of the tannery effluent. Ref. [29] studied the activated sludge system for treating diluted beam house effluent. Their system achieved 99% BOD removal efficiency at an organic loading rate lower than 2 kg COD/m^3/d, whereas COD removal was approximately 80%.

The reactor operation was stable for this loading rate. For higher loading rates and F/M ratio more than 0.15, the system was less efficient (COD and BOD removals were lower than 40%). These results show that high organic loading rate and F/M ratio are not suitable for aerobic treatment of tannery effluent. Ref. [30] Studied the biological nitrogen and organic matter removal from tannery wastewater in pilot plant operations in Ethiopia by pre-denitrification and nitrification process. Ninety eight percentage removal efficiency for Total Nitrogen (TN) and COD, and 95% removal efficiency for NH_4-N were achieved in their system. Ref. [31] studied the treatment of tannery wastewater with high nitrogen content using anoxic/oxic membrane bio-reactor (MBR) and found that the reactor volume required for anoxic denitrification was only 50% of that required by a nitrification reactor. Thus, the pre-denitrification and nitrification process was found to be efficient for simultaneous removal of nitrogen and organic substrates from tannery wastewaters. Though this anoxic-oxic process appears to be suitable for tannery effluent, an external nitrification step and recycling of nitrate bearing effluents to anoxic zone are essential. Tannery effluent normally contains high concentration of sulphide.

The effect of sulphide on this anoxic-oxic process was not mentioned by authors. Ref. [32] described the performance of a full-scale CETP treating tannery wastewater, based on a single-sludge nitrification/denitrification process. The monitoring was carried out for 1.5 years. Their results indicated instability and a periodic failure of nitrification/denitrification process due to several reasons. Small deviations from the optimal pH in nitrification or denitrification basins, a temperature decrease to 17 °C or an increase of the influent nitrogen content reduced the plant's efficiency from 100% to 40% during certain periods. HRT and the Sludge Retention Time (SRT) seem to be the key parameters for the process control. However, [15], in a laboratory study, showed that the SBR operation was an effective tool for the removal of COD and TKN/NH_4-N (partly by simultaneous nitrification-denitrification) from primary treated tannery wastewater. SBR operation is known for retaining microorganisms having less growth rate [33]. Ref. [20] studied the removal of organics and nutrients from pre-settled tannery effluent by Advanced Integrated Wastewater Pond System AIWPS®. The overall organics removal performance of the AIWPS® was high, with removal efficiencies in the range of 90-98% for BOD and 86-92% for COD, respectively. AIWPS® reactors achieved a cumulative ammonia removal efficiency of 85%. For the overloaded condition, the overall ammonia removal efficiency decreased by 50%, while the BOD removal efficiency dropped by only 6%, indicating the higher vulnerability of ammonia removal mechanism to high loading conditions as compared to the organic matter removal. Though pond systems are considered as low cost systems, they are discouraged for tannery effluent treatment in India because of potential odor problems. Ref. [34] Demonstrated excellent ability of the Wetland to remove the metals present in tannery wastewater. The study showed that the concentrations of trace metals (Pb, Zn and Fe) were reduced by 25-45%, while total Cr was reduced by 95%.

A 3.5 L capacity Membrane Sequential Batch Reactor (MSBR) was used for the removal of organic carbon and ammonia from wastewater coming from the beam house section of a tannery by Ref. [35]. The wastewater, produced after the oxidation of sulphide compounds, contained average COD and ammonium concentrations of 550 and 90 mg/L, respectively. Removal efficiencies close to 100% in case of ammonium and 90% in case of COD were achieved. The total nitrogen removal efficiency ranged from 60 to 90%. This result shows an efficient operation of membrane SBR for organic matter and ammonia removal at lower concentrations from a sulphide free tannery effluent. Ref. [36] employed an innovative biofilm-suspended biomass hybrid membrane bioreactor for tannery wastewater treatment. The growth of nitrifiers in the hybrid system was promoted in the biofilms, while heterotrophs

