



Catalytic Oxidation of Sulphide Laden Tannery Wastewater without Sludge Production

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ABSTRACT

The beam house operations in tanning process of hides / skins comprises of soaking, liming, fleshing and delimiting operations. The removal of animal hair and flesh from skin is facilitated by the liming operation. About 5m³/ton wastewater containing a credible concentration of sulphide and dissolved proteins are discharged. It is highly alkaline and having high BOD/COD ratio. The biological treatment of wastewater that occurs at neutral pH requires neutralization of the wastewater using acidic stream. This results in the emission of hydrogen sulphide which is considered to be highly toxic gas. The present investigation employed **Heterogeneous Peroxide oxidation process (HPO)** for the oxidation of sulphide in the lime sulphide liquor without sludge production with simultaneous removal of COD from wastewater. The screened effluent was adjusted to pH 9.7 using conc. Sulphuric acid and it is catalytically oxidized with Hydrogen peroxide 3.921mM/L and Nano Porous Activated Carbon (NPAC), 30 g/L at HRT 24 hr. The dosage of Hydrogen peroxide, mass of NPAC and HRT were optimized. The integrated catalytic and biological oxidation in FICCO (Fluidized Immobilized Carbon Catalytic Oxidation) reactor eliminated COD, sulfide, Total Kjeldahl Nitrogen, protein, Amino acids and Total organic compound by 66.66%, 98.95%, 75.67%, 44.21%, 48.98% and 62.18% respectively. The sulphide present in the wastewater was catalytically oxidized to sulphate and ammonia content was increased by 78.05% by cleaving protein molecules.

Key words: HPO; NPAC; FICCO; COD.

I INTRODUCTION

Leather industry is the significant contributor to the Indian economy and provides largescale employment opportunity. The total processing capacity of the world tanning industry is more than 10 million tons of hides and skins per year. Totally, 2500 tanneries are located in India including Tamilnadu 50%, West Bengal 20% and Uttar Pradesh 15% (CPCB, 2009). The beam house operations such as soaking, liming, fleshing, delimiting in the process of hides/skins are common irrespective of the types of tanning process. The preservation and processing of raw hides and skins for tanning process cause severe pollution problem towards environment and mankind (Aravindhan *et al.*, 2004). In fleshing and liming process, unhairing is done by chemical dissolution of the hair and epidermis with an alkaline medium of sulphide and lime. After skinning at the slaughterhouse the hide appears to contain excessive meat, fleshing usually precedes unhairing and liming. Liming and unhairing produce the effluent stream with the highest COD value. The removal of hair and flesh from skin is facilitated during the liming operation. Conventional process employs 10% lime (calcium hydroxide) and 2% sodium sulphide on hide/skin weight basis for loosening the hair. About 5 m³ of spent lime liquor is discharged per ton of raw hides/skins processed. Sodium sulphide being a good reducing agent interferes in the oxidation of organic wastes and contributes significantly to the BOD and COD concentrations in the wastewater. Lime sulfide is most environmental harmful chemical in tanning process (Schraeder *et al.*, 1998 and Huber *et al.*, 1990). The spent lime liquor is highly alkaline (pH 10-12) and 100% toxicity (Taylor *et al.*, 1987 and Marsal *et al.*, 1999). The major amount of pollution in terms of BOD (5,000-10,000 mg/l), COD

(10,000-25,000 mg/l), sulphide (500-800 mg/l), Total solids (24000-48000 mg/l), suspended solids (6,000-18,000 mg/l), chloride (4000 – 8000 mg/l) and sulphate (600 – 1200 mg/l) is contributed by sulphide-liming process. This sulfide containing wastewater has extensive hazardous to environment and treatment plant also (Davies *et al.*, 1997).

