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**REVIEW**

# Treatment of Tannery Wastewater by Various Oxidation and Combined Processes

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**ABSTRACT:** A general overview on the prospective of various oxidation and combined processes in the treatment of tannery industry effluent are reported. Various oxidation and combined processes such as UV/$H_2O_2$/Hypochlorites, Fenton and Electro-oxidation, photo-chemical, photo-catalytic, electro-catalytic oxidation, wet air oxidation, ozonation, biological followed by ozone/UV/ $H_2O_2$, coagulation or electro-coagulation and catalytic treatments have been considered. The tannery wastewater with sulphide as main sources of pollutant, electro-coagulation is the best removal efficiency process among the other oxidation processes, whereas for chromium, photo catalytic oxidation process using nano-$TiO_2$ and wet air oxidation in the presence of manganese sulphate and activated carbon as a catalyst are more efficiency processes. The integrated combined processes described permit to meet disposal limits, health quality standards and the recovery of several chemicals utilized in the tanneries.

**Key words:** Pollution, Chromium, Sulphide, Integrated water

## INTRODUCTION

Treatment of various wastewaters are become more important due to diminishing water resources, increasing wastewater disposal costs, and stricter discharge regulations that have lowered permissible contaminant levels in waste streams (Metcalf and Eddy, 1979; Matsumoto *et al.*, 1992; ESCWA, 2003). Tannery industry is the significant contributor to the economy and provides large scale employment opportunity for people of economically weaker part of the society. Tanning involves a complex combination of mechanical and chemical processes. The general flow sheet for tanning process was given in Fig. 1. The preservation and processing of raw hides and skins for tanning process cause severe pollution problem towards environment and mankind, rather than being important from economic and employment consideration (Aravindhan *et al.*, 2004). The tanning operation in which organic or inorganic materials become more chemically bound to the available substance and preserve it from deterioration. The substances generally used to accomplish the tanning process are chromium or extracts from bark of trees, such as chestnut. Two types of tanning operations based on tanning agents are chrome and vegetable tanning (Sarkar, 1981; Aravindhan *et al.*, 2004). The general process of tanneries are vegetable tanning employs the use of extracts from the bark of various trees as the tanning agent. Mostly leathers are produced by chrome tanning compare to vegetable tanning (Sarkar, 1981). Chrome tanning produces leather better suited for certain applications, particularly for the upper parts of boots and shoes, and requires less processing time than traditional vegetable tanning (Sarkar, 1981).

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The World production of leather product was 22700.5 M $ft^2$/yr (FAO, 2008). Totally, 2500 tanneries are located in India including Tamilnadu 50%, West Bengal 20% and Uttar Pradesh 15% (CPCB, 2009). In India, the production of leather product was 1738 M $ft^2$/yr (FAO, 2008). The characteristics of tannery effluent vary considerably from tannery to tannery depending upon the size of the tannery, chemicals used for a specific process, amount of water used and type of final product produced by a tannery effluent from a typical tannery. Wastewater from the tannery industry contains large quantities of biochemical oxygen demand (BOD), chemical oxygen demand (COD), sodium sulphide and suspended solids (SS) from the tannery process (Unick *et al.*, 1981; Abdel-Shafy et al, 1995; Vijayaraghavan and Murthy, 1997; Iqbal *et al.*, 1998; Szpyrkowicz *et al.*, 2001). Some of tannery wastewater characteristics are given in Table 1.

