Development of the Sulphidogenesis Cum Ammonia Removal Process for treatment of tannery effluent

P. C. Sabumon

ABSTRACT

The present paper describes the development of Sulphidogenesis Cum Ammonia Removal Process (SCARP) with a simple sulphide inhibition control. The process was developed using synthetic effluent and its application for treatment of primary treated tannery effluent was demonstrated. This paper also discusses the effects of HRT and loading rates. The developed SCARP could treat efficiently the primary treated tannery effluent with influent concentrations of COD, SO_4^{2-} and NH_4^+ equal to 3,900 mg/L, 3,000 mg/L and 300 mg/L, respectively. An HRT of 10.5 hours was found to be adequate for COD, NH_4-N and SO_4^{2-} loading rates of 8.9 kg COD/m^3/d, 0.68 kg NH_4^+/m^3/d, 6.84 kg SO_4^{2-}/m^3/d, respectively. The overall removal efficiencies of COD, NH_4-N and SO_4^{2-} for the above loading rates were in the ranges of 90.8–91.8%, 84–88.3% and 64.2–70.2%, respectively. The system performance was satisfactory for different loading rates and low COD/SO_4^{2-} ratios. The developed SCARP has good potential as a cost effective alternative treatment process to existing extended aeration process with nitrification–denitrification for the secondary treatment of tannery effluent.

Key words | ammonia removal, organic loading rate, sulphides inhibition control, sulphidogenesis, sulphur, tannery effluent

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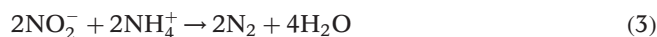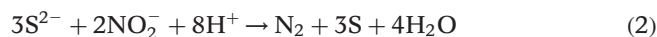Fax: 91-44-22574252
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INTRODUCTION

Leather tanning is an important economic activity in many developing and developed countries. The tannery effluent produced from conventional leather processing contains high concentration of organics (COD/BOD), suspended solids and inorganics like TKN/NH_4—N, SO_4^{2-}/S^{2-}, Cr(III) and chlorides(UNIDO 2000; Kaul *et al.* 2001; Boshoff *et al.* 2004). The discharge of untreated or partially treated tannery effluent to the environment causes adverse environmental impacts. In developed countries, expensive extended aeration process with nitrification and denitrification is usually employed so that the treated tannery effluents meet the discharge norms for BOD, NH_4-N and sulphides (European Commission 2001).

Such a costly process is not attractive in developing countries like India. On the other hand, direct anaerobic treatment is not successful due to low COD/SO_4^{2-} ratio of tannery effluents and severe sulphide inhibition to the anaerobic process (Wiemann *et al.* 1998; European Commission 2001; Hulshoff Pol *et al.* 2001; Hussain & Sabumon 2007). Sulphidogenesis process removes COD at the rate of 0.67 g COD per gram of sulphate reduced and produces sulphide instead of methane. Therefore, enhancement of sulphidogenesis with proper sulphide inhibition control will reduce organic pollution in case of effluents having low COD/SO_4^{2-} ratio. It is also possible to remove ammonia in anaerobic process in presence of sulphate (Polanco *et al.* 2001). Polanco *et al.* (2001) postulated that the nitrite formation and subsequent anaerobic ammonia oxidation (ANAMMOX) reactions were responsible for anaerobic nitrogen removal as per

the following equations:

$$3SO_4^{2-} + 4NH_4^+ \rightarrow 3S^{2-} + 4NO_2^- + 4H_2O + 8H^+ \qquad (1)$$

$$3S^{2-} + 2NO_2^- + 8H^+ \rightarrow N_2 + 3S + 4H_2O \qquad (2)$$

$$2NO_2^- + 2NH_4^+ \rightarrow 2N_2 + 4H_2O \qquad (3)$$

By combining Equations (1) to (3), one can obtain a global biochemical reaction as per Equation (4)