were in suspension. This made it feasible to operate the unit at higher SRT for nitrifies than that for heterotrophs. During the treatment of the tannery wastewater, organic loading rate (OLR) and ammonia loading rate (ALR) were increased stepwise up to 4.5 kg COD/m^3/d and 1.2 kg NH_4-N/m^3/d, respectively. COD removal efficiency was 95%, while ammonia removal efficiency was 97%. The concentration of ammonia in the effluent was as low as 10 mg NH_4-N /L. Moreover, the membrane filtration unit made it feasible to operate the reactor at high OLR, without affecting either the settling properties of the sludge or the nitrogen conversion efficiency. Though this process is promising, costs of membrane treatment and maintenance are prohibitive at present scenario. Therefore membrane treatments may not be an attractive option for developing countries. Ref. [11] reported the results of an investigation on combining the biological degradation (sequential batch biofilm reactor (SBBR)) with chemical oxidation by ozone. The combined treatment was carried out in a laboratory scale reactor using the primary effluent from a centralized plant treating the wastewater from a large tanning district in Northern Italy. SBBR performance with ozonation was satisfactory with average COD, NH_4-N and TSS removal efficiencies of 97%, 98% and 99.9%, respectively. Compared to suspended growth systems, the main advantages of biofilm systems are:

(a) greater biomass concentration in the reactor with corresponding higher specific removal rates,

(b) greater volumetric loads,

(c) increased process stability towards shock loadings and

(d) biomass enrichment of slow growing organisms such as nitrifies.

Ref. [14] assessed the quality of treatment of tannery wastewater in India in two CETPs, constructed for two tannery clusters, at Jajmau (Kanpur) and at Unnao in the state of Uttar Pradesh, India. The Jajmau plant employs an upflow anaerobic sludge blanket (UASB) process, while the Unnao plant employs two stage activated sludge process (ASP). Investigations indicated that the performance of the ASP was superior. The treated effluent from the UASB had higher BOD/COD and considerable amounts of chromium (Cr) and sulphide, as compared to that in the effluent from the ASP. The reason for less amount of chromium in ASP was the prior removal of chromium in primary treatment, whereas there was no prior removal of chromium in the UASB based plant. The results of this study did not agree with the conventional wisdom that anaerobic processes are superior in tropical countries like India for treatment of tannery effluents. The major reason for this could be the sulphide inhibition while treating tannery effluent having low COD/SO_4^{2-} ratio. From Table 1, it is evident that tannery effluent is having lower COD/SO_4^{2-} ratio. This ratio becomes lower than 1.5 after primary treatment, as there is removal of COD in primary treatment excluding SO_4^{2-} removal. At COD/SO_4^{2-} ratios lower than 10; anaerobic process failures are reported due to sulphide inhibition [37].

An Up flow Anaerobic Fixed Biofilm Reactor (UAFBR) has been developed to treat tannery wastewater by Ref. [38]. Effects of major process variables such as HRT, Organic Loading Rate (OLR), and temperature on the COD removal in the reactor were evaluated. This technology ensures the retention of the active methanogenic biomass within the reactor, independent of the HRT. COD removal efficiency (60-75%) remained stable for a wide range of organic loading rates and operating temperatures. Their results showed that fixed biofilm reactor is a promising alternative to the anaerobic treatment of tannery effluents. However, the author has not addressed the sulphide toxicity with details of COD/SO_4^{2-} ratio. Table 3 summarizes the performances of various technologies for anaerobic treatment of tannery effluents. It can be seen from this Table that adoption of sulphide inhibition control [39] results in better treatment efficiency at lower HRT. It can also be observed that the treatment performance improves with HRT and biomass retention inside the reactors. However, the maximum treatment performance achieved by direct anaerobic treatment is lower as compared to that in extended aeration process. This is because of sulphide toxicity developed in anaerobic process while treating high sulphate containing tannery effluent. A separate section 4 is provided to deal with anaerobic treatment of sulphate bearing effluent in this paper. Ref. [40] studied biological sulfate removal from tannery wastewater in a two-stage pilot scale anaerobic treatment system. The concentration of sulfate in the influent had a significant effect on the sulphate reduction in both the stages. The removal efficiency of sulfate in the first stage was approximately 30%. In the second stage, sulphate reduction decreased with higher concentrations of sulfate in the influent. Ref. [6] studied the feasibility of using tannery effluent as organic carbon source for sulphate reduction process to produce sulphide, which has the potential for metal precipitation. Such an approach can be employed for acid mine drainage treatment. In their reactor, sulphate reduction varied from 60-80 % for a feed sulphate concentration of 1800 mg/L.