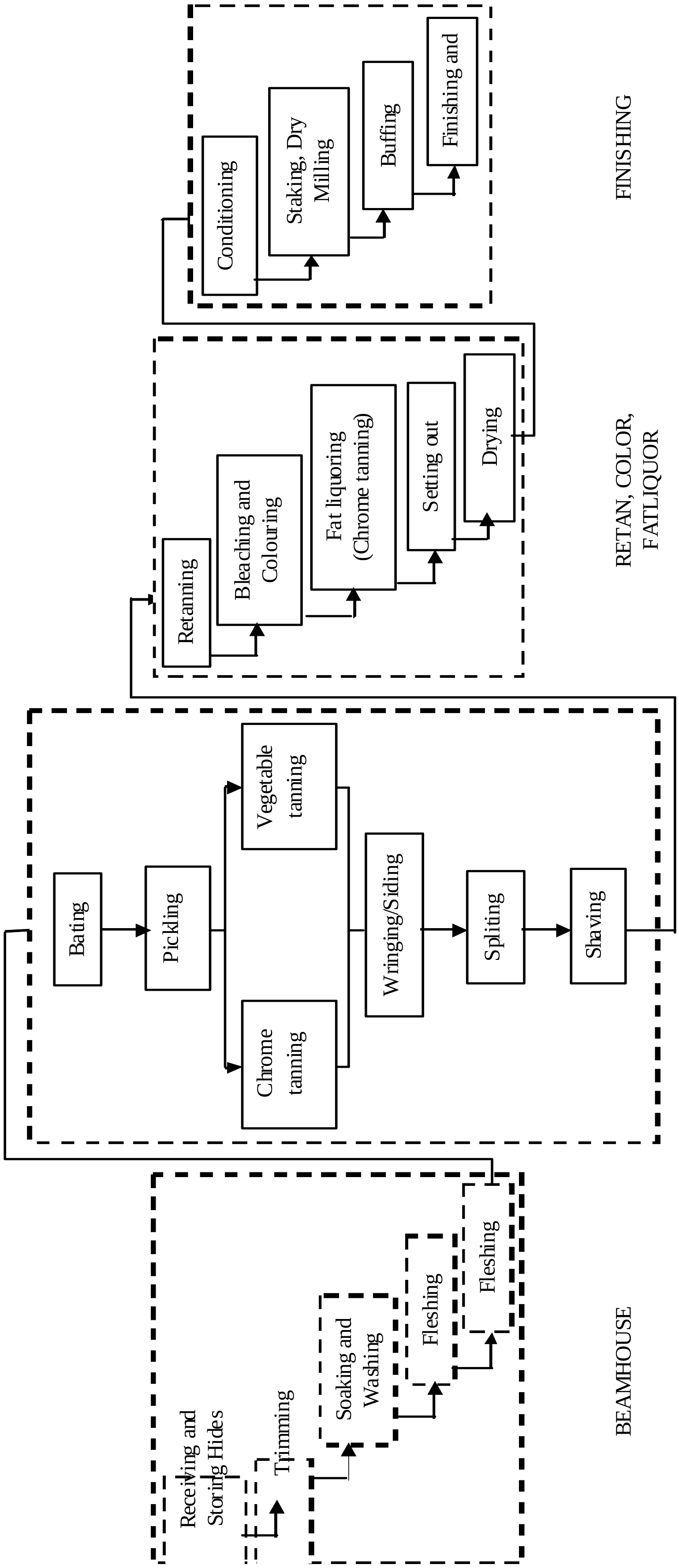


**Fig. 1. General flow diagram for leather tanning and finishing process**

**Table 1. Characteristics of different types of tannery wastewater**

| | Vijayaraghavan and Murthy (1997)* | | Iqbal et al. (1998)* | Szpyrkowicz et al. (2001)* |
|---|---|---|---|---|
| Types of tannery process | Vegetable | Chrome | Chrome | Chrome |
| COD | 19700 | 20000 | 1187-2794 | 561-1450 |
| TN | - | - | 34-312 | - |
| $N-NH_4^+$ | - | - | 18-157 | 207.5-350 |
| Phenols | - | - | 45-282 | - |
| pH | 7.3 | 3.5 | 6.6-8.1 | 5.46-8.9 |
| $Cl^-$ | 1697 | 1728 | 1890-4810 | 5383 |
| $S^-$ | 195 | 150 | 3-80 | 32-192 |
| TSS | - | - | 130-1240 | - |
| VSS | - | - | 217-1030 | - |
| Chromium | - | 178 | - | 1.3 |
| Tannin | 2900 | 1700 | - | 23.9-83.7 |
| TKN | - | - | - | 244.8-418.9 |
| TOC | - | - | - | 131-425 |

