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Removal of Sulphide in Tannery Wastewater by Wet Air Oxidation

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ABSTRACT: Tannery industry is one among the foremost important and rapidly developing industrial sectors. The transformation of hides into leather is typically highly turbid, colored and foul smelling wastewater is generated during this process. The varied components present within the effluent can affect citizenry, agriculture and livestock besides. Sulphide is one among the foremost poisonous components within the wastewater. The Sulphide has more concentration, present in treated wastewater may render aerobic biological treatment unsuitable. Hence, it become essential to incorporate Sulphide removal unit operation proceeding aerobic biological unit. One among the methods of detoxification of Sulphide in wastewater (WW) of tanneries might be their oxidation by use of MoO_3. This material, also because the merchandise of the reaction between Sulphide and this material isn't left in WW and doesn't pollute it.

The Sulphide and thus the pH of solution have an influence on oxidation process duration; it's longer when the Sulphide amount and pH within the WW is higher. Optimal temperature of the treatment is 30°c.Oxidation goes faster if the size of MoO_3 particles doesn't exceed 0.1mm. The chances of repeated use of MoO_3 were investigated. The stableefficiency of the MoO_3 might be obtained by putting initially 0.6% of $MoO_3$and additionally 0.06% of MoO_3 of the answer mass for each following cycle of the treatment.

KEYWORDS: Anaerobic Treatment, Detoxification, Sulphide, Temperature, Wet air Oxidation.

I. INTRODUCTION

Rapid climb of industries has not only enhanced the productivity but also resulted in release of toxic substances into the environment, creating health hazards. It's seriously affected normal operations of ecosystems, flora and fauna. In recent years, considerable attention has been paid to the economic wastes, which are usually discharged ashore or into different water bodies. This is often likely to end in the degradation of environment. Tanning is that the chemical process that converts animal hides and skin into leather and related products. The transformation of hides into leather is typically done by means of tanning agents and therefore the process generates highly turbid, colored and foul smelling wastewater. The major toxic components of the effluent include Volatile organic compounds, Sulphide, chromium, large quantities of solid waste, suspended solids like animal hair and trimmings. For each kilogram of hides processed, 30 liters of effluent is generated and thus the entire quantity of effluent discharged by Indian industries is about 50,000 m3 /day. The varied components present within the effluent affect citizenry, agriculture and livestock besides causing severe ailments to the tannery workers like eye diseases, skin irritations, kidney failure and gastrointestinal problems. Sulphide is one among the main components of the tannery effluent. It causes an irritating, rotten-egg smell above 1 ppm (1.4 mg m^{-3}), and at concentrations above 10 ppm, the toxicological exposure limits are exceeded. It's highly toxic to citizenry. It can cause headaches, nausea and affect central nervous system even at low levels of exposure. It causes death within 30 min at concentrations of only 800–1000 mg/L, and instant death at higher concentrations. The environmental protection regulations stipulate that industries aren't allowed to emit Sulphide within the wastewater. Thus, removal of Sulphide from the wastewater is extremely important.

II. MATERIALS

Pure MoO_3 (Russia, Gost 4470–70) was used for the experiments. MoO_3 (98% pure) used as

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catalyst in Experimental test setup, NaOH solution is employed for adjusting the pH of the sample, Pure Oxygen Cylinder (99.5% pure).

2.1 REAGENTS FOR SULPHIDE TESTING

Hydrochloric acid, concentrated (sp gr 1.19), Iodine standard solution 0.010N, Potassium iodide, Sodium thiosulfate standard solution 0.010N, Starch indicator solution.

2.2COLLECTION OF TANNERY WASTEWATER

The raw effluent wastewater has been collected from Sembattu in Tiruchirapalli District, as per standing operating procedure, the study area known for its location of the airport within the district may be a fast developing urban site. Then the collected samples were delivered to the laboratory and therefore the samples are stored in deep-freeze at 4^{0}C until analysis.

III. EXPERIMENTAL PROCEDURE

3.1 WET AIR OXIDATION

Wet oxidation may be a sort of hydrothermal treatment. It's the oxidation of dissolved or suspended components in water using oxygen because the oxidizer. It's mentioned as "Wet Air Oxidation" (WAO) when air is used. The oxidation reactions occur in superheated water at a temperature above the normal boiling point of water (100 °C), but below the juncture (374 °C).