II PROBLEMS ASSOCIATED WITH PRESENCE OF SULPHIDE IN EFFLUENT

Under alkali conditions sulphide largely remain in solution. When the pH of the effluent falls below 9.5, hydrogen sulphide is evolved from the effluent. The rate of evolution of hydrogen sulphide increases with decrease in pH and is characterized by severe odor problem. This gas is toxic similar to hydrogen cyanide and even low-level exposure will cause headaches and nausea, and there is a danger of attack to the surface of the eye. At higher levels death can rapidly result and there are many deaths recorded from sulphide build up in sewage systems. Hydrogen sulphide gas is also fairly soluble, and when dissolved by condensation weak acids can be formed with resultant corrosion. This typically weakens metal roofing, girders and metal building supports. In sewers major problems can result by corrosion of metal fitting, reinforcement and pipe work. If discharged to surface water, there are toxicological dangers even at low concentrations. Sulphide can also be oxidized into non-toxic compounds by certain bacteria in rivers, but this creates an oxygen demand and if excessive there is damage to aquatic life. It also inhibits the methanogenesis process. Soluble sulfide ranging from 50 – 100 mg/l. can be tolerated in anaerobic treatment with little or no acclimation. Sulfide has

high oxygen demand of 2 molO₂/mol sulfide and causes depletion of oxygen in water.

III TREATMENT OF LIME SULPHIDE LIQUOR

The presence of sulphide in wastewaters may dramatically interfere with microbial activities and consequently disturb the function of the system (Mesdaghinia *et al.*, 1991). Biological processes can be carried out only when concentration of sulphide is not exceeding 50 mg/L (Valeika, 2006). Aerobic treatment was not effective method for treatment of tannery effluent (Sekaran *et al.*, 1996; Ganesh and Ramanujam, 2009). Sekaran *et al.* (1996) have reported that anaerobic treatment of tannery wastewater in high rate close type reactors leaves sulfides in the range 31-795 mg/l, COD 395-1886 mg/l, BOD 65-450 mg/l and total organic carbon (TOC) 65-605 mg/l. So high sulphide concentration present in treated wastewater may not suitable for aerobic biological treatment. In order to remove sulfide from wastewater streams, a number of physicochemical methods like direct air stripping, chemical precipitation and oxidation are in common use today. Many of the metals such as iron, zinc, copper etc could be used to precipitate the sulfide into insoluble metal sulfide. Oxidation processes used for sulfide removal are aeration (catalyzed and un-catalyzed), chlorination, ozonation and hydrogen peroxide treatment (Valeika *et al.*, 2006; Anglada *et al.*, 2009). During the sulfide oxidation by aeration, there is some loss of sulfide directly into the atmosphere. Sulfide consumes the oxygen in the aeration and reduces the effectiveness of the equipment. In chlorination, chlorine reacts with certain metals and organic matter in the water to form hazardous chlorinated organic chemicals. Catalytic chemical oxidation of the sulfide with air removes the sulphide quantitatively but it is a time consuming and expensive process. (Valeika *et al.* 2006) used manganese oxide to oxidize sulphide in tannery effluent. The oxidation of Na₂S proceeds in two stages. In the first stage Na₂S reacts with MnO₂, to give manganese hydroxide. In the second stage, the catalysis reaction between Na₂S and air O₂ is taking part. Sekaran *et al.* (1995) was reported that removal of sulphide in lime yard wastewater by wet aeroxidation in the presence of manganese sulphate as a catalyst. During the oxidation of sulphide in lime yard wastewater, 92% of the total oxygen demand and 90% of the dissolved protein were also removed. But manganese sulphate results in formation of Manganese hydroxide sludge and also when the level exceeds 0.01g/100 g of water, it gets solubilized (solubility of Manganese hydroxide at pH 9.5 = 5.9 x 10⁻⁴ g/l), thus Mn level in the water increases contributing to increase in metal pollution load. Hence, there has been a constant research on the development of methods for the removal of sulphide from lime sulphide liquor without sludge production. The focal theme of the present investigation was to employ heterogeneous

peroxide oxidation process (HPO) and fluidized immobilized cell carbon oxidation reactor (FICCO) for the oxidation of sulphide in the lime sulphide liquor without sludge production.