* All are mg/l unit except pH

In India, especially, Kanpur tannery industry polluted the environment. In 2003 the main tanneries effluent disposal unit was dumping 22 tonnes of Chromium laden solid waste per day. In tannery industry, effluents are produced upto 64 kilo tonnes of wastewater per year (Trujillo *et al.*, 2008). Conventional chrome tanning results in wastewater containing at high as 1500-3000 mg/l of chromium (Suresh *et al.*, 2001; Aravindhan *et al.*, 2004). The tanning industry is an especially large contributor of chromium pollution in India (Sarkar, 1981; Ramasami *et al.*, 1995). It was estimated that in India alone, ~ 2000–3000 tonnes of chromium escape into environment annually from the tanning industries, with chromium concentration ranging between 2000 and 5000 mg/l in the aqueous effluent, compared to the recommended permissible limit of 2 mg/l (EPA, 1990). Chromium has low acute and chronic toxicity to humans at high doses (Aravindhan *et al.*, 2004). Chromium toxicity is dependent on chemical speciation and thus associated health effects are influenced by chemical forms of exposure. Cr (VI) compounds are much more soluble than Cr (III) and are much more toxic (mutagenic and carcinogenic) to microorganisms, plants, animals and humans (Friberg *et al.*, 1980; Aravindhan *et al.*, 2004). The excess of Cr (III) is proven to be a potential soil, surface water, ground water and air contaminant under specific condition (Rao *et al.*, 1999; Aravindhan *et al.*, 2004). The number of tanneries in the United States has significantly decreased in the last 40 years due to the development of synthetic substitutes for leather, increased leather imports, and environmental regulation (EPA, 1990; Bienkiewicz, 1983). The potential environmental standards for tannery effluents given by agencies were pH levels from 6.5 to 9, chromium value, sulphides and oil & grease in the wastewater should be less than 2 mg/l, 1 mg/l and 10 mg/l respectively, $BOD_3$, SS leaves from a tannery should be less than 100 mg/l and the wastewater generation 28 $m^3$/tonne quantum per raw hide processed (EPA, 1990).

Wastewater treatment methods are broadly classified into physical, chemical and biological processes (Metcalf and Eddy, 1979; Matsumoto *et al.*, 1992). Various treatment for tannery wastewater like physico-chemical methods such as sedimentation (Song *et al.*, 2000), Electro floatation (Murugananthan *et al.*, 2004), Filtration (Cassano *et al.*, 1999; Tiglyene *et al.*, 2008) and Membrane filtration (Justina *et al.*, 2009), Precipitation (Kabdasli *et al.*, 2003; Esmaeili *et al.*, 2005) and Coagulation (Jing-Wei *et al.*, 2007; Haydar *et al.*, 2009; Zhi *et al.*, 2009; Espinoza-Quinones *et al.*, 2009; Sengil *et al.*, 2009), Adsorption (Santosa *et al.*, 2008; Covarrubias *et al.*, 2008), Ion exchange (Tiravanti *et al.*, 1997; Kabir and Ogbeide, 2008) and Biological methods such as (Martinez *et al.*, 2003; Farabegoli *et al.*, 2004; Murat *et al.*, 2006; Lefebvre *et al.*, 2006; Banu and Kaliappan, 2007; Munz *et al.*, 2008; Munz *et al.*, 2009; Zupancic and Jemec, 2010).

Schrank et al. (2004) has suggested that many organic compounds contained in wastewater are resistant to conventional chemical and/or biological treatment. The degradation of inhibitor substance such as tannin during the anaerobic digestion was investigated by Banu and Kaliappan (2007).

Polyelectrolyte precipitation was not yield satisfactory results for the treatment of leather tanning industry wastewaters (Kabdasli *et al.*, 2003). Generally, tannery effluents contain mostly sodium sulphide and (or) sodium hydrosulphide (EPA, 1990; Valeika *et al.*, 2006) which has significantly contributing for environmental pollution. 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 process can be carried out only when concentration of sulphides 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 sulfide concentration present in treated wastewater may not suitable for aerobic biological treatment. Sankar et al. (1998) and Yoochatchaval et al. (2008) has reported that a cost effective method was needed to remove the residual organics in biological treated wastewater as it received public attention from the neighborhood of discharge.

The choice of wastewater treatment process depends on several factors like efficiency, cost and environmental capability (Costa and Olivi, 2009). Moreover, the wastewater characteristics should also be considered when choosing the best process (Costa and Olivi, 2009). Few authors have previously reviewed the various techniques for treatment of tannery wastewater (Cassano *et al.*, 2001; Aravindhan *et al.*, 2004; Sharma *et al.*, 2008). Mostly, the sulphides are removed by using $H_2O_2$ and Electro oxidation process (Valeika *et al.*, 2006; Anglada *et al.*, 2009). Oxidation of sulfide by air using activated carbon as catalyst gained importance for its removal of COD, BOD and TOC in addition to elimination of sulfide in wastewater (Sekaran *et al.*, 1996). So, in this context, the tannery industry is review various oxidation and combined processes for the recovery and recycle of chemicals and water in order to avoid discharging of these products into the environment.

Tannery effluents are oxidized by four different reagents like ozone, hydrogen peroxide, Fenton oxygen, and air, in precise, pre-programmed dosages, sequences UV radiation. These procedures may also be combined with any one of oxidation process or agents are known as advanced oxidation process (AOP). The AOP procedure is particularly useful for cleaning biologically toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents, and volatile organic compounds in wastewater (Metcalf and Eddy, 1979; Matsumoto *et al.*, 1992). The contaminant materials are converted to a large extent into stable inorganic compounds such as water, carbon dioxide and salts, i.e. they undergo mineralization. Table 2 . lists out the various types of studies performed for treatment of tannery wastewater by various oxidation processes.