$$SO_4^{2-} + 2NH_4^+ \rightarrow S + N_2 + 4H_2O \qquad (4)$$
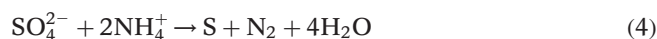
However, to the author's knowledge, employment of sulphidogenesis for COD/BOD removal along with anoxic ammonia removal from tannery effluent has not been attempted earlier, though a good potential for such a process exists. So far, no alternative cost effective treatment process to extended aeration process with nitrification–denitrification has been reported to remove COD/BOD/NH_4-N and SO_4^{2-}/sulphides simultaneously from tannery effluents. The major objective of present work was to develop a Sulphiodogenesis Cum Ammonia Removal Process (SCARP) for simultaneous removal of organic carbon (COD/BOD), SO_4^{2-}/S^{2-} and ammonia and study its performance in treatment of primary treated tannery effluent.

METHODOLOGY

Description of SCARP

The process flow diagram of SCARP is shown in Figure 1. SCARP employs two non-clogging up flow hybrid reactors

(suspended growth cum biofilm growth) of 1.75 L and 1.2 L capacity, respectively, with a sulphide oxidation reactor (0.5 L capacity) in between. The volume provided for suspended growth at the bottom of the first stage reactor was 0.5 L, while it was 0.2 L in the second stage reactors. The remaining reactor volume (in the upper portion) was filled with plastic rings (bulk density = 150 kg/m³; porosity = 90%, area available for microbial attachment = 3,555 cm²/L of reactor volume) as non reactive media for biomass attachment. In the sulphide oxidation reactor, there was a provision for air supply at a rate of 0.2 L/min. to the head space of 0.2 L of effluent volume to aid formation of elemental sulphur film.

The effluent was fed to the first stage sulphidogenesis cum ammonia removal reactor (SCARR-I) for sulphidogenesis and anoxic ammonia removal. Air at rate of 0.2 L/min. was injected to first stage reactor at 40 cm from the bottom of the reactor (0.8 L capacity from the bottom) for Sulphide Inhibition Control (SIC) in the reactor. The off-gas and effluent containing sulphide were taken to Sulphide Oxidation Reactor (SOR), where part of the sulphide was oxidized to elemental sulphur and the sulphur thus formed was removed daily. The off-gas from SOR was injected to the second stage reactor (SCARR-II) at 27 cm from the bottom of the reactor (0. 5 L capacity from the bottom). The effluent from SOR was taken to the bottom of the second stage reactor for further sulphidogenesis cum ammonia removal. Air was supplied at a rate of 0.1 L/min. to the second stage reactor at 44 cm from the bottom of the reactor
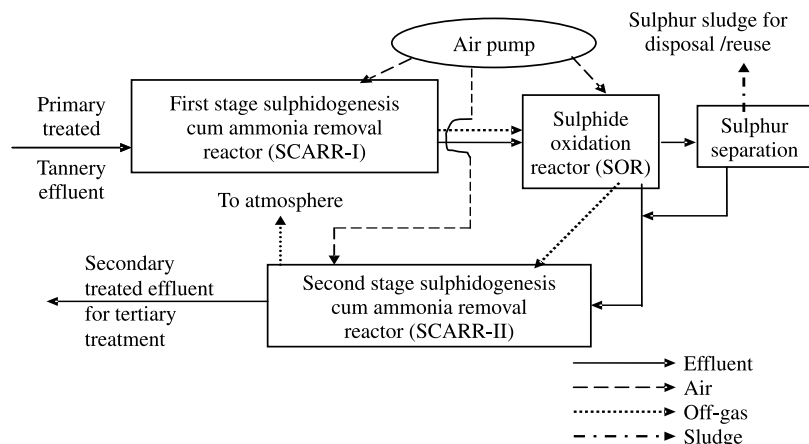

Figure 1 | Process flow diagram of sulphidogenesis cum ammonia removal process (SCARP).

(0. 8 L capacity from the bottom) for oxidation of any residual sulphides present in the second stage reactor. The treated effluent was collected from the top of the second stage reactor and the off-gas, free of sulphides, was released to atmosphere.

Seed biomass

Flocculent type extended aeration process sludge (48.3% volatile fraction) employed for treatment of combined tannery effluent (seed biomass-I) and anaerobically digested cow dung sludge (70.4% volatile fraction; seed biomass -II) were used for the development of SCARP.