It can be seen from the appraisal of biological treatment of tannery effluent that the aerobic treatment of tannery effluent is superior to anaerobic treatment. However, the aerobic treatment requires extended aeration time for satisfactory removal of COD/BOD. Anaerobic treatment of tannery effluent performs well when sulphide produced in the process is properly controlled. SBR and/or MBR technology appear to be suitable for combined removal of organic carbon and nitrogen. However, they require sulphide removal as a pretreatment to obtain

Author	Substrate	Treatment	HRT, days	Influent COD, mg/L	Volumetric loading rate, Kg COD/m^3/d	% COD Removal
[39]	Beam house	Fixed bed reactor-1 with sulphide inhibition control (30 mg/L H_2S) by external biogas stripping and cleaning	1.9	6100	3.2	80
		Fixed bed reactor - 2 without sulphide inhibition control (140 mg/L H_2S)	2.1	6100	2.9	58
[40]	Wastewater	Fixed film	4.6	5250	1.14	66.1
[46]	Wastewater	Fixed bed	2.44	4440	1.82	66.2
[50]	wastewater	Stirred reactor	15	4163	0.28	36.4
			25	4074	0.16	59.6
			30	4074	0.14	60.3
[39]	Beamhouse	Contact process	2.5	2000-15000	1.27-3.89	62
[40]	Beamhouse	Fixed bed reactor	1	3000	3	51
		Fixed bed reactor with circulation	1	3000	3	39

Table 3: Anaerobic treatment of tannery wastewater (Adapted from Weimann et al. [39]).

improved performance. Also an extended period of aeration is required for nitrification. The above limitation of developed processes calls for an effective alternate treatment of tannery effluent.

Following sections discuss relevant literature related to anaerobic treatment of sulphate bearing effluents and recent developments in biological oxidation of ammonia and denitrification processes for nitrogen removal from wastewaters. The knowledge in these sections will be helpful in possibilities of developing an alternate effective effluent treatment system for tannery effluent and other similar kind of wastewaters.

Anaerobic treatment of sulphate bearing effluents

Sulphates bearing waste streams are generated by many industrial processes such as tannery, food processing (e.g., molasses, sea food, edible oil, etc.), pharmaceutical, pulp and paper, and petrochemical [39-41]. Under anaerobic conditions, sulphate can act as an electron acceptor for a group of bacteria that can couple the oxidation of reduced organic or inorganic compounds to the reduction of sulphate for bioenergetic purposes. This process is known as dissimilatory sulphate reduction (Sulphidogenesis) and the bacteria involved are known as the sulphate reducers or sulphate- reducing bacteria [42,43]. Based on the metabolic capacities, sulphate reducing bacteria can be classified into two categories - those species or genera that are capable of complete oxidation of organic compounds to CO_2 and those that carry out incomplete oxidation, usually to acetate as end-product [42]. The majority of sulphate-reducing bacterial species can also utilize sulphite, thiosulphate, organic sulphur compounds and elemental sulphur as electron acceptors [44,45].

Anaerobic treatment of sulphate bearing wastewater imposes severe toxicity to methane producing bacteria (MPB) because of the generation of high levels of sulphide in the process [46-49] and/or by direct sulphide load [39] along with the effluent. Toxicity of sulphide is pH dependent since only the unionized hydrogen sulphide can pass through the cell membrane and therefore, free H_2S is more toxic compared to other sulphide species [50,51]. Hydrogen sulphide dissociates in water according to the following equations [52]:

