ANAEROBIC TREATMENT OF TANNERY WASTEWATER WITH SULFIDE REMOVAL AND RECOVERY OF SULFUR FROM WASTEWATER AND BIOGAS

by

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ABSTRACT

Tannery wastewater contains high concentrations of sulfur compounds. Feasibility studies of pilot plant Sulfur Recovery Unit (SRU) integrated with Upflow Anaerobic Sludge Blanket (UASB) reactor, which is first of its kind in India, were carried out to study the sulfide removal efficiency for tannery wastewater. SRU consists of a stripper column, absorber column, regeneration unit and sulfur separator. Stripper efficiency of about 80-95 percentage in terms of sulfide removal was achieved for a sulfide load of 1-4 kg/d at a influent pH between 7.5-8.5. At sulfide load of 10 kg/d sulfide removal efficiency of about 65 percent was observed in the stripper unit. The absorber efficiency was more than 99.8 percent throughout the study period. The presence of SRU improved the COD removal efficiency in the UASB reactor. Elemental sulfur was obtained as a useful byproduct. Sulfate present in the wastewater is converted to sulfide in the UASB reactor. The sulfide in the dissolved form is stripped, absorbed and converted to elemental sulfur in the SRU. By this process, total dissolved solids (TDS) due to sulfate `in the wastewater is also reduced. Biogas generated can be used as a fuel after scrubbing the hydrogen sulfide from it in the sulfur recovery system.

INTRODUCTION

Anaerobic treatment is considered as one of the successful method, which generates less sludge compared to aerobic system and it is suitable for tropical countries. Each type of wastewater has its own specific characteristics. Tannery wastewater contains high concentration of sulfur compounds. In anaerobic treatment, Sulfate present in the wastewater is utilized by sulfate-reducing bacteria as an electron acceptor and sulfide is the end product of the reduction.[1] Sulfide when present in appreciable concentrations, is corrosive, gives rise to odourous and toxic vapours, increases the oxygen demand in the post-aerobic treatment and can precipitate trace elements.[2]

The presence of high concentration of sulfide in the anaerobic reactor, inhibits the activity of the methane producing methenogenic bacteria, resulting in lower amount of biogas production.[3,4] As the organic compounds in the anaerobic reactor are degraded only under methenogenic condition,[5] inhibition of methenogesis due to the presence of sulfide, lowers the COD reduction efficiency in the reactor. The influence of sulfide on methenogenesis appear to vary from reactor to reactor, but it is believed to inhibit methenogenesis at concentration above 100 mg/L.[4,6,7] The intensity of inhibition depends on the concentration of undissociated hydrogen sulfide present in reactor. The degree of dissociation depends on pH.

Due to the various problems engendered by sulfide, their elimination is very important. In fact, the presence of sulfate in tannery wastewater has retarded the development and application of anaerobic biological treatment. Broadly, sulfide removal techniques that can be employed are, physio-chemical techniques (stripping and absorption), chemical precipitation and biological oxidation (partial oxidation to elemental sulfur). Stripping can be adopted in the treatment system without disturbing the anaerobic process where as chemical precipitation causes several disadvantages[8] and biological oxidation is not a reliable process because it does not always result in sure and complete oxidation to elementary sulfur.[9,10] Although, aerobic biological processes are known to convert the sulfide into elemental sulfur at near neutral pH, these processes refer to effluent post-treatment and not to an integrated process for reduction of the sulfide concentration in the anaerobic reactor. This process produces the sulfur, as poorly recoverable impure sols. Comparing biological oxidation, precipitation and stripping, Wiemann et al. 1998 found stripping as the most suitable technique for a combination of anaerobic wastewater treatment and sulfide removal.