The system must be maintained struggling to avoid excessive evaporation of water. This is often done to manage energy consumption because of the warmth of transformation of vaporization. It's also done because liquid water is vital for several of the oxidation reactions to occur. Compounds oxidize under wet oxidation conditions which may not oxidize under dry conditions at the same temperature and pressure. The WAO of organic compounds occurs in two steps :(1) Physical step (2) Chemical step.

3.1.2 PHYSICAL STEP

The physical step involves the transfer of oxygen from the gas phase to the liquid phase and therefore the second step is that the reaction between organic compounds and the dissolved oxygen. The general mechanism of WAO is therefore hooked in to both of the stages and depends on the speed of oxygen transfer from gas phase to liquid phase and therefore the ability of organics present and various intermediates formed thanks to the oxidation, to react with dissolved oxygen. The migration of oxygen across the gas-solid interface and concluded that the sole significant resistance to oxygen transfer is found at the junction (film model) with three limiting cases.

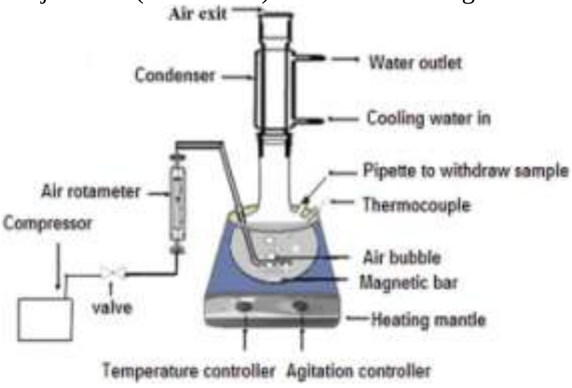

Fig 3.1 Wet air oxidation experimental setup

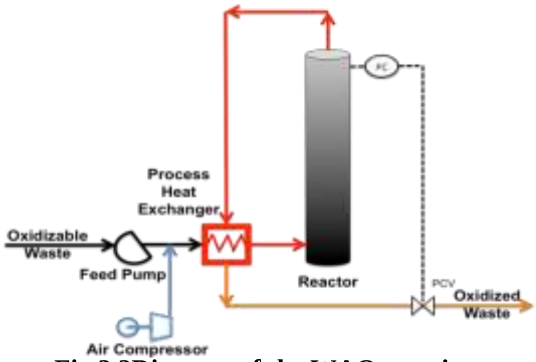

Fig 3.2Diagram of the WAO reaction

Pathway of organic compounds

- Oxygen reacts within the film thanks to a rapid reaction. During this way, the oxygen transfer rate is enhanced.
- Oxygen reacts within the majority liquid where its concentration is on the brink of Zero. The general rate is adequate to the physical step of oxygen transfer.
- Oxygen concentration within the majority liquid is adequate to the interface (or equilibrium) concentration. The general rate is that the chemical step rate, and typically low.

3.2.2 CHEMICAL STEP

The final step, reaction of organic compounds with dissolved oxygen, is understood as a chemical step. The WAO process converts organic compounds into CO_2, water and biodegradable, short-chain organic acids. Inorganic constituents like sulfides and cyanides also can be oxidized.

IV. RESULTS AND DISCUSSION

The experimental work on the tannery wastewater was planned to work out the quantity of Sulphide removed by using wet air oxidation process. Then an equivalent wastewater sample was analyzed to work out the physico-chemical parameters present in it.

4.1 CHARACTERISTICS OF TANNERY WASTEWATER

Wastewater of every tannery process consists of pollution of varying pH values. Similarly, an outsized variation exists in every parameter BOD, COD, Chloride, Sulphide, etc. Discharge of those chemicals into wastewater is hazardous for the environment. Analysis of physical and chemical characteristics of the tannery wastewater collected from Sembattu.

Table 4.1 Raw Effluent Characteristics

S.NO	PARAMETERS	APHA STANDARDS VALUE
1.	pH	11.14
2.	Total Suspended Solids	1040 mg/l
3.	Total Dissolved Solids	6395 mg/l
4.	Biological Oxygen Demand	1520 mg/l
5.	Chemical Oxygen Demand	3640 mg/l
6.	Sulphide	210 mg/l

The above listed parameters were exceeded the tolerance limits of tannery wastewater for reuse. So it's to be treated well to urge it within the tolerance limits. Since there are several standard limits for reuse water given by TamilNadu Pollution control panel (TNPCB), treatment need to be done to satisfy it. That's what we've wiped out this study.