A search of the ISI web of knowledge shows a number of research articles on oxidation and combined process on treatment of tannery wastewater. Fig s 2 and 3 shows the yearly progress of publications and citations in the late twentieth century and during the present decade. These figures clearly indicate the increasing in the area of various oxidation and combined process to treat the tannery wastewater. Results of the investigation on treatment of tannery wastewater by various oxidation and combined processes have been reported in this study.

The various oxidation techniques (UV, $TiO_2$/UV, $O_3$, $H_2O_2$/UV and $O_3$/UV) to degrade tannery wastewater were reported by Schrank et al. (2004). The removal efficiency of COD, TOC, ammonia and sulphate were found to be 3%, 8.5%, 10% and 6% respectively by $TiO_2$/UV process at pH 7. In the $H_2O_2$/UV treatment, the COD removal was 60% in 4 h as a reaction time (Sauer *et al.*, 2006). *Artemia salina* (Dantaset *et al.*, 2003; Sauer *et al.*, 2006) and *Daphnia magna* (Schrank *et al.*, 2004) toxicity testing performed in parallel proved a decrease in toxicity after treatment of the tannery wastewater. Awan et al. (2003) was analysed that the recovery of chromium from tannery wastewater by $H_2O_2$, sodium hypochlorite and calcium hypochlorite oxidants to soluble chromate. $H_2O_2$ was potentially a suitable oxidant as it could oxidize a suspension of Cr $(OH)_3$ to chromate to 98% and 88% in the synthetic and real wastewater. Awan et al. (2003) and Sauer et al. (2006) were observed that degradation rate of tannery pollutants increased as the $H_2O_2$ increased, but excessive $H_2O_2$ concentration was harmful because it acted as a hydroxyl radical forager since it can contend for the active sites of the $TiO_2$. The percentage removal by the hypochlorites was lower than $H_2O_2$ (Awan *et al.*, 2003). Calcium hypochlorite was potentially a suitable oxidant as it COD removal was 76% (Awan *et al.*, 2004) when initial COD was 3413 mg/l in the tannery wastewater. Chlorine dioxide was used to removed the benzidine pollutants from tannery dyeing wastewater (~90%) (Cao *et al.*, 2007). Dantas et al. (2003) was evaluated that the efficiency of Fenton and Photo-Fenton processes for the treatment of wastewater from leather industry. 90% of COD removal was achieved in 4 h. The concentration of hydroxyl radicals (•OH) increases as increase in the

**Table 2. Some of Literature review for optimum conditions of Tannery wastewater treatment by various oxidation processes**

| Type of Oxidation process | Pollutants | Optimum conditions | References |
|---|---|---|---|
| Catalytic oxidation ($MgSO_4$ or $NiSO_4$) | Sulphide | Air flow rate = 0.8 l/min; Aeration time = 450 min; $MgSO_4$ conc. = 270 mg/l; $NiSO_4$ conc. = 260 mg/l | Mesdaghinia et al. (1991) |
| Electro-oxidation | Sulphides, Chromium | Anode: Ti/Pt; Cathode: Ti; Current density = 5.56 A /dm$^2$ | Rao et al. (2001) |
| Fenton-photo Fenton process (fast and slow process) | COD | Ferrous ions =1 g/l; Hydrogen peroxide = 15 g/l; Time = 20 and 240 min | Dantas et al. (2003) |
| Hydrogen peroxide | Chromium | Time = 5 min; Temperature = 100 $^oC$ | Awan et al. (2003) |
| $TiO_2$/UV | COD, TOC, $NH_4^+$, $SO_4^{2-}$ | Ozone dosage = 2.6 g $O_3$ /h; pH = 7 | Schrank et al. (2004) |
| $O_3$/UV | COD, TOC, $NH_4^+$, $SO_4^{2-}$ | Ozone dosage = 2.6 g $O_3$/h; pH = 11 | Schrank et al. (2004) |
| Electro oxidation | COD, Color | Ti/$PbO_2$; Ti/Ti$RuO_2$ | Panizza et al. (2004) |
| Hydrogen peroxide | COD | Oxidant = Calcium Hypochloride; Time = 5 min; Temperature = 100 $^oC$ | Awan et al. (2004) |
| Photo oxidation | COD, Chromium | Nano-$TiO_2$ dosage = 100 mg/l; pH = 6; Radiation time = 480 min | Shi et al. (2006) |
| Photo oxidation | COD, Chromium | Time = 6 h; $FeCl_3$ dosage = 3.36 mg/l; nano-$TiO_2$ dosage = 100 mg/l | Yajun et al. (2006) |
| Fenton photo Fenton process | COD | $H_2O_2$ dose = 840, 1679 mg/l; pH = 3,5; Reaction time = 90 min | Kurt et al. (2007) |
| Electro oxidation | COD, TOC | Current = 2.8 A; pH = 3.25; Electrolysis time = 60 min, Ti-Pt electrode | Ouejhani et al. (2008) |
| Electro coagulation and Electro fenton | COD and sulphide | Electric current = 33.3 mA /m$^{2;}$ Electricity consumption = 1.8 and 1.5 kWh/kg COD removed; 27.7 and 8.3 kWh/kg sulphide removed | Apaydin et al. (2008) |
| Ozonation | COD | Ozone flow rate = $6 \times 10^{-3}$ $m^3$/min; Ozonation time = 60 min; pH = 11 | Preeti et al. (2009) |
| Photo oxidation | Chromium and Leather | Sodium sulphate = 0.1 mol/l; Nanoporous Ti/$TiO_2$ electrode; pH = 2 | Paschoal et al. (2009) |