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Some of the main advantages in adopting sulfur recovery system are its efficiency in reducing the obnoxious gases, corrosion problem, the total dissolved solids in the effluent, and also the cost of post-aerobic treatment. It also yields sulfur as the by-product, which can be used as a raw material in the production of rubber and sulfuric acid. Sulfur recovery unit (SRU) integrated in the anaerobic wastewater treatment process renders possible, the removal of sulfide produced in the anaerobic process (and the sulfide contained in the raw material wastewater) and recovery of elemental sulfur as the useful by-product.

In this study, feasibility studies of a sulfur recovery unit (SRU) integrated to upflow anaerobic sludge blanket (UASB) reactor (first of its kind in India for tannery wastewater), was carried out to remove hydrogen sulfide from wastewater and biogas (generated from UASB reactor) and convert it into elemental sulfur.

EXPERIMENTAL

Wastewater characteristics

The composite tannery wastewater excluding pickle and chrome liquors was used for the study. Table I depicts the characteristics of untreated tannery wastewater and after UASB treatment.

TABLE I
Characteristics of Raw Tannery Wastewater and After Anaerobic Treatment

Parameter	Tannery wastewater (soak, pickle and chrome streams segregated)	UASB Treated Effluent(Influent to SRU)
COD_T (mg/L)	3000-4000	1000-1400
Temperature (° C)	30-38	30-38
pH	7.5-8.5	7.4-8.0
Sulfate (mg/L)	700-1500	100-250
Sulfide (mg/L)	100-120	300-550
Chloride (mg/L)	5000-7000	5000-7000
Ammonia (mg/L)	300-500	350-600
TKN (mg/L)	400-700	400-700

Provision was made to introduce sulfide in the form of Na_2S prior to sulfur recovery unit, in addition to the sulfide present in the wastewater, when the influent sulfide concentration had to be increased.

Pilot plant setup

The schematic of the pilot scale SRU used is shown in Figure 1. The SRU consists of stripper column, absorber column, regeneration unit, sulfur separation tank and sulfur storage tank. Treated wastewater from UASB system was conveyed to a stripper feed tank of capacity 1000 liters. From the stripper feed tank, wastewater was pumped to the top of the stripper column. The stripper column of capacity 2 m^3 was filled with polypropylene packings. Liquid pumping rate of 5 m^3/hr was maintained in the stripper and absorber columns.

Wastewater was fed from the top and is distributed uniformly throughout the plan area of the stripper column. Wastewater from the stripper column was recirculated back into the stripper unit along with the effluent from the UASB reactor. A blower was working at its maximum capacity of 250 m^3/hr and was used for circulating the stripper gas (counter current to the liquid flow) through the stripper and absorber columns. The stripper gas after removing/stripping the hydrogen sulfide from the wastewater in the stripper unit of SRU was carried over to the absorber unit. In the stripper column, there is no chemical reaction involved. Only phase change occurs (aqueous phase to gaseous phase). The stripper gas is the biogas containing very low concentration of hydrogen sulfide. Biogas from the UASB system was introduced into the SRU in the absorber column (Figure 1) and the hydrogen sulfide was removed. Biogas with almost negligible quantity of Hydrogen sulfide was then sent to the stripper column to strip H_2S from wastewater, is termed as stripper gas. In the absorber column, iron(III) chelate was used to absorb the H_2S selectively by means of fast chemical oxidation. In this study, Nitrilotriacetic acid (NTA) was used as the chelating agent, mainly because it is relatively inexpensive and fairly stable. The redox solution consists of ferric ions to oxidise the sulfide into sulfur, a chelating agent (NTA) to prevent the iron to precipitate, thiosulphate as a stabilizer to prevent NTA degradation and CO_2 to maintain the pH and stabilize the redox solution.