4.2 INVESTIGATION OF THE REACTION BETWEEN Na_2S AND MoO_3

It is known that MoO_3could also be a really strong oxidizer, but it’s also utilized in various chemical reactions as a catalyst. MoO_3 can oxidise H_2S during this way:

$2MoO_3 + 3H_2S + 2O_2 \rightarrow MoSO_4 + MoS_2O_3 + 3H_2O$

Analyzing old literature uncovered another interesting reaction which proceeds in boiling solution of Sulphide.

$4R_2S + 4MoO_3 + 10H_2O \rightarrow 2R_2S_2O_3 + 4ROH + 4MoO_3$

No more possible reactions were found which could to travel in strongly alkaline medium between Sulphides and MoO_3.

Adding of 0.15% MoO_3 into the strongly alkaline (pH 13.2) solution of Na_2S (solution contained 10 g/l NaOH and 5.6 g/l Na_2S) and treating it in air or nitrogen atmosphere has shown the interest course of the tactic.

It are often seen that the Na_2S concentration quickly decreases within the primary quarter-hour and practically doesn't change then,when treating a solution in nitrogen atmosphere.

When treating in conventional atmosphere, the rapid decreasing of Na_2S concentration is additionally observed, but the method doesn't stop then and goes further until no Na_2S is left within the answer. This character of reaction proceeding allow us to suppose that the tactic of oxidizing Na_2S using MoO_3 goes by two stages. Within the primary stage the reaction between MoO_3 and Na_2S predominates. Within the second stage only the catalysis reaction between Na_2S and air oxygen takes part. (By the way, during this stage the catalyst isn't MoO_3 but the merchandise of reaction between MoO_3 and Na_2S).
The further investigation (IR spectroscopy and DT analysis) has shown that within the primary stage MoO_3 turns insoluble in alkaline solution MoOOH which acts as a catalyst within the second stage. After the investigation of products of oxidation of Na_2S after treatment of solution the suggestion was made that within the primary stage the subsequent reactions are possible:

1) $2Na_2S + 2MoO_3 + 2H_2O \rightarrow 2MoOOH + 2S + 4NaOH$
2) $5Na_2S + 4MoO_3 + 5H_2O \rightarrow 4MoOOH + 4Na_2S_2O_3 +$
$2NaOH + 2S$
3) $Na_2S + 4MoO_3 + 3H_2O \rightarrow 4MoOOH + Na_2SO_3$
4) $Na_2S + 6MoO_3 + 4H_2O \rightarrow 6MoOOH + Na_2SO_4$

The analysis of the decreasing Na_2S concentration in air atmosphere has confirmed that within the first stage this reaction prevails:

$2Na_2S + MoO_3 + 2H_2O \rightarrow MoOOH + 2S + 4NaOH$

We suppose that within the second stage the reaction takes part, where MoOOH acts as catalyst:

$2Na_2S + 2H_2O + O_2 \rightarrow 2S + 4\ NaOH$

In parallel, the reactions of further sulfur oxidation went on, because not only free sulfur was found within the solution after finish of oxidation, but also thiosulphates, Sulphides and sulphates.

4.3 EVALUATION OF THE ADDITION OF VARIOUS AMOUNTS OF MoO3

It is known that Sulphides get into wastewater after liming, pelt washing and deliming-baiting processes. There aren't only alkalis and Sulphide in these solutions, but products of hair and collagen degradation, as well. The foremost aim of this investigation was to work out how the oxidation of Sulphide in WW proceeds using MoO_3, and what factors during which way influence this process.

At first, the influence of MoO_3amount on duration of Sulphide oxidation in WW was investigated. Two assays using two different WW of tanneries there have been carried out:

– ww after liming (I), which contained 24.8 g/l $Ca(OH)_2$, 2.87 g/l Na_2S, its pH was 13.11;

– Mixture of solutions after liming, washing of pelt and deliming (II): 8.9 g/l Ca $(OH)_{2,}$ 1.32 g/l Na_2S, its pH was 11.92.