removal efficiency was observed, either before or after coagulation. The reduction of ammonia nitrogen amount for both processes not significant different was observed, because of attributed to the oxidation of nitrogen organic compounds, possibly forming $N_2$ and nitrate ions (Dantas *et al.,* 2003).

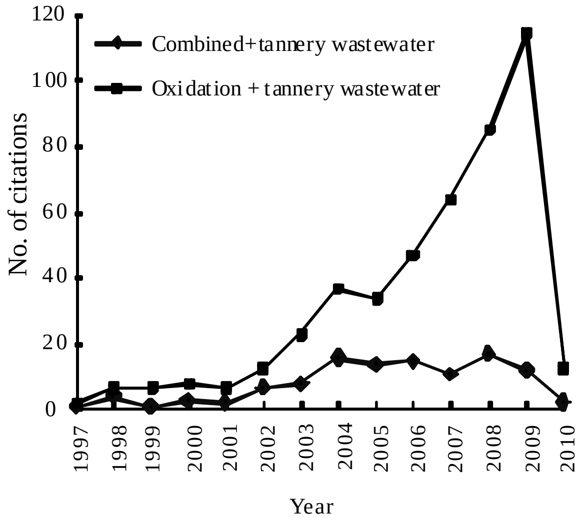


**Fig. 2. Number of citations appearing with 'Oxidation', '*Combined*' and *Tannery wastewater* in the topic as listed in the ISI Web of Science database for 'All Years' (1983–2010) (out of a total of 461 and 113 articles appearing: database searched 23.03.10). Note that early adsorption articles appeared in the late 1997s. The small number of papers in pre-1996 years means they cannot be properly shown in the figure**

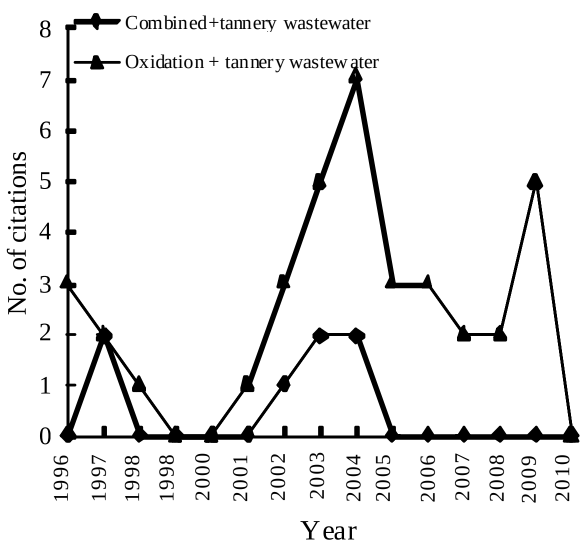


**Fig. 3. Number of research papers appearing with 'Oxidation', '*Combined*' and *Tannery wastewater* in the topic as listed in the ISI Web of Science database for 'All Years' (1983–2010) (out of a total of 38 and 7 articles appearing: database searched 23.03.10). Note that early adsorption articles appeared in the late 1990s. The small number of papers in pre-1989 years means they cannot be properly shown in the figure**

