



Original Research Article

Characterization of Physicochemical Parameters and heavy metal Analysis of Tannery Effluent

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ABSTRACT

Keywords

Effluent,
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Tanneries generate various pollutants depending upon the process used. The present study deals with the analysis of physicochemical parameters of both untreated and treated tannery effluent for two years at monthly intervals. All the parameters were more or less higher for untreated effluent compared to that of the treated. The pH was lower in the untreated and higher in the treated effluent. Heavy metals such as copper, chromium and zinc was also analyzed. Higher amounts were recorded in the untreated effluent which indicates that it may be become major source of water pollution which will affect the flora and fauna inhabiting such environments.

Introduction

Tannery is an oldest and fastest growing industry in India. There are about 2161 tanneries which process 500,000 tons of hides and 314 kg of skins annually. These industries spread mostly across Tamilnadu, West Bengal, Uttar pradesh, Andhra pradesh, Karnataka, Maharashtra, Rajasthan, Punjab and Kanpur (Vijayanand and Hemapriya, 2014). In Tamilnadu alone there are about 1120 tanneries located in Vellore, Ranipet, Trichy, Dindugal, Erode and Pallavaram in Chennai (Noorjahan, 2014).

Nearly 30 m³ of waste water is generated during processing of one tone of raw skin/hide (Suthantrarajan *et al.*, 2004). A total annual discharge of waste water from these tanneries is 9,420,000 m³, which generates about 100,000 m³ of waste water

per day (Mohan *et al.*, 2006). The waste water is highly polluted in terms of biological oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), nitrogen, conductivity, sulphate, sulphide and chromium (Mondal *et al.*, 2005) and in most developing countries tannery effluents are discharged directly into aqueous system without treatment (Verheijen *et al.*, 1996; Favazzi, 2002). The high BOD content of the effluent will affect the survival of gill breathing animals of the receiving water body and high COD value indicate toxic state of the wastewater along with presence of biologically resistant organic substances. The high level of ammonia-N is toxic to aquatic organisms and nitrogen may cause eutrophication. The high salinity and TDS of the effluent may

result in physiologically stressful conditions for some species of aquatic organisms due to alterations in osmotic conditions. Studies show that increase in salinity causes shifts in biotic communities, limit biodiversity, exclude less tolerant species and cause acute or chronic effects at specific life stages. Changes in the ionic composition of water can also exclude some species while promoting population growth of others (Weber-Scannell and Duffy, 2007). The pollutants are hazardous to human and aquatic life resulting in bioaccumulation.

One of the major emerging environmental problems in the tanning industry is the disposal of chromium contaminated sludge produced as a by-product of waste water treatment. For instance, in India alone about 2000–3000 tons of chromium is released into the environment annually from tanneries, with chromium concentrations ranging between 2000 and 5000 mg/L in the aqueous effluent compared to the recommended permissible discharge limits of 2 mg/L (Altaf *et al.*, 2008). In view of the negative impact of tannery effluent on the environment, the present study aimed at determining the levels of physicochemical pollutants in untreated and treated effluent samples and assessing its impact on the ecosystem.

Materials and Methods

Study area

The selected study area of this present study is Nagalkeni, which is situated in Kanchipuram district, Tamilnadu. The groundwater of Nagalkeni is polluted by untreated sewage and waste water from tannery industry.

Collection of tannery effluent

100 mL of untreated and treated tannery

effluent was collected each month from a common treatment effluent plant, PTIET (Pallavaram Tanners Industrial Effluent Treatment) for two years (May 2009–April 2011) in a sterile plastic container, transported to the laboratory and was stored at 4 °C.

Determination of physicochemical parameters

The effluent samples were analyzed for their physicochemical properties such as appearance, odour, turbidity, total solids, total suspended solids, total dissolved solids, electrical conductivity, pH, alkalinity pH, alkalinity total, total hardness, calcium, magnesium, sodium, potassium, iron, manganese, free ammonia, nitrite, nitrate, chloride, fluoride, sulphate, phosphate, tidity's test (as O), silica, chemical oxygen demand (COD), biological oxygen demand (BOD), total kjeldhal nitrogen, oil and grease. Heavy metals such as chromium, copper and zinc were also analyzed (Clesceri *et al.*, 1998).

Results and Discussion

In the present investigation, untreated and treated tannery effluent was collected from a common treatment effluent plant each month for two years (May 2009-April 2011). The physicochemical parameters of the effluents were analyzed (Table 1). The result of the study revealed that colour of the untreated effluent was blackish in colour with offensive odour. Similar results were reported by Noorjahan (2014) for the untreated tannery effluent collected for a period of 6 months (May 2011 to October 2011). A large number of pollutants can impart colour, taste and odour to the receiving water, thereby making them unaesthetic and unfit for domestic consumption (Jamal *et al.*, 2011). However in the present study, treated effluent was

slightly brownish but the odour was similar to that of the untreated. Brown colour of the tannery effluent was also reported by Smrithi and Usha (2012). The colour of the effluent might be due to the presence of biodegradable and non-biodegradable high molecular weight organic compounds and high amount of inorganic chemicals like sodium and chromium used during the processing and the odour may be due to putrefaction of the organic residues from the processed skin and hides (Smrithi and Usha, 2012).