Start-up, acclimatization and operation of SCARP

The start-up and acclimatization of first stage sulphidogenesis cum ammonia removal reactor (SCARR-I) and second stage sulphidogenesis cum ammonia removal reactor (SCARR-II) were carried out independently using seed biomass-I (total volatile suspended solids $= 8.33$ g) and seed biomass-II (total volatile suspended solids $= 17.6$ g), respectively.

Both reactors were operated in recycling mode during start-up and acclimatization (with intermittent feeding/drawing effluent from recycling vessel) and operated for 120 days to develop required microbial flora for sulphate reduction and anoxic ammonia removal using synthetic effluent. An oxidation reduction potential (ORP) of -220 ± 25 mV was maintained during the start-up phase.

After 120 days, SCARR-I and SCARR-II were operated independently, but continuously (for daily loading rate studies), without sulphide inhibition control (SIC) until 185 days. On 186th day, SOR was introduced between SCARR-I and SCARR-II, with an air supply at the rate of 0.2 L/min. to the head space of SOR, and the entire operation of SCARP was made continuous. Off-gas from SOR was injected to SCARR-II. From 190th day onwards, air was supplied at a rate of 0.2 L/min. to the SCARR-I as a SIC measure and off-gas containing sulphides, along with SCARR-I effluent, were taken to SOR for sulphide oxidation. From 205th day onwards, air was supplied at a rate of 0.1 L/min. to the upper part of the SCARR-II for oxidation of residual sulphides. After 220 days of successful operation of SCARP with synthetic effluent, primary treated tannery effluent was fed and the system was operated under different loading conditions until 450 days. The operational details of SCARP are presented in Table 1.

Analytical methods

All physico-chemical parameter analyses were carried out as per *Standard Methods* (APHA 1998). NH_4^+, SO_4^{2-} and NO_3^- analyses were carried out using an ion chromatograph (Dionex, USA) with ED50 electrochemical detector and results were processed with integrated Chromeleon software. The samples for sulphate and sulphide analyses were fixed immediately upon drawing with 2N zinc acetate (C_2H_5COOZn) in alkaline condition to avoid sulphide oxidation. The fixed samples were centrifuged at $5,000 \times g$ for 5 minutes and supernatant was analyzed for sulphate and precipitate was analyzed for total sulphides. The COD analysis of centrifuged sample (without zinc acetate) was carried out after acidifying the sample to pH less than 1 with sulphuric acid for releasing sulphides as H_2S by stirring and then fixed with potassium dichromate. The COD of tannery effluent was determined by sufficient dilution of sample to have the chlorides concentration in digestion tube less than 2,000 mg/L. ORP was measured using double junction platinum ORP electrode connected to a calibrated Cyber Scan pH (1,100) meter in mV mode (EUTECH Instruments, Singapore). ORP electrode was calibrated using Quinhydrone 86.

RESULTS AND DISCUSSION

Start-up and acclimatization

Start-up and acclimatization of reactors (SCARR-I and SCARR-II) as per the loading conditions given in Table 1 were successful. The percentage removals of COD, SO_4^{2-} and NH_4^+ during this period were in the ranges of 82–96, 70–85 and 50–68, respectively. After acclimatization of the process, from day 121 to day 450, the reactors were operated continuously under various operating conditions as given in Table 1. There was no recycling of effluent during this period.