The redox liquor (iron(III) chelates) oxidises the sulfide to elemental sulfur in the absorber column. In this reaction Fe(III) is reduced to Fe(II) while sulfide is oxidised to sulfur which can settle down. Redox liquor along with sulfur was collected in a sulfur separation tank. In the sulfur separation tank, with slow stirring, sulfur was separated from the redox liquor. The separated sulfur was then stored in the sulfur storage tank. After separation of sulfur, the redox liquor was sent to the regeneration column where Fe(II) was converted back to Fe(III) by means of controlled aeration. The above reactions can be explained in the form of equations, as follows.

$$2\ \text{Fe(III)chelate} + H_2S \xrightarrow{\text{absorption}} 2\ \text{Fe(II)chelate} + 2H^+ + S^0$$

$$2\ \text{Fe(II)chelate} + \tfrac{1}{2}\ O_2 \xrightarrow{\text{regeneration}} 2\ \text{Fe(III)chelate} + 2OH^-$$

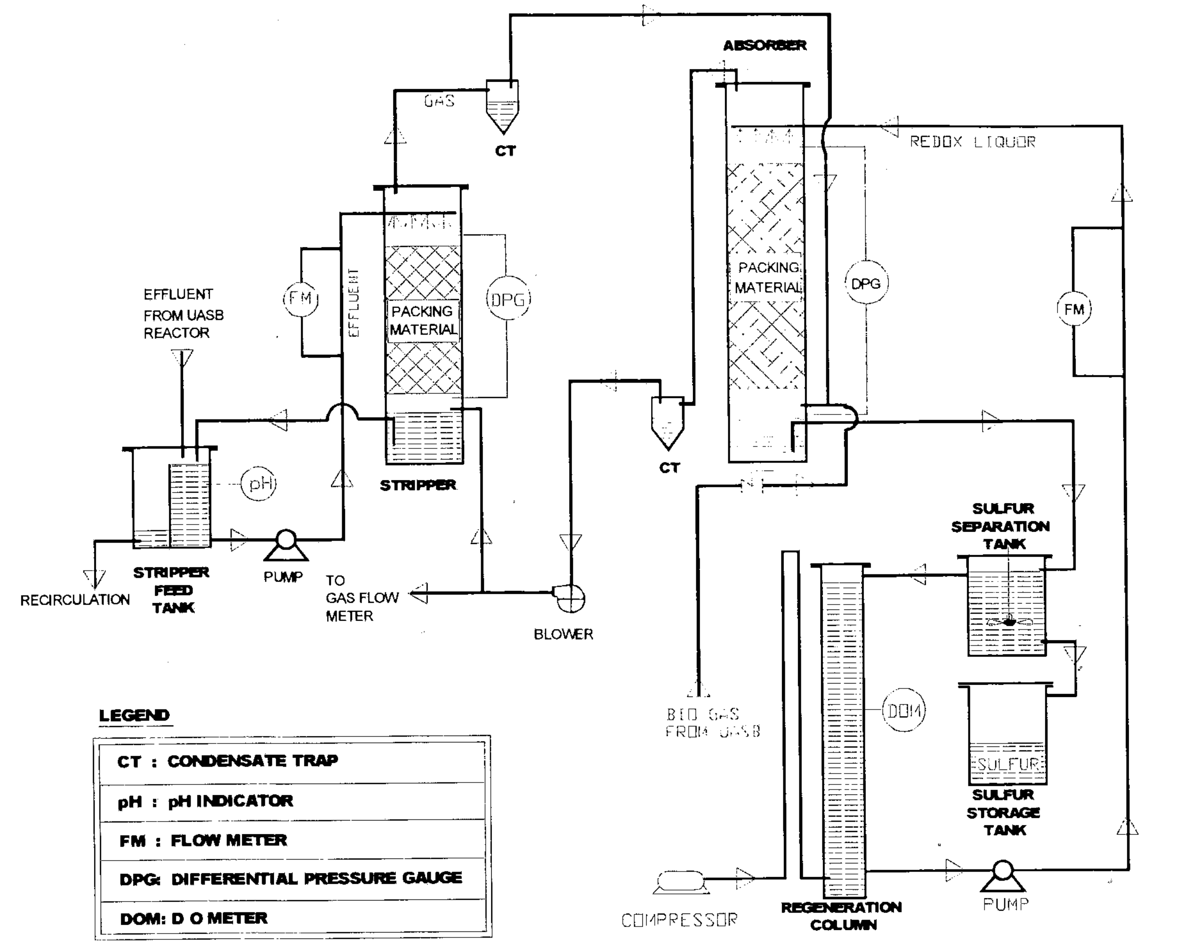

Figure 1. - Schematic of the pilot plant sulfur recovery unit

Regenerated redox liquor, which is now again at maximum oxidizing capacity was then pumped to the absorber column. The biogas from the absorber, having low H_2S concentration, was returned to the stripper again to take up another load of H_2S from the wastewater.