Total solids of the untreated effluent and treated effluent was about 6867.3 & 5457.4 mg/L (I year) and 6640.7 & 5627.9 mg/L (II year) respectively which exceeded the permissible limit (110 mg/L). These solid impurities cause turbidity in the receiving streams. The composition of solids present in tannery effluent mainly depends upon the nature and quality of hides and skins processed in the tannery (Islam *et al.*, 2014). Level of average suspended solids was found to be higher in the untreated effluent, 492 mg/L (I year), 357.8 mg/L (II year) when compared to the permissible limit (100 mg/L) prescribed by CPCB (1995) for effluent discharge. Even in treated effluent of first year, the value was higher (135.3 mg/L) than the permissible limit. High amounts of suspended particles have detrimental effects on aquatic flora and fauna and reduce the diversity of life in aquatic system and promote depletion of oxygen and slitting in ponds during rainy season (Goel, 2000). Similar reports were given by Noorjahan (2014) where the values were 5174-6908 mg/L. High level of total suspended solids present in the tannery waste water could be ascribed to their accumulation during the processing of finished leather (Deepa *et al.*, 2011). Somnath (2003) reported that larger solid particulate matter remains suspended as a

result of charges on the surface of small particles in the effluent.

Presence of Total Suspended Solids (TSS) in water leads to turbidity resulting in poor photosynthetic activity in the aquatic system (Goel, 2000). In the present study, turbidity of untreated effluent was 28.9 and 3.6 NTU whereas 17.8 and 14.8 NTU for treated effluent of I year and II year respectively. The turbidity of the effluent might be due to the discharge of high concentration of carbonates, bicarbonates and chlorides of calcium, magnesium and sodium (Chakrapani, 2005). The composition of solids present in a natural body of water depends on the nature of the area and the presence of industries nearby. Total dissolved solids of untreated effluent was found to be 6375.3 mg/L (I year), 6282.8 mg/L (II year) very high compared to that of the treated. The value was much greater than the tolerance limits (2100 mg/L) prescribed by Bureau of Indian Standards. Total Dissolved Solids (TDS) is the measure of total inorganic salts and other substances that are dissolved in water (Nasrullah *et al.* 2006). High levels of TDS are aesthetically unsatisfactory and may also produce distress in human and livestock (Patel *et al.*, 2009).

Total dissolved solids are mainly due to carbonates, bicarbonates, chlorides, sulphates, phosphates, nitrates, nitrogen, calcium, sodium, potassium and iron (Kannan *et al.*, 2009). Noorjahan (2014) reported TDS value as 5758 - 6672 mg/L. The presence of high level of TSS and TDS may be due to the insoluble organic and inorganic present in the effluent (Nagarajan *et al.*, 2005). In our study, maximum level (318.5 mg/L) of potassium was recorded in untreated effluent of I year under study which was very much higher than the previous study conducted by Smrithi and Usha (2012), where the level was 600 mg/L.

It was reported that the levels of exchangeable cations (sodium and potassium) in the soil irrigated with tannery waste water were found to be high (Krishna, 2008). Untreated effluent showed higher level of electrical conductivity, 9070.3 $\mu\text{mhos/cm}$ (I year), 8924.4 $\mu\text{mhos/cm}$ which indicates that the discharge of chemicals as cations and anions were higher in the waste water. The higher conductivity alters the chelating properties of water bodies and creates an imbalance of free metal availability for flora and fauna (Akan *et al.*, 2008). It may be due to high concentration of acid base and salt in the effluent (Jamal *et al.*, 2011). Noorjahan (2014) reported electrical conductivity value as 8344-9138 $\mu\text{mhos/cm}$. However, the electrical conductivity of the treated effluent was also higher, 7561.5 $\mu\text{mhos/cm}$ (I year), 7889.08 $\mu\text{mhos/cm}$ (II year).

The average pH of the untreated tannery effluent was found to be within the range (7.08 (I year), 7.07(II year)) similar to that of Rabah and Ibrahim (2010). This could explain the high counts of microorganisms because most of them thrive well in such pH value. Hemamalini and Sneha (2014) reported the pH of the gold electroplating effluent to be 7.5. However, pH of the treated effluent is slightly alkaline. Discharge of such effluent with alkaline pH into ponds, rivers, etc. for irrigation may be detrimental to aquatic biota such as zooplankton and fishes. According to Saxena and Shrivastava (2002), alkaline nature of the tannery effluent may be due to the presence of carbonates and bicarbonates present in the effluent. Total alkalinity is higher in untreated effluent [1021.5 mg/L (I year), 1187.2 mg/L (II year)] than the treated effluent [516.8 mg/L (I year), 665.5 mg/L (II year)]. Alkalinity of water is its acid neutralizing capacity. It is the sum of all the bases. The alkalinity of natural water

is due to the salt of carbonates, bicarbonates, borates, silicates and phosphates along with hydroxyl ions in the free state. In the tannery effluent under study, maximum phosphate content (2.7 mg/L) was observed in the untreated effluent of II year. However, the major portion of the alkalinity is due to hydroxides, carbonates and bicarbonates (Islam *et al.*, 2014).

