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Tannery Waste Water Treatment: A Review

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ABSTRACT
The transformation of hides into leather is usually done by using tanning agents and a highly turbid, colored and foul smelling wastewater is generated in the process. The major components of the effluent include sulphide, chromium, volatile organic compounds, large quantities of solid waste, suspended solids like animal hair and trimmings. The various components present in the effluent affect human beings, agriculture and livestock besides causing severe ailments to the tannery workers. The environmental protection regulations stipulate that industries be not allowed to emit sulphide and chromium in the wastewater. Thus, removal of sulphide and chromium from the wastewater is very important. A number of researchers worked on the removal of sulphide and chromium from the wastewater streams, but little has been reported on the sulphide, chrome and other toxic components removal from the tannery wastewater. In this review, characteristics of tannery wastewater and methods tannery wastewater treatment have been discussed.
Key words: *Tannery, Hexavalent Chromium,Wastewater, Chemical, Biological, Physical*

1. INTRODUCTION

Tanning is the chemical process that converts animal hides and skin into leather and related products. The transformation of hides into leather is usually done by means of tanning agents and the process generates highly turbid, colored and foul smelling waste water [1]. The major components of the effluent include sulphide, chromium, volatile organic compounds, large quantities of solid waste, suspended solids like animal hair and trimmings [2]. For every kilogram of hides processed, 30 litters of effluent is generated and the total quantity of effluent discharged by Indian industries is about 50,000 m^3 /day. The various components present in the effluent affect human beings, agriculture and livestock besides causing severe ailments to the tannery workers such as eye diseases, skin irritations, kidney failure and gastrointestinal problems [3].

Tannery waste material also varies considerably in volume and concentration due to continuous operation and intermittent discharge. Sulphide is one of the major 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 [4]. It is highly toxic to human beings. 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 on 800–1000 mg/L, and instant death at higher concentrations [5]. The upper concentration [2] limit of sulphide in water intended for human consumption is 250 mg/L. The corrosive properties of sulphide are apparent in the damage done to concrete walls of reactors, sewer systems and steel pipelines. It also inhibits the methanol genesis process [6.7]. Soluble sulphide ranging from50 – 100 mg/L can be tolerated in anaerobic treatment with little or no acclimate ion [8].Sulphide has high oxygen demand of 2 moles O_2/mol sulphide and causes depletion of oxygen in water [9].

Chromium salts used during the tanning process generate two forms of chrome; Hexavalent chromium and trivalent chromium. Hexavalent chromium is highly toxic to living organisms even at low concentration causing carcinogenic effect [3]. Trivalent chromium may be present in the waste or can be produced from the Hexavalent chromium by chemical treatment. Soluble trivalent chromium causes toxicity in anaerobic digestion due to the accumulation of the metal in the intracellular fraction of biomass [2]. Several components in the effluent contain nitrogen as part of the chemical structure, which can lead to development of anaerobic conditions harmful to the aquatic life. The environmental protection regulations stipulate that industries are not allowed to emit sulphide and chromium in the wastewater. Thus, removal of sulphide and chromium from the wastewater is very important. A number of researchers worked on the removal of sulphide and chromium from the wastewater streams, but little has been reported on the sulphide removal from the tannery wastewater [2]

Manufacturing of leather, leather goods, leather boards and fur produces numerous by-products, solid wastes, high amounts of wastewater containing different loads of pollutants and emissions into the air. The uncontrolled release of tannery effluents to natural water bodies increases health risks for human beings and environmental pollution. Effluents from raw hide processing tanneries, which produce wet blue, crust leather or finished leather, contain compounds of trivalent chromium (Cr (III)) and sulphides in most cases. Organic and other ingredients are responsible for high BOD (Biological Oxygen Demand) and COD (Chemical Oxygen Demand) values and represent an immense pollution load, causing technical problems, sophisticated technologies and high costs in concern with effluent treatment [3].