IV MATERIALS AND METHODS

(a) Source and collection of lime sulphide liquor and methods

The lime sulphide liquor was collected from model tannery in CLRI, Chennai. The wastewater was screened to remove the floating solids such as hair, flesh, trimmings etc. The screened effluent was taken to adjust pH 9.7 which was optimized using con. Sulphuric acid on magnetic stirrer then allowed to remove grit solids in imhoff cone for two hours. Then supernatant liquor was siphoned off without disturbing the settled grit solids. That liquid catalytically oxidized with Hetero Peroxide oxidation (HPO) process using 0.4ml/L of 30% Hydrogen peroxide and 30 g/L of Nano Porous Activated Carbon (NPAC) for 24 hr dosage amount and time were optimized then neutralized using lime after that it carried to FICCO (Fluidized Immobilized Carbon Catalytic Oxidation) using microorganism with NPAC 30g/L.

(b) Materials

All the reagents were purchased from Merck, India and nanoporous carbon was prepared in lab using two stage processes.

(c) Preparation and characterization of Nanoporous activated carbon (NPAC)

Rice husk, the precursor, was pre-carbonized at 400°C and activated using phosphoric acid at 800 °C. It was washed with hot distilled water several times and dried at 110 °C for 1 h in a hot air oven and stored over dehydrating agent in the desiccators (Swarnalatha *et al.* 2009). The prepared nanoporous activated carbon (NPAC) was used as base catalyst for the removal of sulphide and COD simultaneously.

(d) Physico-chemical analysis of the wastewater

The wastewater samples were analyzed for pH, BOD₅ (biochemical oxygen demand), COD (chemical oxygen demand), sulphide, sulphate, total organic carbon and total dissolved solids, in accordance with standard methods of analysis of wastewater (American Public Health Association, 1998). TOC analyzer used to measure presence of Total Organic Compound and Total Nitrogen (TN), UV/Visible spectroscopy done to know the degradation and FT-IR spectroscopy also done to initial and final treated water, TGA for Total solids also done Ammonia Distillation unit were used to measure Total kjeldahl Nitrogen and Ammonia present in the sample during all treatment processes.

(e) Treatment methods for lime sulphide liquor

The lime sulphide liquor was oxidized NPAC/H₂O₂ in FBR optimization of the dosage of NPAC/H₂O₂ and pH were carried out.

V RESULTS & DISCUSSION

The characteristics of initial wastewater samples are presented in table 1.

Table 1
Characteristics of Initial effluent

Parameters	Values
pH	12.59 ± 0.523
ORP	-524.8± 11.682
COD , mg/L	11523 ± 1657.88
BOD , mg/L	6975± 1372
TOC, mg/L	1644± 1155
NH ₃ , mg/L	96.55± 76.076
TKN, mg/L	624.1±393.69
Total Solids , mg/L	66626± 69248
Total Dissolved Solids, mg/L	25513± 14082
Total Suspended Solids, mg/L	41113 ± 55166
Sulphide , mg/L	1211± 402.43
Sulphate , mg/L	958.4± 962.19
BOD:COD	0.339± 0.0906
Protein, mg/L	7331±1262.9
Amino acid	52702 ± 72022

(a) Characteristics of NPAC

The NPAC samples were characterized by surface area 291.15 (m²/g), average pore diameter 25.91 (Å), carbon 48.45 (%) and free electron density 16.052 x 10¹⁸ (spins/g).

(b) Fluidized bed Reactor (FBR)