Various types of electrodes like 3D (Rao *et al.,* 2009) and graphite electrode (Vijayalakshmi *et al.,* 2009) was used for oxidation of tannery wastewater by electrochemical treatment. Application of noble metals and metal oxides electrodes for treatment of tannery wastewater (Szpyrkowicz *et al.,* 2005). Marco et al. (2004) and Rao et al. (2001) found that electro oxidation method can be applied effectively for were vegetable tannery wastewater, allowing the complete removal of COD, tannin, and ammonium and decolourization. For example, the removal of chromium and sulphides was found to be 76% and 88% respectively and the energy consumption was 5.77 kWh/kg COD and 16.63 kWh/kg of $NH_4^+$ in a two-electrode stirred batch reactor. The order of efficiency of anodes was found to be Ti/Pt > Ti/$PbO_2$ > Ti/$MnO_2$ (Rao *et al.,* 2001). Szpyrkowicz et al. (2005) showed highest rate of ammonia removal was achieved while compared with other conventional electrodes. The reduction in TKN, protein and COD was 78.52%, 83.02% and 79.35% respectively and complete disinfection was also achieved (Vijayalakshmi *et al.,* 2009). In order to estimate the optimum conditions, some design methodology has been applied for treatment of tannery wastewater. A Doehlert design was used to optimize the significant experimental variables temperature, pH, current intensity and time over yields Cr (III) to Cr (IV) from aqueous and tanning baths effluents reported by Ouejhani et al. (2008). The results have shown that the current intensity and the electrolysis time were the main influent parameters on the removal ratio of COD, TOC and electrochemical oxidation of trivalent chromium. Another study was also shown by increasing the rate of oxidation by increasing the current density, pH and temperature of the solution in the presence of Ti/$TiRuO_2$ anode electrode (Marco *et al.,* 2004). Ozonation is a treatment process that destroys bacteria and other microorganisms through an infusion of ozone, a gas produced by subjecting oxygen molecules to high electrical voltages. The COD removal efficiency was 47% achieved even with low feeding time of 5 min at the selected ozone flow-rate of 42.8 mg/min by ozonation process (Dogruel *et al.,* 2004). The COD removal efficiency was 92% achieved by ozonation process (Preeti *et al.,* 2009).

Wet oxidation is the oxidation of dissolved or suspended components in wastewater using oxygen as the oxidizer. It is referred to as 'wet air oxidation', 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 critical point (374° C). Sekaran et al. (1995) was reported that removal of sulphide in limeyard wastewater by wet air oxidation in the presence of manganese sulfate 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. The removal efficiency of sulphide increases to 99% when an activated carbon packed counter current reactor was used. Sankar et al. (1998) and Paschoal et al. (2009) was investigated the feasibility of the photo electrocatalytic oxidation of residual organic and leather acid dye, acid red 151. The photo electrocatalytic oxidation promotes 100% decolourization, reducing around 98-100% of Cr (VI) and achieving an abatement of 95% of the original total organic carbon (Paschoal *et al.*, 2009). The photocatalytic oxidation process using nano-$TiO_2$, the COD and chromium removal was 65% and 91.4% respectively, and the effluent biodegradability was great improved (Yajun *et al.*, 2006). Catalyst may be accelerates the rate of a chemical reaction without itself being consumed. It lowers the operating and or capital costs. The removal of sulphides was $\geq$ 98% by catalytic oxidation (Mesdaghinia *et al.*, 1991).

AOPs, which are very effective in oxidization, decolorization and degradation of organic pollutants. The main drawback of advanced oxidation technologies is their operating cost high as compared to other conventional physicochemical or biological treatments. Therefore AOPs cannot achieve complete mineralization due to this constraint. One of the most reasonable solutions to this problem is coupling AOPs with other treatment methods. Advanced oxidation processes often are employed as a pre-treatment method in an integrated system. This integration is acceptable commercially when intermediates are easily degradable in another process. The various integration AOPs and biological processes has been reviewed (Matsumoto *et al.*, 1992; Scott and Ollis, 1995; Kang and Hoffmann, 1998; Tabrizi and Mehrvar, 2004; Mohajerani *et al.*, 2009).

Physicochemical followed by biological treatment, especially activated sludge or lagoon systems are usual technology for wastewater treatment (Moura Alencar *et al.*, 2004; Mohajerani *et al.*, 2009). Generally these conventional treatments are incapable and donot often reach the limits to reduce all of the polluting parameters, COD, chlorides, sulphates and ammonia (Molinari *et al.*, 1997; Molinari *et al.*, 2001; Mohajerani *et al.*, 2009). Table 3. lists out the various types of studies performed for treatment of tannery wastewater by various combined process.