2. LITERATURE REVIEW

2.1 Manufacturing of leather

The manufacturing of leather can be divided into two parts; beam house operations and tanning process. In beam house operations, the removal of dirt and blood by washing is the first step after which the hides are then soaked in water for softening and removal of salts. After the removal of salts, fatty tissue is removed by fleshing. Liming is done to swell the hides for the better penetration of tanning agents and hair removal. Chemical dissolution of the hair and epidermis with an alkaline medium of sulphide and lime takes place. During liming, a high concentration of sodium sulphide, lime and organic matter is delivered to the effluent [1]. Hides are then neutralized with acid ammonium salts and treated with enzymes to remove the hair remnants and to degrade proteins. This results in a major part of the ammonium load in the effluent. Pickling is usually done to prepare the hides for tanning. The pH value of hides is adjusted by addition of acids (main sulphuric acid). Salts are added to prevent the hides from swelling. Tanning is the reaction of the collagen fibres in the hides with tannins, chromium, alum or other chemical agents. Alums, syntans, formaldehyde, glutaraldehyde and heavy oils are used as tanning agents. During the tanning process, about 300 kg chemicals are added per ton of hides. Based on the tanning agents, tanning operations are further divided in to vegetable tanning and chrome tanning. Vegetable tanning is usually done in series of vats by using natural organic substances [2, 3].