Analyses

All standard analyses were performed according to the procedure given in Standard Methods.[12] Sulfide was determined by iodometric method (No. 450012). Gas analyses for H_2S and CO_2 were carried out using DRAGER tubes. The efficiency of hydrogen sulfide removal in the stripper and absorber columns was constantly monitored to evaluate the performance of SRU.

RESULTS AND DISCUSSION

The wastewater from the UASB reactor was fed into the SRU without any pH adjustment. The pH values of the wastewater from UASB effluent and SRU influent is shown in Figure 2.

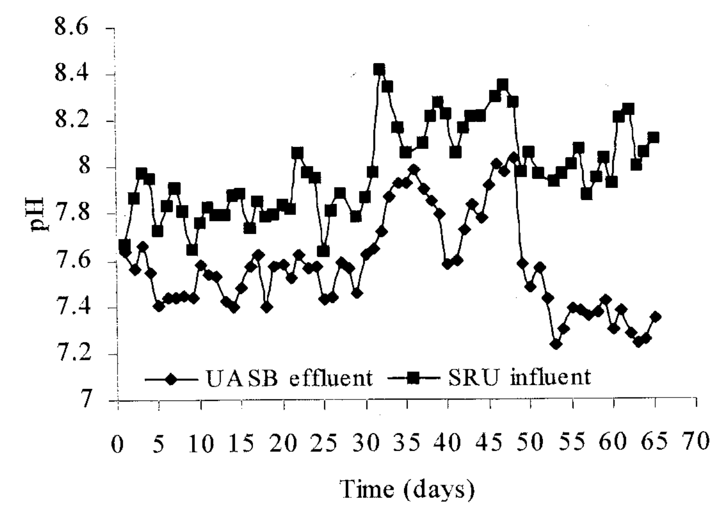

Figure 2. - Variations in pH of UASB effluent and SRU influent with time

The pH of the redox liquor from the absorber column and the wastewater from the stripper unit of the SRU is shown in Figure 3. The pH of the wastewater entering the SRU (i.e. stripper unit influent) from the stripper feed tank was between 7.5 and 8.5. This pH of the SRU influent was higher than the UASB effluent because of the mixing of recircu-

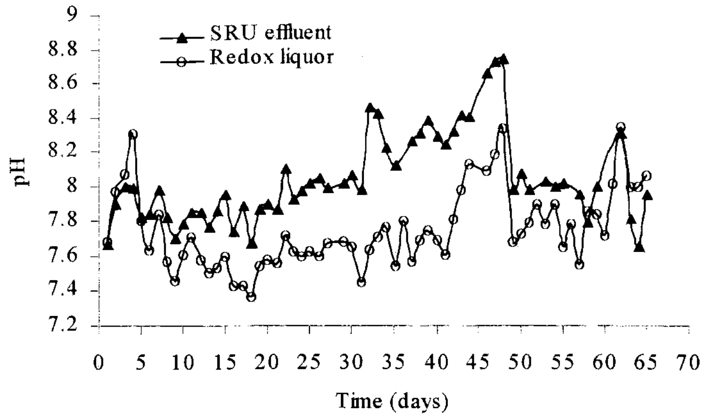

Figure 3. - Variations in pH of SRU effluent and redox liquor with time.

lation wastewater from the stripper unit into the stripper feed tank.