$$H_2S \leftrightarrow H^+ + HS^- ; (K_1 = 1.0 \times 10^{-7}) \quad (1)$$

$$HS^- \leftrightarrow H^+ + S^{2-}; (K_2 = 1.0 \times 10^{-14}) \quad (2)$$

Virtually all dissolved sulphide is present in the ionised form when pH is more than 8-9. At neutral pH values, typical of methanogenic systems, approximately 20-50% of the dissolved sulphide is present in the undissociated H_2S form. Much of the published literature on sulphide toxicity does not take pH and bacterial adaptation into consideration, which makes general conclusions about toxicity levels difficult. Literature on H_2S inhibition of methanogenesis is inconclusive (Table 4). Ref. [51] summarizes a few of the reported data, from which it can be concluded that total dissolved sulphide in the range of 150-1100 mg/L and free hydrogen sulphide in the range of 50-250 mg/L can cause inhibitory effects. Also, the sulphide inhibition depends on the type of substrate [53] and has different degrees of effect on various bacterial groups [54]. Ref. [47,55] have found that sulphide toxicity is experienced at lower concentrations in suspended growth systems as compared to that in anaerobic filters. In general, it was found that the sulphide inhibition often leads to a complete process failure since methanogenesis is crucial for anaerobic organic stabilization [46,56].

Sulphide also precipitates all essential trace metals required for methanogens as metallic sulphides. The other most obvious effect on methanogenesis is a reduction of the methane yield per unit COD converted. In terms of sulphate, the reduction of 1.5 g SO_4^{2-} requires oxidation of 1 g COD, resulting in a decrease of 0.233 m^3 in the methane (STP) yield for every kg of SO_4^{2-} reduced during anaerobic treatment [57].

Other problems associated with anaerobic treatment of high sulphate bearing wastewaters result from the presence of sulphide in the biogas and in the effluent. Hydrogen sulphide, even at concentrations ≤ 2 ppm causes malodor. Though burning of H_2S-containing biogas is feasible, it produces acidic gases. The presence of H_2S in biogas may also cause severe problems of corrosion, necessitating costly sulphide stripping techniques. The presence of dissolved sulphide in the effluent after anaerobic treatment also gives rise to malodor and enhanced oxygen demand. Post-treatment of the effluent may be necessary, depending on the sulphide concentration, and is generally accomplished either by chemical precipitation with iron salts or biological or chemical oxidation [50].

Available information on the sensitivity of sulphate reducing bacteria (SRB) to sulphide toxicity is also inconclusive. In general, methanogens are known to be more sensitive compared to SRBs [58]. Ref. [59] concluded that SRBs were not affected by high concentrations of hydrogen sulphide. However, Ref. [42] reported inhibition of *Desulfotomaculum acetooxidans* at hydrogen sulphide concentrations more than 85 mg/L. Ref. [60] indicated that SRBs are more sensitive to elevated levels of dissolved total sulphide than Methane Producing Bacteria (MPB).

Competition between sulphate reducers and other bacteria involved in anaerobic mineralization

Figure 2 illustrates the possible anaerobic pathways of organic compound degradation under methanogenic and sulphidogenic conditions. In the presence of sulphate, competition between sulphate reducers and the anaerobic bacteria involved in methanogens [61] can occur at different levels in the stepwise degradation process as listed below:

1. Competition between sulphate reducers and fermentative bacteria for monomeric compounds, such as sugars, amino acids, etc.
2. Competition between sulphate reducers and Obligate Hydrogen Producing Acetogens (OHPA) for intermediate fermentation products, such as propionate, butyrate, ethanol, etc.

Biomass	Substrate	DS	FS	Inhibition	T	pH
Suspended	DW	390	130	50%	37	7.0-7.2
Suspended	Acetate	295	125	50%	35	6.5-7.4
Suspended	Acetate	1060	100	50%	35	7.7-7.9
Suspended	Lactate	250	100	50%	35	7.0
Suspended	Lactate	1630	100	50%	35	8.0
Suspended	C_2, C_3	145-195	60-65	*	35	7-0-7.2
Suspended	C_2, C_3	150-200	60-75	**	35	7.0
Biofilm	Propionate	1000	200	**	35	7.4
Biofilm	Acetate	400	125	NR	35	7.2
Granular	Acetate	676	250	50%	30	6.4-7.2
Granular	Acetate	1045	90	50%	30	7.8-8.0

T in °C, Dissolved Sulphide (DS) and Free hydrogen Sulphide (FS) in mg S/L
NR-Not reported, DW- distillery wastewater, C_2-acetate, C_3-propionate.
*Process failure, **Inhibition threshold for adapted sludges.

Table 4: Sulphide toxicity in methanogenic process (Adapted from Karhadkar et al. [103], McCartney and Oleskiewicz [48], Parkin et al. [46], Maillacheruvu et al. [47]).