The fluidized Bed Reactor in this present investigation to oxidize sulphide in lime sulphide liquor is presented in Fig.1, consists of three zones. The first zone is known as “react zone” comprised of the catalyst (either MnSO₄ or NPAC) which can be fluidized by air and wastewater at upflow velocity of 5 m/min. The quantity of air required for the oxidation of organics in wastewater is decided on the kinetics of oxidation of organics in wastewater. The air required for the fluidization and oxidation of organics is supplied through the perforated pipe lines provided at the bottom of the reactor. The pressure of air required is a function of upflow velocity, viscosity of medium, total solids content of the medium, temperature and height of the reactor. The second zone is the fluid separation zone. The unspent oxygen and nitrogen in air are separated using a triangular septum provided at the optimum height of the reactor. The separated air is collected through the perforated chamber. The third zone is the settling zone. The treated wastewater enters through the aperture is allowed to settle in the inclined baffled zone. The angle of the inclined plate was decided on the zone settling velocity of the suspended solids present in the wastewater. The settling tendency of the suspended solids was enhanced by providing the extended surface area to capture the particles. The media used to increase the surface area for interception of the suspended particles are by poly propylene plastic media of defined geometry. The screened suspended solids are sloughed off from the media on exceeding a critical thickness. The sloughed suspended solids slides back into the reactor through the aperture. The sludge accumulated in the reactor is withdrawn daily through sludge withdrawal pipe line provided in the reactor.

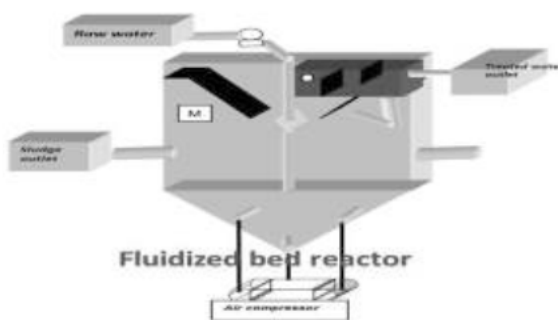


Fig. 1 Fluidized Bed reactor

VI OPTIMIZATION TECHNIQUES

(a) Optimization of pH

Hetero Peroxide oxidation process was optimized by batch process for 24hr with 0.4 ml/L of 30% H₂O₂ to know which would give better result accordance with pH, so the sample were taken in different pH say 12,11,9.7,8 and 7. The removal of

COD is represented in fig. 2. Initial COD value was 11040mg/L and the residual COD after treatment at pH 12, 11, 9.7, 8.0 and 7.0 were 6760mg/L, 7520mg/L, 5500mg/L, 6080mg/L, 5600mg/L respectively. It clearly indicates that almost the removal of COD at pH 7.0 and 9.7 is greater than any other pH, but at the pH 7.0, the liberation of hydrogen sulphide is greater, thus we fixed the optimum pH as 9.7.

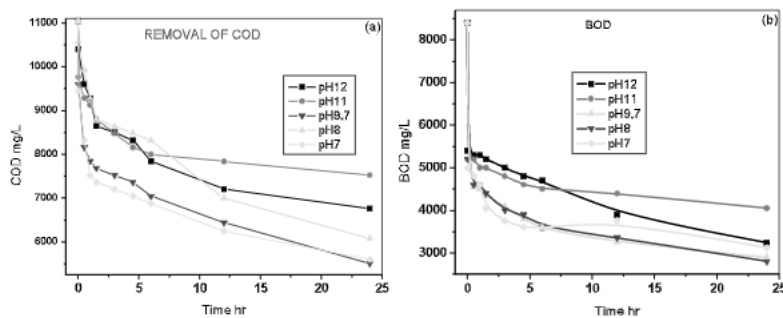


Fig. 2 Optimization of pH for the removal of (a) COD and (b) BOD on HPO process

Fig 2(b) indicates the removal of BOD and the removal was better in pH 7.0 and 9.7. In order to avoid the liberation of sulphide, optimum was fixed to be pH 9.7. The BOD:COD of initial sample was

0.25 and it increased during the process at different pH (Fig. 3a) and NH_3 formation was also increased by varying the pH (Fig. 3b).