During the stripping operation, in addition to hydrogen sulfide, CO_2 was also stripped off and this increased the pH of the wastewater. The biogas containing H_2S and CO_2 from the stripper unit reduces the pH of the redox liquor during its interaction in the absorber unit. The reduction of pH of the redox liquor in the absorber column was compensated during aeration (when CO_2 was again eliminated), when the redox liquor was regenerated in the regeneration column.

About 80 percent of sulfate in the tannery wastewater is converted to sulfide in the UASB reactor. Sulfide concentration varied from 300-550 mg/L in the effluent from the UASB reactor. Sulfide loading rate to the SRU was varied from 1.0-10 kg/d by additionally introducing sulfide in the form of Na_2S, if necessary. The performance of the stripper and absorber units in removing hydrogen sulfide at different sulfide loads are shown in Figure 4.

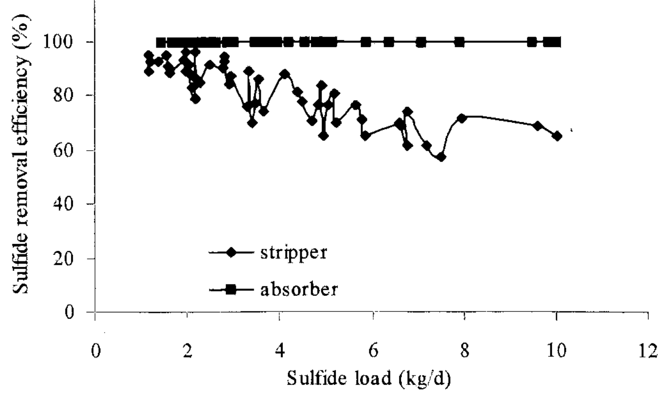

Figure 4. - Sulfide removal efficiency of stripper and absorber units of SRU at various sulfide loads (SRU influent pH 7.5-8.5, gas circulation rate 250 m³/hr).

The efficiency of the stripper unit depends on many factors including pH of the SRU influent, gas flow rate, sulfide loading rate, wastewater flow rate, efficiency of the absorber in removing H_2S from the gas etc. Stripper efficiency of 80-95 percentage sulfide removal was observed when sulfide loading rate was around 1-4 kg/d was applied. Stripper efficiency dropped to 60-80 percent when the loading rate was increased to 4 -10 kg/d. The reduction in hydrogen sulfide removal efficiency can be mainly attributed to the increase in sulfide loading rate and high pH (8.0-8.5) of SRU influent.

Theoretically, there exists an equilibrium between H_2S, HS^- and S^{2-} at various pH levels as shown in Figure 5. Sulfide can be removed only when it exists as free undissociated H_2S. According to the Figure 5, maximum removal of sulfide is effected when the solution pH is between 6.5-8.0. At pH value of 8 and above, most of sulfide present is in solution as HS^- and S^{2-} ions and the amount of H_2S is very low. In the current study, SRU influent was in the pH range of 7.5-8.5 and no pH correction was made. Hence removal

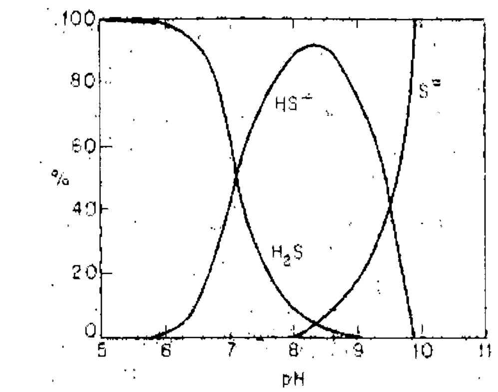

Figure 5. - Effect of pH on hydrogen sulfide - sulfide equilibrium.

efficiency found to be very low.