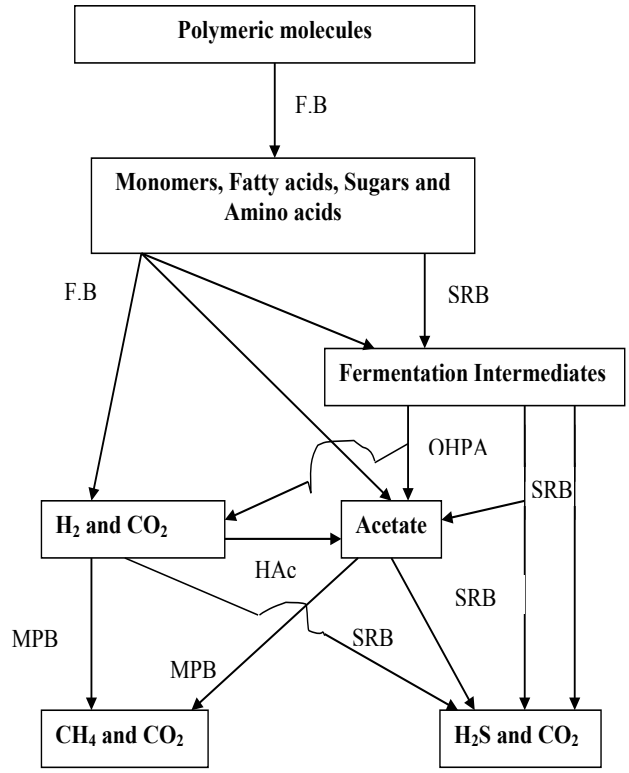

Figure 2: Pathways of organic compound degradation under methanogenic and sulphidogenic conditions.

3. Competition between sulphate reducers and homoacetogenic bacteria for H_2.

4. Competition between sulphate reducers and methanogens for direct methanogenic substrates, such as H_2 and acetate.

Competition between sulphate reducers and fermentative bacteria: Usually sulphate reducers do not effectively compete with the fast-growing fermentative bacteria involved in polymer hydrolysis and monomer degradation in anaerobic environments [42,62]. However, there is evidence of malate and fumarate fermented by a number of SRB species irrespective of the H_2 partial pressure [42,44] and fermentation of some other substrates, such as ethanol, lactate, glycerol, propionate, etc., only if the H_2 partial pressure is maintained at a low level [42,62]. It is likely that, in natural ecosystems and in anaerobic digesters, sulphate reducers are more likely to be involved in the ultimate and penultimate stages of mineralization than in the initial fermentative stage [63].

Competition between sulphate reducers and OHPA bacteria: Several researchers have reported that SRB can compete with OHPA bacteria for substrates such as butyrate [42,64] and propionate [46,65]. Complete or partial sulphidogenic oxidation of fermentation intermediates is favored over the OHPA syntrophic route due to the insensitivity of the former to hydrogen partial pressures, thermodynamic and kinetic parameters [42,62,66]. In marine sediments, between 75 to 99% of organic substrate electrons appear to be scavenged by SRB species [59].

Competition between sulphate reducers and homoacetogenic bacteria: Ref. [61] reported that from thermodynamic and substrate affinity considerations, H_2 oxidizing sulphate reducers should effectively out-compete homoacetogens under the conditions prevailing in digesters.

Competition between sulphate reducers and methanogens: In natural environments and in anaerobic reactors, hydrogen and acetate are the key intermediates through which organic matter is channeled during both methanogenic and sulphidogenic mineralization [42]. Thermodynamic considerations are often used to predict the outcome of competition between SRB and MPB species for both the substrates [42,48,61]. As presented in Table 5, ΔG^o values predict that sulphate reducers could out-compete methanogens for both H_2 and acetate.