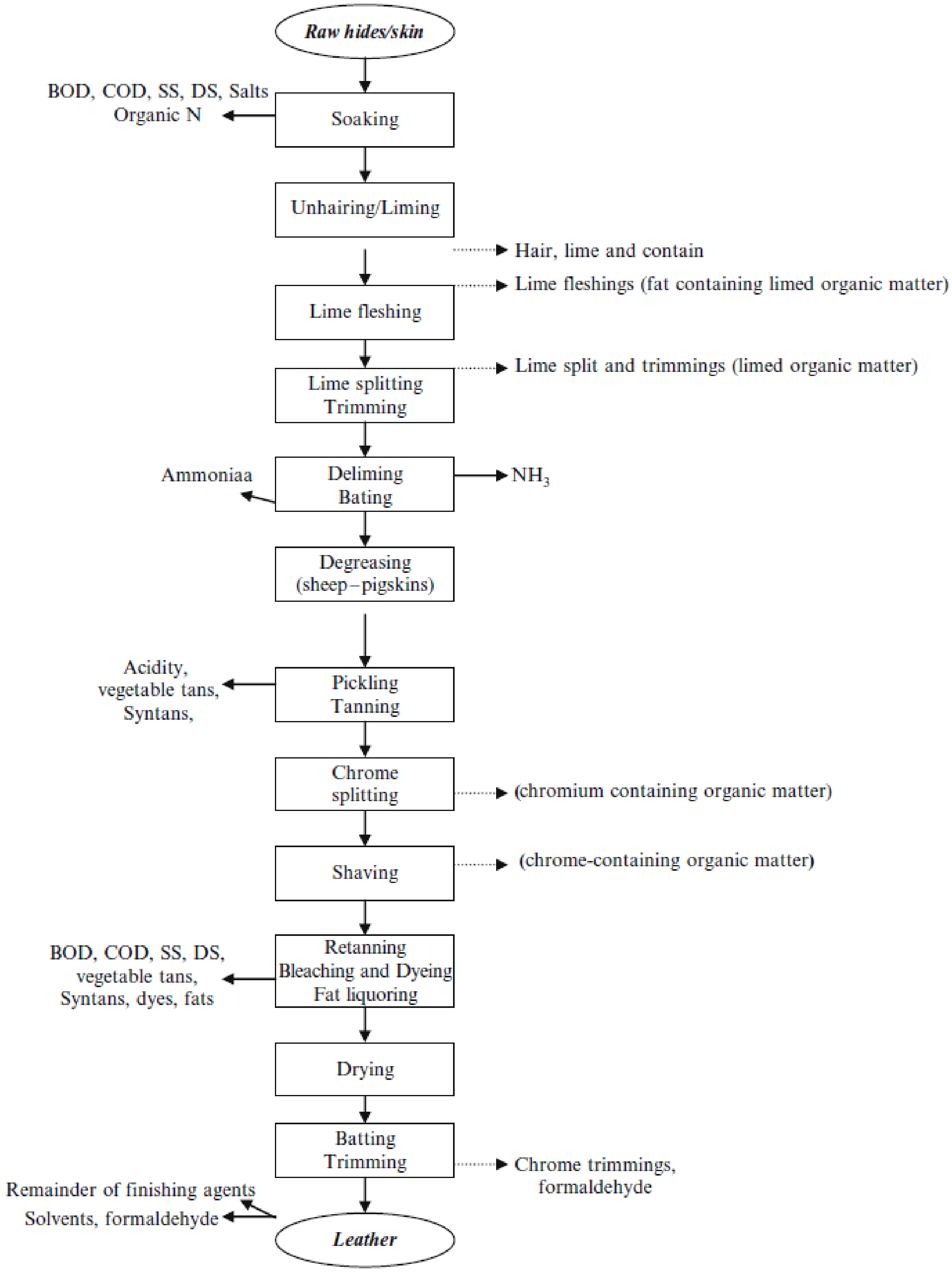

Fig. 1: Manufacturing of leather

Chrome tanning is done at a higher pH using chromium salts. After tanning, tanned leather is piled down, wrung and graded for thickness and quality, split into flesh and grain layers and shaved to desired thickness. In chrome tanning, retaining, dyeing and fat liquoring are the additional steps as compared to the vegetable tanning. Fat liquoring is the process of introducing oil into the skin before the leather is dried to replace the natural oils lost in beam house and tan yard processes. After drying, a number of finishing operations like buffing, plating and embossing are carried out to make the leather softer and aesthetic[8].

In the tanning industry leather processing involves conversion of put rescible hide or skin into leather. Tanning agents could help permanent stabilization of the skin matrix against biodegradation. This industry has gained a negative image in society with respect to its pollution potential and therefore is facing a severe challenge. The unit processes that cause tanneries the most difficult with regard to perceived environmental impact are unharing and chrome tanning. Basic chromium sulfate (BCS) is a tanning agent, which is employed by 90%of the tanning industry. Conventional chrome tanning results in wastewater containing as high as 1500−3000ppm (parts per million) of chromium; however, the present day high-exhaust chrome tanning methods lead to a wastewater containing 500−1000 ppm of chromium. But, the discharge limits for trivalent chromium vary broadly ranging from 1 to 5 mg/l in the case of direct discharge into water bodies and 1 to 20 mg/l in the case of discharge into the public sewer system [10]

2.2 Tannery Wastewater treatment methods

One of the emerging problems faced by the world today is management of all types of wastes and energy crisis. Rapid growth of population and unhampered and unmonitored urbanization has created serious problems of energy requirement and solid waste disposal. tannery wastes cause to a great amount of pollution; hence, there has been a strong need for appropriate tannery waste management systems. Tannery wastes that consist of high fraction of appreciable organic matter cause serious environmental and health risks [11].

Tannery waste water effluent is treated in many different ways. There are situations in which an individual tannery applies all the below described wastewater treatment steps on site. In an individual tannery may apply only pre-treatment or a part pre-treatment or no treatment at all, sending the effluent to a centralist effluent treatment plant .Nevertheless, a treatment is necessary due to the wide range of toxic effluents and sludges [2].The following stapes are necessary and will be described in more detail after wards.

2.2.1 Biological wastewater treatment

Various physiochemical techniques used for wastewater treatment can be applied to tannery wastewater (to the entire process or to individual step in the process) but these processes are expensive. Biological treatment of wastewater is more favourable and cost effective as compared to other physiochemical methods. Various microorganisms are capable of reducing the content of pollutants significantly by utilizing them as energy and nutrient source in the presence or absence of oxygen [1] 2].