In the absorber column more than 99.8 percent H_2S removal efficiency was observed throughout the study period. The redox liquor absorbs the sulfide from the biogas from the stripper unit, as well as the sulfide present in the biogas entering the SRU and oxidises the sulfide to elemental sulfur. The purity of dry sulfur obtained after water washing was found to be more than 99 percent. H_2S in the biogas, which was connected to the inlet of the absorber column, contained 0.7-2.7 percent v/v. By adopting this sulfur recovery system, H_2S concentration in the biogas was also reduced from 2.7 percent v/v to less than 0.06 percent v/v and rendered the biogas suitable for its use in the duel fuel engines to convert it into electrical energy.

The removal of sulfide using SRU also helps in solving the odour problem by preventing the harmful gases to be let out into the environment, prevents corrosion problem due to

hydrogen sulfide, reduces the energy requirement in the aerobic treatment (post anaerobic treatment) and also helps in the reduction of total dissolved solids as sulfates are removed from the tannery wastewater (after conversion to sulfide).

Removal of sulfide by SRU, which was integrated with the UASB reactor, lowers the toxic effect of sulfide on the methenogenic bacteria in the UASB reactor and thereby helps in improving the COD removal efficiency in the UASB reactor. The COD removal efficiency in the UASB

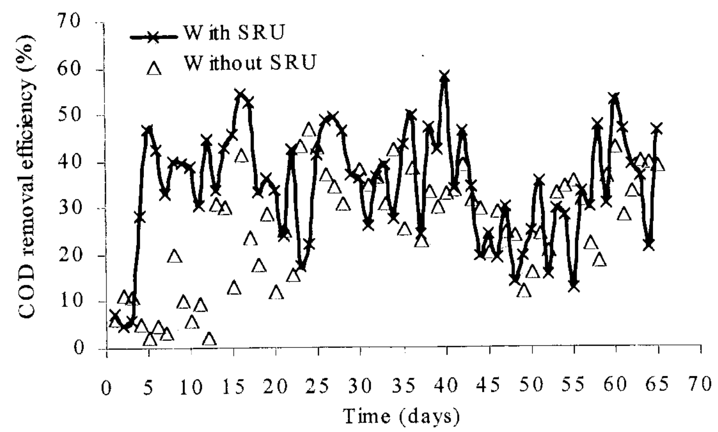

Figure 6. - COD removal efficiency of UASB reactor with and without SRU.

reactor with and without SRU is shown in Figure 6.

The maximum COD removal efficiency, when SRU was present was 45-55 percentage and when SRU was not present, the maximum COD removal efficiency ranged from 30-45 percent. The COD removal efficiency was calculated based on the results obtained without taking into account the COD demand for sulfide. However, if the concentration for sulfide interference during COD estimation were to be taken into account, the COD removal efficiency would be higher at least by about 10 %. In this study, the presence of SRU did not improve the COD removal efficiency significantly.

Further studies on the optimization of operating pH of the SRU influent and redox liquor and the gas circulation rate is being currently carried out.

CONCLUSIONS

Sulfur recovery unit proved to be an effective treatment system for sulfide removal from tannery wastewater, which is rich in sulfur compounds. The sulfide removal efficiency of about 80-95 percent was observed by the stripper unit of the SRU at a sulfide load upto 4 kg/d at SRU influent pH of 7.5-8.0. The absorber efficiency of more than 99.8 percent was achieved throughout the study period. The H2S concentration in the biogas reduced from 2.7 percent v/v to less than 0.06 percent v/v.

Adopting SRU or tannery wastewater helps in effectively reducing sulfide and thereby controlling odour problem, preventing corrosion, reducing the energy cost in the aerobic treatment, reducing total dissolved solids, and making the biogas fit for use in duel fuel engines for the conversion to electrical energy. Recovering sulfur as a useful byproduct is an added advantage of this system.

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