SRB species have a higher affinity for hydrogen than methanogens (Table 5) and this higher affinity, coupled with yield coefficient data, suggest that SRB should effectively out-compete MPB under normal digester operating conditions and at limiting substrate levels [42,48]. Ref. [67] proposed that SRB have a higher affinity for hydrogen than MPB. This is because the hydrogenase enzyme is located in the periplasmic space in the former and it is located in the cytoplasm in the latter. SRB could reduce sulphate with H_2 as substrate even at HRT of 2 hours in an acidogenic chemostat [58]. Kinetic data (Table 5) also suggest that SRB could successfully out-compete *Methanosarcina* Sp. at low acetate concentrations prevailing in natural environments and anaerobic reactors. Given the very low levels of H_2 and acetate that may prevail in natural environments and in steady state anaerobic digesters, a comparison of minimum substrate threshold values may be a more useful guide for prediction of the outcome of competition between SRB and MPB species [61]. Ref. [68] determined threshold concentrations for H_2 for a variety of anaerobes and concluded that there was an inverse correlation between the free energy available for the reaction and the threshold value. Threshold values for H_2 for sulphate reducers were found to be lower than those for methanogens (Table 5), indicating that SRB species can lower the H_2 partial pressure to a lower level such that it cannot be utilized by hydrogenophilic methanogens. Similarly, threshold values of acetate for sulphate reducers were lower than methanogens making SRBs more competitive at lower acetate concentrations. In the study conducted by Ref. [69], SRB out-competed methanogens in the acetate-fed chemostats because sulfate reducers have lower half-velocity constant (Ks) than methanogens for acetate-utilization.

From the above discussion, it is seen that SRB have an advantage over MPB in utilizing the common substrates. The COD/SO_4^{2-} ratio appears to be a key factor in the regulation of the competition between methanogenic and sulphate-reducing bacteria [40,48,64]. A common recommendation for a successful anaerobic treatment of wastewater is to operate the system at COD/SO_4^{2-} ratio higher than 10 [50]. For such wastewaters, the H_2S concentration in the anaerobic reactor will never exceed the critical value of inhibition due to the stripping effect of the biogas produced. At COD/sulfate ratios lower than 10, process failures of anaerobic reactors have been reported [37,46] and the process

Biochemical Reaction	Δ G° (KJ/ Reaction)	Apparent Km (μM)	Minimum threshold (nM)
$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$	-135	5-13	23-75
$4H_2 + HSO_4^- \rightarrow HS^- + 4H_2O$	-152	2	7
$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$	-31	$(3\text{-}5)10^3$	$(0.5\text{-}1.2)10^6$
$CH_3COO^- + SO_4^{2-} \rightarrow HS^- + 2HCO_3^-$	-47	0.2×10^3	1×10^3

Table 5: Free energy, apparent Km and minimum substrate threshold values for hydrogenophilic and acetoclastic methanogens and sulphate reducers (Source: Widdel [42], Cord-Ruwisch et al. [68], Zinder [61]).

proceeds successfully when precautions are taken to prevent sulphide toxicity. Addition of ferric salts to precipitate sulphides, dilution of the influent H_2S concentration, decrease of unionized H_2S concentration at elevated pH, separation of H_2S production and methanogenesis, selective inhibition of SRB, aerobic biological sulphide oxidation to elemental sulphur, and recycling of effluent containing low sulphide concentration to anaerobic process, Oxidation-Reduction Potential (ORP) based oxygenation for sulphide control by injecting controlled oxygen to biogas recycling line, are some of the sulphide inhibition control measures [37,70-73]. So far, no sustainable method has been developed for selective inhibition of SRB to drive the anaerobic process towards methanogens [37]. Also, many of the developed sulphide inhibition methods are not economically feasible or sustainable. For example, separation of H_2S production and methanogenesis may be costly because it requires an additional reactor and accessories, which increases the complexity of treatment system [73].

Anaerobic digestion of low COD/SO_4^{2-} ratio bearing industrial wastewaters

Ref. [74] used a laboratory-scale UASB reactor in which 5 mg/L chloroform was added for 5 days to terminate methanogenesis and then fed it with an influent containing 2,500 mg/L COD and 5,000 mg/L SO_4^{2-} for a 180 day trial period. No methane production was detected from this 'sulphidogenic' reactor throughout the experiment and, towards the end of the trial; a COD conversion rate of 0.9-1.0 g COD/gVSS/d was achieved. In a parallel 'sulphidogenic/methanogenic' (i.e., mixed) reactor which had not been treated with chloroform, the percentage of organic COD used by SRB in similar feeding conditions was about 50% at the start of the experiment and gradually increased to 80% over the first 150 days of feeding. This was correlated with an increase in the proportion of acetate being used for sulphate reduction. Ref. [75] were the first to demonstrate the feasibility of treating industrial wastewaters which contain a very low COD/SO_4^{2-} ratio in sulphidogenic reactors in which methanogenesis is completely suppressed. Ref. [20] conducted a pilot scale experiment using advanced facultative pond system to study the competition between SRB and *Methanogenic Archaea* (MA) in anaerobic treatment of tannery wastewater. The relative electron flow towards sulphate reduction was higher (59-83%) than that towards methanogenesis (41-17%), although the COD removal within the reactor varied from 15 to 90%. Results from this study also demonstrated that the flow of electrons towards SRB increased with an increase in sulphate concentration and a decrease in COD/SO_4^{2-} ratio.