For each WW the effect of the addition of varied amounts of MoO_3 on the speed of the reaction was evaluated. The amounts of MoO_3 added for treatment was 0.3, 0.5 and 1% (control treatment without MoO_3).Treatment was administered at 18-20°c. The duration of Sulphide oxidation without MoO_3 was 26-28 h, using MoO_3 it had been remarkably shorter: 0.6-1h in WW II and 1.5-2.5h in WW II. The duration of this process trusted the quantity of MoO_3.We suppose that counting on the concentration of Sulphide in solution, optimum amount of MoO_3 for treatment is 0.3-0.5% from the solution mass. It's more getting to have slightly longer duration of oxidation than to feature 2-3 times more (1%) of MoO_3.

4.4 ESTIMATION OF TIME REACTION BETWEEN Na_2S AND MoO_3 FOR DIFFERENT pH

WW utilized in this assay contained 21.7 g/l Ca $(OH)_2$, 3.16 g/l Na_2S, its pH was 11.92. By use of solution NaOH (10%) or Hcl (10%) the pH was adjusted to values 9, 11 and 13.The amount of MoO_3 added for treatment was 0.15% (control treatment proceeded without MoO_3).The treatment was administered at 18-20°c. The results obtained are presented within the graph. One can see that Sulphide are totally removed during 5 or 7 hours when treating without MoO_3 the ww, pH of which was 9 or 11. It's known that Na_2S is converted to H_2S when pH is 10 and lower.

The smell of H_2S was slightly perceptible within the vessel with the answer having pH 11 and therefore the strong smell was within the vessel with the answer having pH 9.This means that in the treatment of those solutions the Sulphide aren't only oxidized but also removed as H2S.In summary, it should be said that Sulphide are removed sooner when the pH of solution is lower.

Time duration (hr)	Na_2S Concentration (g/l)	Na_2S Concentration (g/l) with MoO_3
0	5.6	5.6
1	5.2	4.87
1.5	5.1	3.82
2	5	3.16
2.5	5	3.02
3	4.9	2.9
3.5	4.7	2.5
4	4.6	2.3
4.5	4.6	1.8
5	4.6	1

Table 4.2 Time reaction between Na_2S and MoO_3

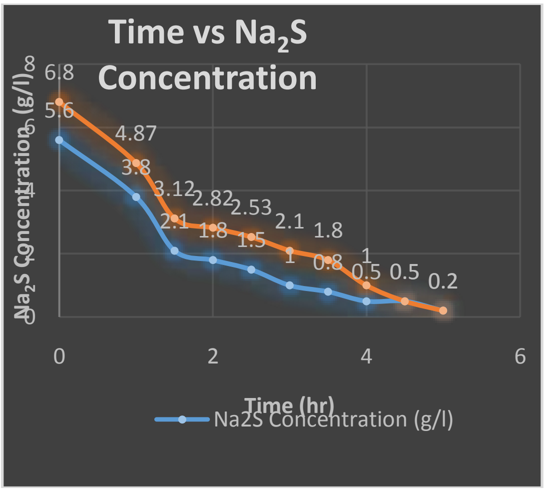

Fig 4.1 Estimation of time reaction between Na_2S and MoO_3

The results obtained have shown that the case of treatment the WW having pH 10 and lower (generally the mixture of solutions after beam house processes had pH about 10) an outsized amount of H_2S gets into atmosphere. To escape that, the Sulphide should be treated during a mix of used liming-unhairing and pelt washing solution, which has pH. 11-12. This wastewater takes about 14-20% of all WW of tanneries which suggests distinctly less amount of solutions should be treated compared to total WW during this case.

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4.5 EVALUATION OF TEMPERATURE ON SULPHIDE OXIDATION

The second factor, which naturally has influence on the reaction, is temperature. For the investigation of this influence the used unhairing liquor containing 24.8 g/l Ca $(OH)_2$ with the combination of Na_2S (pH was 12.8) was treated. The quantity of MoO_3 added for treatment was 0.15%. The treatment was administered at the 18, 30, 40 and 50°c. It had been established that temperature had an influence on the duration of Sulphide oxidation. This influence is ambivalent. The chemical process between Na_2S and MoO_3 proceeded sooner when temperature was being increased, but then the rise of the temperature decreases the speed of the catalysis reaction between Na_2S and air oxygen. Total duration of the oxidation process became shorter when increasing the temperature from 18 to 30°c. The shortest time of process was obtained at 30°c. The further increase of temperature from 30°c increased the entire duration of Sulphide oxidation. We suppose that to warm up ww to 30°c isn't worth trying because such warming allows shortening the method just for about 10 minutes.