Table 1 | Operational details of SCARP

Sl. No.	Operational phase	Period of operation, days	Influent values, mg/L			Loading rate, Kg/m³/d			COD/SO$_4^{2-}$ ratio	HRT, h	Remarks
			COD	SO$_4^{2-}$	NH$_4^+$	COD	SO$_4^{2-}$	NH$_4^+$			
1	Start-up and acclimatization	1–120	2,500	1,390–1,900	25–280	1–1.25	0.56–0.95	0.01–0.14	1.80–1.32		In recycling operation, Synthetic effluent
Loading rate studies											
2	Phase-1	121–148	2,500	1,900	280	1.52	1.16	0.17	1.30	39	No SIC
3	Phase-2	149–185	3,750	2,850	450	2.29	1.74	0.27	1.30	39	
4	Phase-3	186–220	3,750	2,850	450	2.14	1.63	0.26	1.30	42	SOR introduced
5	Phase-4	221–240	3,900	3,000	300	2.22	1.71	0.17	1.30	42	Tannery effluent feeding started
6	Shut down	241–320									
7	Phase-5	321–334	3,900	3,000	300	2.22	1.71	0.17	1.30	42	
8	Phase-6	335–356	3,900	3,000	300	2.22	1.71	0.17	1.30	42	
9	Phase-7	357–365	3,900	3,000	300	4.45	3.42	0.34	1.30	21	Varying OLR & HRT
10	Phase-8	366–370	3,900	3,000	300	8.9	6.84	0.68	1.30	10.5	
11	Phase-9	371–373	3,900	3,000	300	17.8	13.7	1.36	1.30	5.25	
12	Phase-10	374–379	3,900	3,000	300	13.34	10.3	1.03	1.30	7.8	
13	Phase-11	380–383	3,900	1,950	300	13.34	6.67	1.03	2.0	7.8	COD/SO$_4^{2-}$ ratio varied
14	Phase-12	384–391	3,900	1,950	300	8.9	4.45	0.68	2.0	10.5	
15	Phase-13	392–397	3,900	1,300	300	8.9	3	0.68	3	10.5	
16	Phase-14	398–403	2,000	1,500	150	4.56	3.42	0.34	1.33	10.5	
17	Shut down	404–423									
18	Phase-15	424–430	3,900	3,000	300	8.9	6.84	0.68	1.3	10.5	
19	Phase-16	431–436	1,500	3,000	300	3.42	6.84	0.68	0.5	10.5	
20	Phase-17	437–450	2,000–8,077	1,733–2,700	300	4.56–18.42	3.95–6.16	0.68	1.2–4.7	10.5	Daily varying OLR

SIC-Sulphide Inhibition Control, SOR-Sulphide Oxidation Reactor, OLR-Organic Loading Rate, HRT-Hydraulic Retention Time Synthetic effluent contained all required minerals and trace metals for bacterial growth. Primary treated tannery effluent was amended with carbon (sucrose/milk powder), SO$_4^{2-}$ and NH$_4^+$ to get maximum concentrations expected in combined tannery effluent.

Performance of SCARR-I

Performance of SCARR-I in terms of removals of SO_4^{2-}, COD and NH_4^+ under various operating conditions (Table 1) is shown in Figure 2. It is evident from Figure 2 that for loading rates in phase-1, SO_4^{2-} reduction at steady state of operation varied from 97% to 100%. However, at increased loading rates in phase-2 at the same COD/SO_4^{2-} ratio of 1.30, the sulphate reduction was affected. The percentage removal of sulphate decreased to the extent of 70%. This decreased performance of sulphate reduction was gradual and might be due to sulphide toxicity to sulphate reducing bacteria (SRB). At increased loading rates (Phase-2), the pH in SCARR-I varied between 6.00 and 6.86, with high concentrations of dissolved sulphides in the effluent as shown in Figure 3. Here, it is to be noted that at a pH of 6.0 and at 30°C, approximately 93% of total dissolved sulphide could be present as free H_2S as compared to a value of 60% at a pH of 7.0 at similar conditions (Metcalf & Eddy 2001). The free H_2S concentration during this period could be varying between 476–518 mg/L. The high concentration of free H_2S (more than 250 mg/L) is highly toxic to all bacteria including sulphate reducing bacteria (Parkin *et al.* 1990; Hulshoff Pol *et al.* 2001) as compared to ionic form of sulphides. There are reports and experimental evidence that sulphate reduction can proceed well when pH is maintained above 6.0 (Sipma *et al.* 1999). From the above discussion, the decrease in performance of sulphidogenesis process at increased loading rates in SCARR-I could be attributed to the free H_2S toxicity at reduced pH conditions.