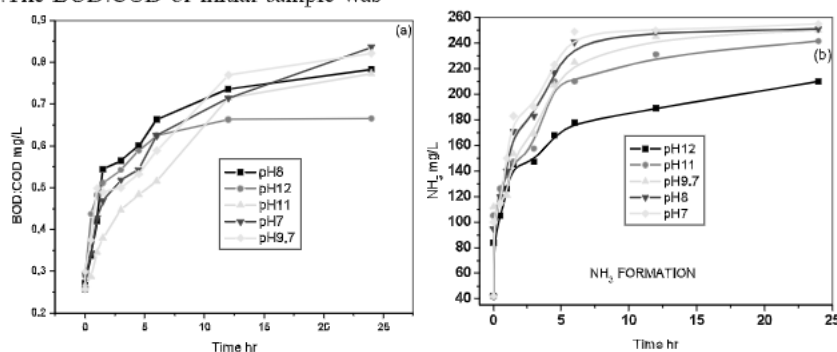


Fig. 3 Optimization of pH on the values of (a) BOD: COD and (b) NH_3 formation in HPO process

Fig 4(a) and (b) represents the removal of TN and TOC at various pH. The removal of total organic compound (TOC) and Total Nitrogen (TN) was

decreased throughout the entire process irrespective of the pH also given below.

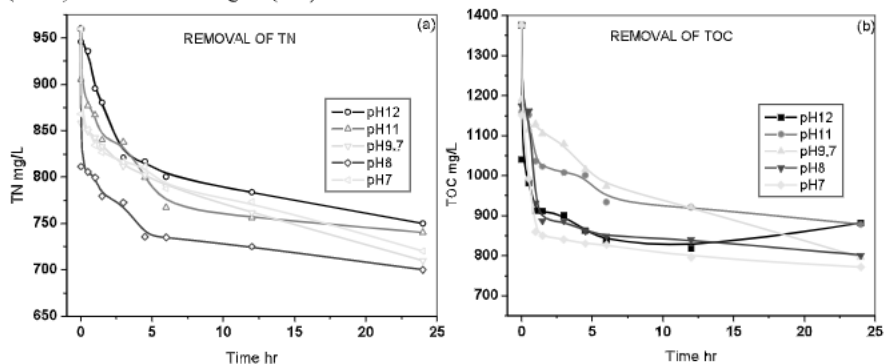


Fig. 4 Optimization of pH for the removal of (a) Total nitrogen and (b) Total Organic Carbon in HPO process

Sulphide removal is considered to be one of the important criteria in pH optimization. Though it decreases drastically in pH 7 and pH 8 (Fig 5), pH

9.7 was considered as optimum in order to avoid the evolution of H_2S gas (results in rotten egg smell) by decreasing the pH.

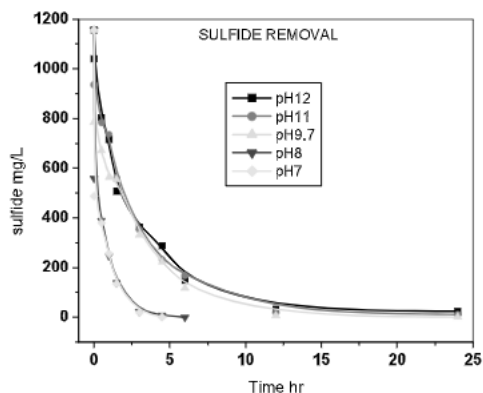


Fig. 5 Optimization of pH for the removal of sulfide on HPO process.

(b) Optimization of H₂O₂

Optimization of peroxide (0.2, 0.4, 0.6 and 0.8 ml of 30% hydrogen peroxide/L) was done at the optimum pH (pH 9.7) and the result showed the optimum was 0.4 ml of 30% hydrogen peroxide/L.

Though sulphide removal is high at 0.8 ml of 30% hydrogen peroxide/L, there is no considerable COD removal at this dosage when compared with the optimized peroxide volume.