The liming unhairing is typically administered at 23-25°c and therefore the washing of limed pelt accordingly at 20°c. If leather is processed in winter- time, the treatment is to be administered while the answer of Sulphide has not cooled down. Since one among the components of the oxidation process may be a solid material (MoO_3), the dimensions of particles of this material also has influence on the progress of oxidation.

Table 4.3 Temperature on Sulphide oxidation

Time duration (hr)	Na_2S Concentration (g/l)	Na_2S Concentration (g/l) with MoO_3
0	5.6	6.8
1	3.8	4.87
1.5	2.1	3.12
2	1.8	2.82
2.5	1.5	2.53
3	1	2.1
3.5	0.8	1.8
4	0.5	1
4.5	0.5	0.5
5	0.2	0.2

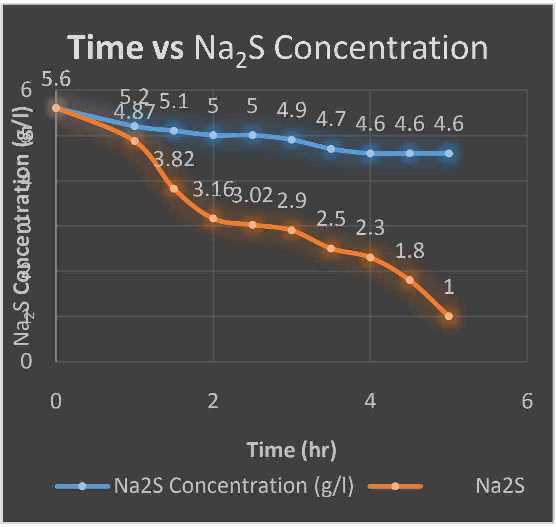

Fig 4.2 Evaluation of temperature on Sulphide oxidation

It are often seen that this factor plays a superb role within the method of Sulphide oxidation. It goes without saying, because the tactic of Sulphide oxidation is based on a heterogeneous reaction during which the planet of surface of a solid-state material influences speed of the reaction. This means that the size of particles of MoO_3 shouldn't exceed 0.1 mm if more rapid process of Sulphide oxidation is required.

After that a replacement portion of WW was poured on the used catalyst for treatment. Together can see from this table, the efficiency of the catalyst decreases when it's used repeatedly. We used it until the duration of treatment reached 10 hours. This duration when adding 0.3% MoO_3 was reached the 5th time of catalyst use, and on the 10th time, when adding 0.6% MoO_3.

V. CONCLUSION

This project deals with the removal of Sulphide and toxic pollutants from the tannery wastewater. The foremost source of Sulphide in tannery industry effluent is beam house operations. Wet air oxidation was effectively used to remove Sulphide in wastewater. We conducted experiments for various conditions. The pollutants were reduced thanks to adding catalyst and continuous supply of air or oxygen (at heat and pressure). The Sulphide removal efficiency were determined. Hence, the Sulphide is removed in wastewater sample using WAO to reinforce rock bottom water quality, to eliminate environmental impacts, to reduce pollution of land and spring water and also to prevent water borne diseases. This treatment shows an honest reduction of pollutants from the tannery wastewater Sample.

Wet air oxidation process is one among the foremost effective method for removal of Sulphide within the tannery wastewater. The optimal temperature of the treatment is 30°c at this temperature the oxidation proceeds sooner. The method becomes a touch longer if the temperature is lower or above 30°c. Not only the quantity of MoO_3, but also the dimensions of MoO_3 particles has an influence on the duration of the Sulphide oxidation process. It's faster if the dimensions of particles doesn't exceed 0.1 mm. the likelihood of reuse of the catalyst was investigated. The efficiency of the catalyst decreased when it had been used repeatedly for a couple of times. Stable efficiency of the method might be obtained by putting initially 0.6% $MoO_3$and additionally 0.06% MoO_3 every following time of treatment.

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