Introduction of SOR on 186th day and subsequent air injection into SCARR-I helped in improving the performance of SCARR-I (Figure 2). SOR could oxidize part of sulphides from SCARR-I to elemental sulphur and sulphur

was recovered daily. After starting the supply of air as SIC measure from 190th day onwards, the sulphide concentration in SCARR-I reduced and pH increased as a result of sulphide oxidation (Figure 3). The air injection could change the ORP in SCARR-I from a value of -320 ± 25 mV in the bottom zone to -290 ± 25 mV in the zone above the air injection point. The control of sulphide concentration inside SCARR-I helped in enhanced sulphate reduction and COD removal during phase-3 to phase-17(Figure 2), for all the loading rates studied. Ammonia removals also improved as a result of SIC measure and it might be as a result of nitrification and denitrification along with anoxic ammonia removal. Once ammonia is oxidized to nitrite/nitrate, denitrification was easier in presence of organic matter and sulphides. There are reports on increased growth rate of ammonia oxidizing bacteria at very low dissolved oxygen concentrations (0.12–0.24 mg/L) (Park & Noguera 2004).

Performance of the system on restarting after a long shut down period (day 241 to day 320) was not adversely affected, as far as removals of COD and NH_4^+ are concerned, though sulphate reduction was affected. However sulphate reduction could be reactivated within 2 weeks. The percentage removals of COD and NH_4^+ were high even during phase-17, though there was a daily variation in organic loading rates. The performance was comparable to the performance during earlier phases.

Overall performance of SCARP

Figure 4 shows the overall performance of SCARP in terms of simultaneous removals of NH_4^+, COD and SO_4^{2-}. From the results it is evident that percentage of ammonia removal
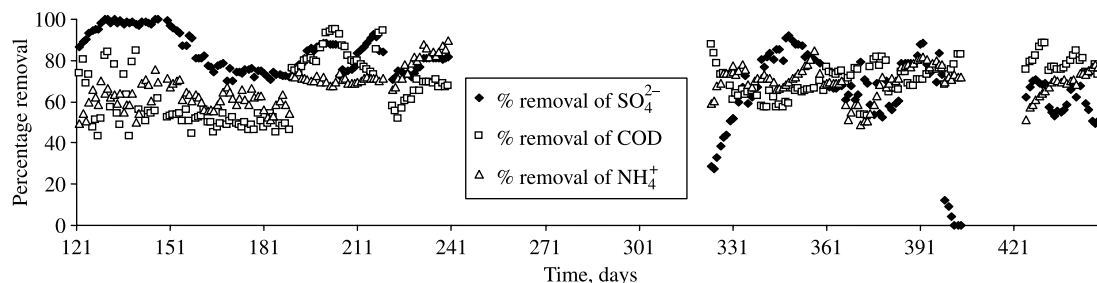

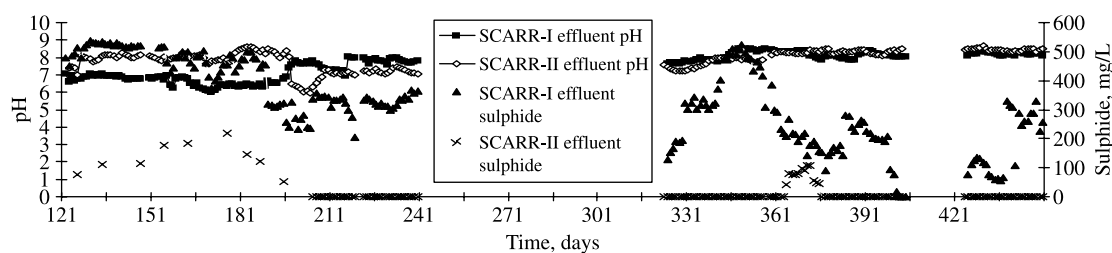**Figure 2** | Performance of SCARR-I.