Overview of biological nitrogen removal process

Discharge of untreated wastewater containing nitrogen compounds (TKN, NH_4-N, oxidized nitrogen compounds) is responsible for promoting eutrophication in receiving water and adversely affects the human health and aquatic life [76,77]. As nitrogen pollution has become a cause for concern in recent times, many countries are enforcing stringent nitrogen discharge standards. As a result, development of techniques for reducing the nitrogen content from wastewaters has attracted a great deal of attention [78].

Conventional wastewater treatment systems for nitrogen removal are based on both aerobic nitrification and anaerobic or anoxic denitrification [79,80]. This combination requires the spatial separation of nitrification and denitrification units or temporal separation of each process by alternating aeration and no aeration in the same unit. The process involves two stages:

(ι) conversion of ammonium into nitrate (nitrification); and

(ιι) subsequent transformation of nitrate into nitrogen gas (denitrification).

Nitrifiers, such as *Nitrosomonas* and *Nitrobacter,* oxidize NH_4-N to nitrite and nitrate using free oxygen [81] as per equations 3 and 4. Then, denitrifiers oxidize organic carbon using nitrate as the electron acceptor under anoxic conditions as per equation 5 [77]. Though conventional nitrification followed by denitrification (with external organic carbon supply) can be carried out as separate processes, combining anoxic and aerobic units with nitrate recycling has been commonly used for nitrogen removal in full-scale wastewater treatment plants [82]. This process may remove up to 80% of the NO_3-N when a 400% recycling rate is used [83,84].

$$NH_4^+ + 1.5O_2 \xrightarrow{\text{Nitrosomanas}} NO_2^- + 2H^+ + H_2O;\ \Delta G^o = -275\ KJ/M$$

$$NO_2^- + 0.5O_2 \xrightarrow{\text{Nitrobactor}} NO_3^-;\ \Delta G^o = -74\ KJ/M$$

$$1.25\ CH_3COOH + 2\ NO_3^- \xrightarrow[\text{Heterotronhic}]{\text{Denitrificans}} N_2 + 2.5CO_2 + 1.5\ H_2O + 2OH^-\ \Delta G^o = -527.4\ KJ/M$$

Conventional nitrification can be implemented only after pre-treating the wastewater to reduce the C/N ratio [85]. In conventional suspended growth biological nitrogen removal system, it is difficult to maintain sufficient nitrifying biomass because of the low growth rate of nitrifying bacteria [86,87]. During biological denitrification of wastewater, external organic carbon is needed as the electron donor for the reduction of nitrate and nitrite to nitrogen gas. The COD/N ratio required for complete denitrification may range from 3.5 to 15 g COD /g N [88]. Biological nitrogen removal can also be achieved by nitrification and denitrification under alternating aerobic-anoxic conditions in the same reactor. A few advantages that can be accrued by a single sludge system over conventional ones are:

i) No prior carbon removal step required before nitrification,

ii) No external carbon source is needed for denitrification,

iii) Lesser buffer quantity is needed as alkalinity generated during denitrification can partly compensate for the alkalinity destroyed in nitrification [89].

For wastewater with a low BOD/N ratio, autotrophic denitrification is a promising alternative to heterotrophic denitrification [90]. Autotrophic denitrifying bacteria include autohydrogenotrophic denitrifiers [91] as well as autosulphurotrophic denitrifiers, which oxidize reduced sulphur compounds (sulphides, elemental sulphur and thiosulphate) to sulphate while reducing nitrate to N_2 gas. Contrary to heterotrophic denitrification, autotrophic denitrification eliminates the need for addition of organic carbon sources, consumes alkalinity and generates high concentrations of sulphate [90]. So in anoxic conditions, the tannery effluent contained nitrates could be denitrified by both heterotrophic and autotrophic route effectively.