Biological treatment is evaluated as a good treatment method of industrial effluents. tretment of wast with bacteria involves the stabilization of wastes by decomposing them into harmless inorganic solids either by aerobic or in anaerobic process. in aerobic process the d decomposing rate is more rapid than the anaerobic process and it is not accompianed by un pleasant odours, where as in anaerobic process longer detection period is required and gives un pleasant odours [1, 2].

Aerobic Treatment

Aerobic microorganisms use organic carbon in the effluent and convert it to biomass and carbon dioxide. A large amount of sludge is generated along with high energy consumption the process. Aerobic treatment of tannery wastewater reduces chemical oxygen demand (COD) by 60-80% and biological oxygen demand (BOD) reduction is 95%, when combined with physicochemical pre-treatment [2].

In a combined biochemical oxidation and chemical coronation step, chemical oxygen demand (COD), total nitrogen (TN) and total suspended solids (TSS) removals of 96%, 92%

and 98%, respectively were obtained. Ozonisation step was integrated with sequencing batch bio film reactor. Ozonisation partially oxidizes there fractory compounds present in tannery wastewater and increases their biodegradability [2].Sludge production was 0.1 kg VSS/ kg COD removed, which is lower than the value reported in the literature for conventional biological systems. Aerobic treatment followed by chemical ozonisation and again aerobic treatment further increases the biodegrability of refractory compounds [3].

A combination of electrochemical and biological treatment can also be used to eliminate ammonia and avoid implementation of biological nitrification. Respirometry combined with sequencing batch reactor is an effective method for the removal of COD in tannery effluent. At 12 h sequencing batch reactor cycle with a loading rate of 1.9-2.1 kg/m3 day, removals of COD, TKN and NH3-N were 80-82%, 78-80% and 83-99%, respectively. The removal efficiencies were much higher than conventional aerobic systems [2].

Anaerobic treatment

Anaerobic treatment of wastewater converts the organic pollutants into a small amount of sludge and large amount of biogas (methane and carbon dioxide).The sulphide present in wastewater inhibits the anaerobic treatment. Methanogenic bacteria are inhibited by sulphide, whereas acidifying and sulphate reducing bacteria do not inhibit. Three inhibiting effects of sulphide or sulphide reduction are known: direct toxicity of sulphide, substrate competition between sulphate reducing and Methanogenic bacteria and precipitation of trace elements by sulphide. The extent of these effects depends on the experimental system used. In a continuous fixed film reactor, the efficiency of degradation was improved by 15% ata hydraulic retention time of 1.9 days when the concentration of undissociated sulphide was reduced from 100 to 30 mg/L[7].

The Advantage and Disadvantage Anaerobic treatments are Removal of sulphate, sulphite and thiosulphate forme the waste stream, Heavy Metal removal Precipitated metal sulphides and Reduce COD removal efficiency, Corrosion, Less methane formation respectively [9].

In two stage anaerobic treatment of tannery wastewater, 30% of the sulphate was reduced independent of the sulphate influent concentration in the first stage. With high concentration of sulphate in influent, percentage of desulfurization decreased in the second stage. Pre treatment of wastewater for reducing the tanning chromium and sulphide levels gives better results in COD removal efficiency. In anaerobic up flow contact filter, COD removal efficiency was in the range of 79-95% after pre treatment compared to 60-86% for untreated wastewater. [2].

2.2.2 Chemical wastewater treatment

Chemical waste water treatment is an individual process that is employed to remove substance and bacteria’s from raw sewage and rain water runoff waste water treatment facilities filter used dirty water , so that it can be recycled back in to natural artificial water sources . Numerous chemicals are used in different phase of the filtration process to separate out solids, kill bacteria and parasites’ and remove dangerous toxins. Chemical compounds of ferric cheloride, alum, ozone, chlorine and lime help to purify even the most polluted concentrations of sewage .after waste water has been filtered disinfected and neutralized ,it no longer poses an environmental treat [4].