Electro-fenton process, electrocoagulation, electrochemical oxidation and Photo Electro Oxidation – Electro Dialysis (PEO-ED) were studied by various researchers (Apaydin *et al.*, 2009; Kurt *et al.*, 2007; Naumczyk and Rusiniak, 2005). Naumczyk and Rusiniak. (2005) were studied that process of tannery wastewater treatment by electrocoagulation and coagulation with $FeCl_3$ followed by advanced

**Table 3. Some of Literature review for optimum conditions of Tannery wastewater using combined treatment**

| Type of combined treatment | Pollutants | Optimum conditions | Reference |
|---|---|---|---|
| SBBR with Chemical oxidation (ozone) | COD, Ammonia and Suspended solids | Ozone flow rate = 8.7 mg $O_3$/min; Sludge production = 4 kg TSS/kg COD | Iaconi et al. (2002) |
| SBBR process with ozonation | COD, TKN, and TSS | Sludge production = 4 kg/kgCOD; Organic loading = 2.6 kg COD/($m^3$ day) | Iaconi et al. (2003) |
| CAACO system | COD, BOD, Sulphide and sulphate | Volumetric loading rate = 0.7376 $m^3/m^3$.day ; Surface loading rate = 0.2438 $m^3/m^2$.day | Kennedy et al. (2004) |
| SBBR with ozone | COD, TKN and TSS | Sludge production = 0.05 kgVSS/kgCOD | Iaconi et al. (2004) |
| AOP with Fenton | COD, Ammonia | Fenton reaction time = 30 min | Naumczyk et al. (2005) |
| Electrochemical with Biological process | COD, Ammonia | Sludge production = 1.37 kg/$m^3$ day; Electrolysis time = 49 min | Szpyrkowicz et al. (2005) |
| Photo electrochemical with electrodialysis | COD; Ammonical nitrogen | Current Density = 36 mA/$cm^2$; Ti electrode; Membrane area = 1.72 $dm^2$; Membrane spacing = 0.75 mm | Rodrigues et al. (2008) |
| SBBR with Ozonation | COD, TSS,TKN, BOD, Color | Sludge production = 0.4 kg TSS/kg COD; Time = 5760 h and 2160 h. | Laconi et al. (2009) |

oxidation processes (Fenton reaction, $O_3/OH^-$, $O_3/H_2O_2$, and $H_2O_2/UV$). Coagulation followed by Fenton reaction in 30 min was recognized as the best method of purification of tannery wastewaters-COD was reduced by 85-88%. The purification effect obtained by AOPs decreased in the order: Fenton reaction $<O_3/OH^- < O_3/H_2O_2 < H_2O_2/UV$. During the Electro-Fenton process, the removal efficiencies of COD and sulphide parameters were 54% and 85%, respectively, and electricity consumptions were also obtained as 1.5 kWh/kg COD removed and 8.3 kWh/kg sulphide removed. Furthermore, the removal efficiencies of total Chrome and suspended solids were found to be 97% and 70%, respectively (Apaydin *et al.*, 2009). During the electro-coagulation process, the removal efficiencies of COD and sulphide were 46% and 90%, respectively. Electricity consumptions were also obtained as 1.8 kWh/kg COD removed and 27.7 kWh/kg sulphide removed (Apaydin *et al.*, 2009). The Electro Fenton process and an electrochemical oxidation process were studied for COD treatment and were reduced by 60–70% within 10 min (Kurt et al, 2007). The application of a PEO-ED process to an effluent from tannery was found to be effective with removal efficiency >98.5% for all ion species in effluent (Rodrigues *et al.*, 2008).

Various biological process followed by various oxidation process were reported for the treatment of tannery effluents (Szpyrkowicz *et al.*, 2005; Iaconi *et al.*, 2002, 2003, 2004; Kennedy *et al.*, 2004; Iaconi *et al.*, 2009). Iaconi et al. (2002) was reported to evaluate the performances of an innovative tannery wastewater process by sequencing batch biofilm reactor (SBBR) with chemical oxidation, performed by ozone. The average COD, $NH_4$–N and TSS removals were 97%, 98% and 99.9%, respectively. Furthermore, it was proved that the combined process is characterised by a very low sludge production was lower than the value reported for conventional biological systems. Similarly, Iaconi et al. (2003, 2004) were found that the average removal of COD, TKN, and TSS were 96%, 92% and 98% respectively. Kennedy et al. (2004) was reported that the combined treatment biological and catalytic oxidation for tannery wastewater by rice husk based mesoporous activated carbon—*Bacillus sp*. It was found that the reduction in COD, BOD, sulphide and sulphate were respectively 87%, 96%, 100% and 40% under an air oxidation of 2 h. Szpyrkowicz et al. (2005) was reported that a combination of electrochemical and biological processes for tannery wastewater. COD 80% reduction. In this case the energy requirement, of 29 kWh/$m^3$ of treated wastewater, is much higher than the 8.47 kWh theoretically needed in a single-sludge biological plant. Iaconi et al. (2009) was investigated that the treatment of tannery wastewater by an aerobic granular biomass system (SBBGR – Sequencing Batch Biofilter Granular Reactor) integrated with ozonation. The results show that the integrated process was able to achieve concentrations much lower than the current discharge limits. Furthermore, the process was characterised by a very low sludge production (i.e., 0.1 kg dry sludge/$m^3$ of treated wastewater) with interesting repercussions on treatment costs (about 1 € per $m^3$ of wastewater).