ANAMMOX is the acronym for anaerobic ammonia oxidation. The ANAMMOX process is the denitrification of nitrite with ammonia as the electron donor. ANAMMOX needs a preceding partial nitrification step that converts half of the wastewater ammonium to nitrite. On laboratory scale, ANAMMOX has been tested in different reactors: fluidized bed [92], fixed bed [93], sequential batch [33] and gas-lift reactors [94]. All the above reactors appeared to be suitable, although the economics of the process differs for different reactor configurations. The temperature range for ANAMMOX is 20-43 °C with an optimum value at 40 °C. The ANAMMOX system performed well in the pH range of 6.7- 8.3. One of the main problems of the ANAMMOX process is the long start-up time. For example, the ANAMMOX planctomycetes grow slowly and it takes about 100 to 150 days for an ANAMMOX reactor inoculated with activated sludge to reach its full capacity [95]. It has also been reported that presence of organic matter (OM) adversely

affects ANAMMOX [96,97] and co-existence of ANAMMOX culture and denitrifiers during start-up could slow down anaerobic ammonia removal [98].

So far NO_2^-, NO_3^- and SO_4^{2-} have been reported as electron acceptors for anoxic ammonia oxidation as per the reactions given in Eqs. (6) to (8) [33,78,99].

$$5\ NH_4^+ + 3NO_3^- \rightarrow 4N_2 + 9H_2O + 2H^+;\ \Delta G^o = -297\ KJ/M \quad (6)$$

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O;\ \Delta G^o = -357\ KJ/M \quad (7a)$$

$$NH_4^+ + 1.31\ NO_2^- + 0.066HCO_3^- + 0.13\ H^+ \rightarrow N_2 + 0.26\ NO_3^- + 0.066CH_2O_{0.5}N_{0.15} + 2H_2O \quad (7b)$$

$$2NH_4^+ + SO_4^{2-} \rightarrow S + N_2 + 4H_2O;\ \Delta G^o = -48\ KJ/M \quad (8)$$

Equation 8 shows the feasibility of anoxic oxidation of ammonia in presence of sulphate. Recently, Ref. [100] observed ammonia removal associated with sulphate reduction. Also, Ref. [101-103] developed a viable process for simultaneous removals of COD/BOD, NH_4-N and sulphide /sulphate with possibility of sulphur recovery for the treatment of tannery effluent. The major processes involved were sulphate reduction, sulphide oxidation, nitrification, ANAMMOX and/or denitrification. The sulphide inhibition control in this process was achieved by controlled air injection to the part of reactor. This air injection could oxidize part of ammonia to nitrite/nitrate and denitrification was effective in presence of reduced organic compounds and sulphides. Such integrated treatment system has the advantages of high loading rates with a mixed consortium of bacteria. More focused research is required for development of such mixed bacterial consortium with involvement of multiple electron donors and electron acceptors for simultaneous removal of multiple pollutants present in many wastewaters. The major advantages of such integrated treatment systems are less reactor volume demand because of higher loading rates obtained.

Conclusions

Primary treated tannery effluent after chromium removal is found to be suitable for secondary stage biological treatment. The inherent nature of tannery effluent demands more aeration time and lesser organic loading rates for efficient aerobic treatment. Lower COD/SO_4^{2-} ratio of tannery effluent is an impediment in successful anaerobic treatment. Sulphide inhibition control is essential for an effective anaerobic treatment of tannery effluent with high cost of treatment with less biogas recovery. Sequencing Batch Reactor (SBR) and membrane reactor technologies are found to be satisfactory for removal of organic matter and ammonia. However, the operational cost of such technologies is high and may not be attractive to developing countries. The use of abundantly available SO_4^{2-} as an alternate electron acceptor for organic matter removal and anoxic ammonia oxidation is worth considering. It is possible to treat tannery effluent by an alternate sulphidogenesis process with proper design and operational control. Such treatment enables simultaneous removals of COD/BOD, NH_4-N and sulphide/sulphate with possibility of elemental sulphur recovery at higher loading rates.

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