The important chemical waste water treatment technique involves neutralizing the acid content of the water. Pure water is demand natural on the pH scale, which a measure of seven .Acidic waste water typically has a pH value lower than seven. And most be made more basic through chemical processes. Vary specific amount of basic chemicals are added to acidic tanks in order to naturalize the contents .Lime is the most commonly used base, as it is easy for specialists to measure.

Chemical oxidation method

Chemical oxidation allows in general complete elimination of the principal organic pollutants but complete removal of total organic carbon is more difficult .The oxidation of phenol with a power full oxidant such as ozone allows only a 30; total organic carbon removes similar level of total organic carbon removal are obtained using H_2O_2 at room temperature [4].

Ozonisation

Ozone is a gas at normal presser and tempreatur .Its solubility in water is function of its partial pressur and temperature. Ozon is generated by high voltage discharge in air and oxygen. Ozone is unable and to tends to react to form [6]

$$O_3 + H^+ + e^- \longrightarrow O_2 + H_2O$$

Ozone is a very strong oxidizing agent and it is very effective as a decolouration agent and as oxidant of organic material.

Electro chemical method

Electro chemical oxidation has been reported to be have in similar way .we have demonstrated that the total organic carbon (TOC) Removal obtained by the electro chemical oxidation at a platinum anode is higher than that obtained by chemical oxidation. This higher Toc removal using electro chemical oxidation has been attributed to the oxidation of adsorbed organic compounds to carbon dioxide [7].

2.2.3 Physical waste water treatment

A physical waste water treatment process does not add any chemical components or biological material to treat .The water can be screened to filter out large object. It can also treated by means of sedimentation, during which solids settle to the bottom under the effluence of gravity .Water that is free of can be then be remove. Other physical process includes the addition air to provide oxygen within the waste water and the water can also be passed through filter to get rid of solid material. There are three method of physical waste water treatment [8]. these are Mechanical treatment, Effluent treatment, Post-purification, and sedimentation a Sludge handling.

Mechanical treatment

Usually the first treatment of the raw effluent is the mechanical treatment that Includes screening to remove coarse material. Up to 30-40% of gross suspended solids in the raw waste stream can be removed by properly designed screens. Mechanical treatment may also include skimming of fats, grease, oils and gravity settling [3].

Effluent treatment

In order to carry out effluent treatment in the most effective manner, flow segregation is useful to allow preliminary treatment of concentrated wastewater streams, in particular for sulphide- and chrome-containing liquors. And although a reduction of water consumption does not reduce the load of many pollutants, concentrated effluents are often easier and more efficient to treat. Where segregation of flows is possible, thorough mixing of chrome-bearing effluents and other effluent streams improves the efficiency of the effluent treatment plant because the chromium tends to precipitate out with the protein during pre-treatment [2].

Post-purification, sedimentation and sludge handling

Post-purification, sedimentation and sludge handling are the last step in wastewater from the water phase by gravity settlement. After dewatering this sludge by means of filter presses, a sludge cake with up to 40% dry solids can be achieved, whereas belt presses produce a sludge cake with up to 20-25% dry solids [3,10].

3. CONCLUSION

Tannery wastewater is difficult to treat because of complex characteristics like high BOD, COD, suspended solids, sulphide and chromium. The main source of sulphide in tannery effluent is beam house operations. Anaerobic treatment of tannery wastewater gives better results but formation of sulphide in anaerobic reactors restricts its application. Various phototrophic and chemotropic have been used for sulphide removal but requirement of light source is the major problem in case of phototrophic. Chemotrophes require careful control of oxygen to produce sulphur instead of sulphate but still some sulphate formation is there.

Biological treatment method is better choice for removal of colour and organic contentes: however, some of the questions are needs chemical and physical methods depends on the process efficiency. This review shows that integrated application of combined process of physical or chemical with the biological process to treat tannery wastewater would give satisfactory results compared to individual treatment processes.

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