Figure 3 | pH and sulphide in effluents during operation of SCARP.

improved after the introduction of SOR and SICs on 190th day. The overall removal of NH_4^+ at a high loading rate of 0.68 kg NH_4^+/m³/d at a HRT of 10.5 h varied in the range of 84–88.3%. It was found that during steady state operation at a HRT of 10.5 hours, treated effluent NH_4-N was meeting India's Central Pollution Control Board (CPCB) discharge standard of 50 mg/L. The overall percentage removal of COD was very good except when organic loading rates were very high during phases-9 to 11 (Figure 4). The overall percentage removal of COD at a high Organic Loading Rate (OLR) of 8.9 kg COD/m³/d at a HRT of 10.5 h varied in the range of 90.8–91.8. It was found that during steady state operation at a HRT of 10.5 hours, treated effluent COD varied in the range of 196–413 mg/L, which is comparable to the treated effluent quality from an extended aeration process with nitrification and denitrification, operated at a HRT of 1–2 days with OLR of 1–2 kg COD/m³/d (European Commission 2001; Vidal *et al.* 2004). Further COD removal of treated tannery effluent by biological process was not possible as the residual COD was refractory in nature.

High effluent COD after biological treatment of tannery effluent has been reported earlier (European Commission 2001; Vidal *et al.* 2004).

The variation in overall percentage removal of SO_4^{2-} is shown in Figure 4. The overall percentage removal of SO_4^{2-} at a high sulphate loading rate of 6.84 SO_4^{2-} kg /m³/d at a HRT of 10.5 h varied in the range of 64.2–70.2. It is to be noted that sulphide was absent in the treated effluent after sulphide control measure was adopted in the SCARR-II on day 205 of operation (Figure 3). The treated effluent pH from SCARR-II (Figure 3) was meeting CPCB effluent discharge standard. Mass balance analysis of sulphur was carried out during steady state operation (day 351 to day 353). It was found that 63–66% of input sulphur (as SO_4^{2-}/S^{2-}) can be recovered as elemental sulphur in SOR. The sulphur escaping in treated effluent (mainly as sulphate) varied in the range of 20 to 23%. The remaining portion of sulphur was deposited inside the reactors. The sulphur can accumulate in the reactor by sulphide oxidation (Buisman *et al.* 1990), autotrophic denitrification by *Thiobacillus denitrificans* (Avila *et al.* 2004) and by
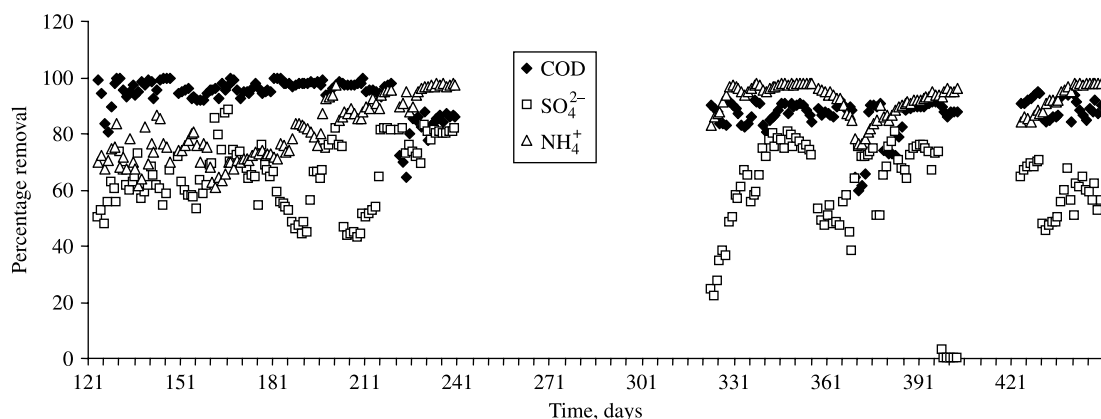

Figure 4 | Overall performance of SCARP.

anoxic oxidation of ammonia with SO_4^{2-} as electron acceptor (Polanco *et al.* 2001).

CONCLUSIONS

Sulphidogenesis cum ammonia removal process (SCARP) can be developed from flocculent type extended aeration process sludge (employed for treatment of tannery effluent) and anaerobically digested cow dung sludge. The sulphide inhibition control with elemental sulphur recovery is essential for satisfactory performance of the SCARP. The SCARP has good potential as a cost effective alternative treatment process to existing extended aeration process with nitrification–denitrification for the secondary treatment of tannery effluent.

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