**CONCLUSION**

The treatment of tannery wastewater by different oxidation and combined processes was reviewed in the present paper. Some of the suggestions made by various author and present study were reported here. The main problem with AOPs is their high operating cost. The application of solar technologies to these processes could help to diminish that problem by reducing the energy consumption required for generating UV radiation. The maximum reduce the TOC content by mineralisation of the organic compounds using combined $H_2O_2/UV$ and the Fenton's oxidation processes for the treatment of tannery wastewater. The $H_2O_2$ and Calcium hypochlorite were the most efficient oxidant while compared to other oxidant for removal of chromium pollutant from tannery wastewater. However, $H_2O_2$ alone is not effective for high concentration of certain refractory contaminants because of low rates of reaction at reasonable $H_2O_2$ concentration. Improvements can be achieved by using metal salts (iron salts) or ozone and UV-light can activate $H_2O_2$ to form hydroxyl radicals which are strong oxidants. Fenton Oxidation was successful in increasing both the extent and rate of biodegradation (soluble COD) in the treatment of tannery wastewater. Drawbacks associated with the use of fenton oxidants are the safety hazards associated with using $H_2O_2$ and the need to firstly reduce the pH, followed by a subsequent neutralisation. Iaconi et al. (2002) was concluded that treated effluent by SBBR with chemical oxidation well below the limit values fixed by the regulations. The electrochemical oxidation can be applied as a post-treatment after the conventional biological process in order to remove the residual ammonia with low energy consumption (Marco *et al.*, 2004; Rao *et al.*, 2001; Szpyrkowicz *et al.*, 2005). Marco et al. (2004) have recommended that the anode Ti/$TiRuO_2$ electrode have more energy consumption for complete COD removal, it was more stable and was not release toxic ions, so it was the best choice for industrial applications. However, Corrosion of electrode reduces the removal efficiency is the drawback of this method.

The advantage of treated tannery wastewater by ozonation can be achieved by enhancing the biodegradable compounds. The oxidation of inorganic pollutants by ozone is usually fast and efficient except ammonia which is only slowly oxidized by ozone and OH radicals. The oxidation of organic pollutants can be directly oxidized by ozone and those which do not react with ozone. For the compounds, Ozonation is very efficient. For ozone resistant compounds, ozone based AOPs can be applied for this oxidation. For example, the ozonated process was higher removal efficiency than that obtained with the non-ozonated effluent by combining biological and chemical oxidation with ozone (Iaconi *et al.*, 1998). In wet air oxidation process, operating costs is low, minimal pollution discharge. However, high capital costs which is limitation of this method for treatment of tannery effluent. Photo oxidized process can be applied only to the transformation of recalcitrant to non-recalcitrant compounds, which subsequently can be easily degraded conventional techniques. More incident photons are require to produce an oxidation/reduction step i.e. Quantum efficiency values are very low, which the main limitation of this method. PEO-ED technique was significant reductions in all parameters tested, showing the success in removing heavy metals and ions present in the effluent (Rodrigues *et al.*, 2008). The photo-oxidized treated effluent was reused in leather processing while potable water was used as control (Sankar *et al.*, 1998).

The membrane process especially, reverse osmosis and nanofiltration are effective method for treatment of tannery wastewater. However, membrane fouling and large quantity of liquid waste and high costs were limitations of this method.

The best combination of process depends upon neither intrinsic advantages nor drawbacks that favours or exclude its utilization. However, individual system treatable testing must be done to find the best technology. From a practical point of view, treatment at source may be pragmatic/down-to-earth option and challenge of the further improve the overall performance, AOPs technology is the acquisition of a cheaper understanding of all the mechanism (example, affects the chemical kinetics and/or the overall efficiency) occurring within the process and then optimization techniques be developed to consistency for the process.

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