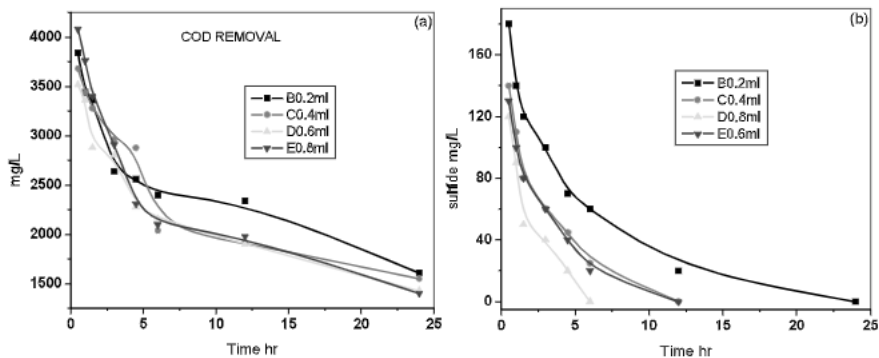


Fig. 6 Optimization of H₂O₂ for the removal of (a) COD and (b) Sulfide

(c) OPTIMISATION OF NPAC (Nano porous activated carbon)

Optimization of NPAC was carried for 20g, 25g, 30g, 40g/L of NPAC, fig 7 showed that the higher

reduction of COD, BOD, protein degradation in 40 g/L taken but the optimum was fixed as 30g/L by comparing the reduction verses cost.

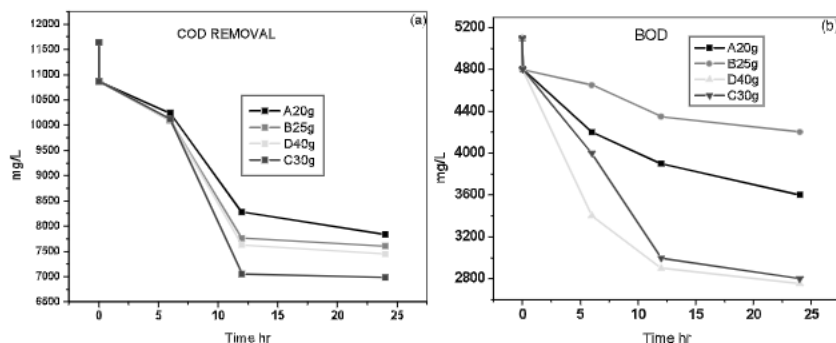


Fig.7 Optimization of NPAC for the removal of (a) COD and (b) BOD

VII OVERALL PROCESSES

HPO process was carried out at the optimum pH, peroxide and NPAC. It has been observed that the sulphide removal in this method might would have

been due to the formation of sulfenic, sulfinic, cysteic acid during the oxidation process⁽⁶⁾ because of the decrease of the pH throughout the process. Then the samples were passed through FICCO reactor for further treatment at neutral pH.

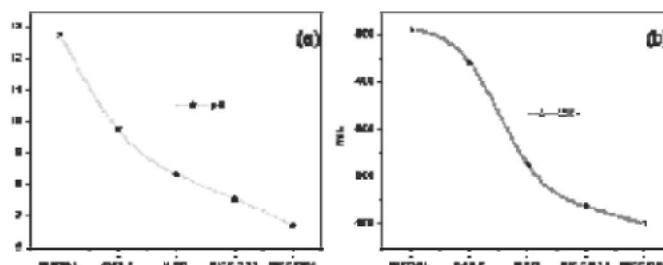


Fig. 8 The values of (a) pH and (b) ORP during the treated processes

During the entire process the oxidation of the sample was examined by the ORP of the sample. ORP of the initial sample was -524 mV and it was

reduced as -100 mV at the end of the treatment, which is the clear evidence for the oxidation.

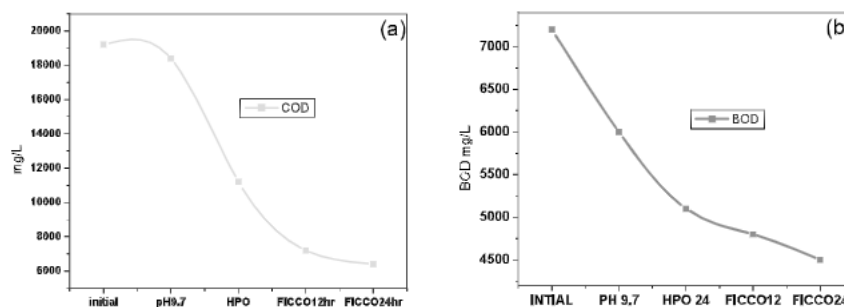


Fig.9 Removal of (a) COD and (b) BOD during the treatment process.

The COD of the initial sample was 19200 mg/L and it was reduced to 6400 mg/L (66.66%) during the various treatment processes. The BOD of the

initial sample was 7200 mg/L, which has been reduced to 4500 mg/L.

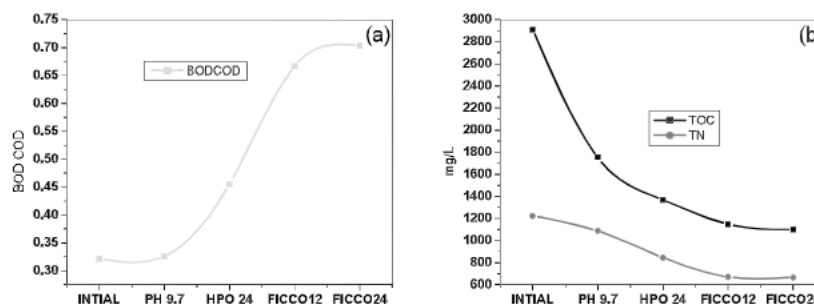


Fig. 10 The values of (a) BOD: COD and (b) Total organic carbon, Total nitrogen during treatment processes

It was found that the initial BOD:COD ratio was 0.33 which has been characterized as moderately biodegradable water because of high COD and low

BOD(O. Dahl et al.,1999, S. Lacorte et al.,and E.T. Barness et al.,1994), this was increased considerably to 0.66 (high degradable samples).

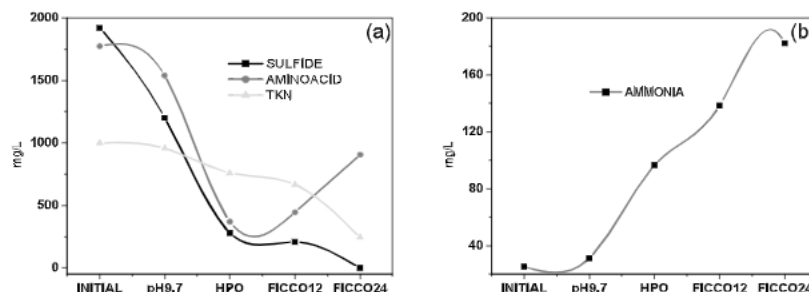


Fig.11 The values of (a) Sulfide, amino acid, Total Kjeldahl nitrogen (b) Ammonia during treatment process.

Amino acid of the sample were analyzed and it was found to be decreased during HPO due to the degradation of free amino acid present in the sample. Further it increases at FICCO which may be due to the degradation of higher molecular

weight protein to amino acids. Initial Protein present in the sample was 8228 mg/L which was decreased to 4590 mg/L at the end of FICCO. Thus most of the residual COD may be due to the non-degraded protein molecules. (Fig. 12)

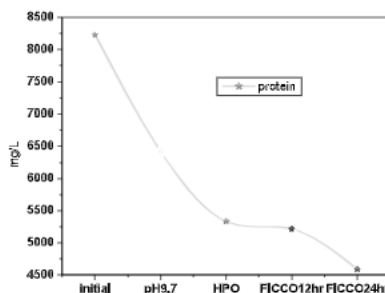
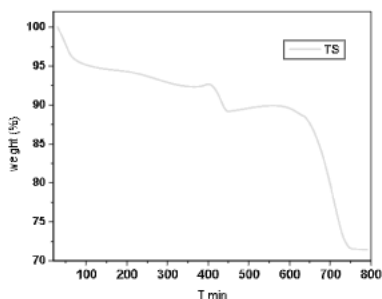


Fig. 12 Removal of protein during treatment processes.

VIII INSTRUMENTAL ANALYSES

(a) Thermo gravimetric analysis (TGA) and UV-Visible spectroscopic studies



Initial sample was dried using Nitrogen Evaporator at 80°C using nitrogen gas and analyzed using TGA from 30°C to 800°C at 5°C/min. It was found that decrease in weight of 28.45% was due to the presence of organic molecules.

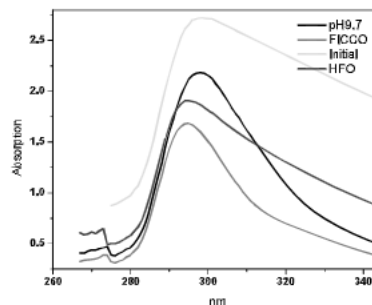


Fig.13 (a) TGA spectrum for Total solids (b) UV-Visible spectrum for the treatment system

UV-Visible spectrum of sample taken out for all processes it was observed that intensity and blue shift found on all processes. Initial sample show characteristic peak at 300 nm it was shifted gradually accordance with treatment process shows removal of organic pollutant taking place by treatment process.

(b) FT-IR spectroscopic studies

FT-IR spectrum of the initial sample and final sample were taken shown in fig No. sample was taken and dried using Nitrogen evaporator at 80°C then analyzed FT-IR spectroscopy.

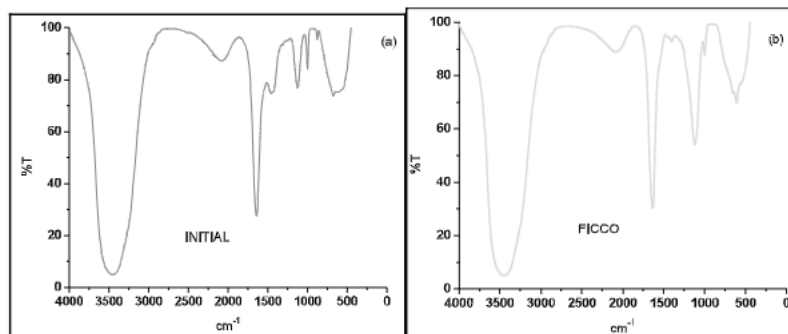


Fig .14 FT-IR spectrum of (a) Initial and (b) final treated lime sulfide water sample

A broad peak at 3460 cm^{-1} conforms the presence of -OH stretch, then at 1638 cm^{-1} sharp peak due to the sec. amide stretch, at 1450 cm^{-1} due to the presence of Aromatic C-C stretching, at 1122 cm^{-1} due to the hydronium sulfonate salts, at 673 cm^{-1} by C-S stretching frequency, at 1453 cm^{-1} due to the Stretching frequency of sulphate salt, at 999 cm^{-1} due to the stretching frequency of S-O-C molecule. When we compare from initial to final some of the peaks shift were observed the above figure shows a broad peak at 3460 cm^{-1} due to -OH stretch, at 1638 cm^{-1} sharp peak due to -sec. amide stretch, at 1405 cm^{-1} due to -Aromatic C-C stretching, at 1120 cm^{-1} due to hydronium sulfonate salts, at 673 cm^{-1} C-S stretching, at 1453 cm^{-1} Stretching frequency of sulphate, at 1000 due to the -S-O-C stretching frequencies were observed.

IX CONCLUSION

Treatment of sulfide laden wastewater processed using Heterogeneous peroxide oxidation (HPO) flowed by FICCO. In HPO, the sample was catalytically oxidized using 0.4 ml of 30% $\text{H}_2\text{O}_2/\text{L}$ (optimized) and 30 g/L NPAC. During the oxidation process high foam produced because of presence of high protein content in the wastewater at end of the process this foaming reduced well due to the removal of protein which was also confirmed using protein and amino acid estimation. With these treatments 66.66% of COD and sulfide (major problem) was eliminated 98.95% with the considerable removal of TOC, TKN and increasing of NH_3 . The ORP of the wastewater remains in negative showed still the presence of some of the reduced species.

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