In the study conducted by Napit (2014), the level of 'O' by Tidy's test was reported as 0.4-68 mg/L which was within the permissible limit, whereas in the present study the value was much higher in both the effluents exceeding the limit. Silica content was maximum (102 mg/L) in the untreated effluent in the II year. Dissolved silica exists as monosilicic acid at low concentrations. As silica concentration increases, polysilicic acid begins to form. Once formed, it will grow to spherical colloidal silica particles or to large polymerized silica networks depending on pH, temperature, silica concentration and TDS (Bergna and Roberts, 2006). In the present investigation, total hardness of untreated effluent was found to be high, 1512.5 mg/L (I year), 1320.8 mg/L (II year) than the permissible limit of CPCB (1995), whereas for treated effluent, the values were 1129.2 mg/L (I year), 1245.8 mg/L (II year), chloride [1026.8 mg/L (I year), 1523.7 mg/L (II year)], sodium [2087 mg/L (I year), 1367.5 mg/L (II year)] and calcium [312.7 mg/L (I year), 314.2 mg/L (II year)] of untreated effluent were higher compared to permissible limit of CPCB (1995). For treated effluent, the level of chloride, sodium and calcium were [842.2 mg/L (I year) & 1147.6 mg/L (II year)], [1760.7 mg/L (I year) & 1120.8 mg/L (II year)] and (259.3 mg/L (I year) & 300.8 mg/L (II year)) reported respectively. Similarly, in the study conducted by Noorjahan (2014), total hardness (1416-3850 mg/L), chloride

(1244-1895 mg/L), sodium (1200-2100 mg/L) and calcium (257-560 mg/L) was observed for untreated effluent.

Chloride is introduced into tannery effluents as sodium chloride usually on account of the large quantities of common salt used in hide and skin preservation or the pickling process. Being highly soluble and stable, they are unaffected by effluent treatment and nature, thus remaining as a burden on the environment. Chloride inhibits the growth of plants, bacteria and fish in surface waters; high levels can lead to breakdown in cell structure. If the water is used for irrigation purposes, surface salinity increases through evaporation and crop yields fall. When flushed from the soil by rain, chlorides re-enter the ecosystem and may ultimately end up in the ground water (Bosnic *et al.*, 2000). Fluoride content (0.3 mg/L) of the effluent samples were within the permissible limits (2 mg/L), whereas the sulphate content of the tannery effluents was exceeding the limit. Sulphate is a component of tannery effluent, emanating from the use of sulphuric acid or products with a high (sodium) sulphate content (Bosnic *et al.*, 2000). Calcium, magnesium, carbonates, bicarbonates, sulphates, chlorides, nitrates, organic matter together associate and form hardness of water (Salim *et al.*, 2013). Magnesium content (140.2 mg/L) was found to be maximum in the untreated effluent of I year.

Determination of Biological Oxygen Demand (BOD) is one of the important parameters used in water pollution to evaluate the impact of waste waters on receiving water bodies. The present study revealed high levels of BOD (1099.2 mg/L, I year; 1130.4 mg/L, II year) in the untreated effluent due to the presence of considerable amount of organic matter. High level of BOD (600-1622 mg/L) was observed by

Noorjahan (2014). High BOD levels have also been reported for effluent discharged from tanneries (Kulkarni, 1992) and dairy effluent (Noorjahan *et al.*, 2004). In the present study, BOD of treated effluent was 856.3 mg/L (I year) and 736 mg/L (II year). Increase in BOD which is a reflection of microbial oxygen demand leads to depletion of Dissolved Oxygen (DO) which may cause hypoxia conditions with consequent adverse effects on aquatic biota (Jerin, 2011). Chemical Oxygen Demand (COD) test is the best method for organic matter estimation and rapid test for the determination of total oxygen demand by organic matter present in the sample. The present investigation revealed high levels of COD (2749.8 mg/L, I year; 3420.3 mg/L, II year) in the untreated effluent than treated effluent. The values were 2260 mg/L, I year and 2281.8 mg/L, II year which exceeded the standard limit for COD (250 mg/L) prescribed by CPCB (1995) for effluent discharge into inland surface waters. Noorjahan (2014) also observed COD values as 2286- 9600 mg/L. Increased amount of COD may be due to high amount of organic compounds which are not affected by the bacterial decomposition (Nagarajan and Ramachandramoorthy, 2002). These results are in agreement with the previous studies (Alvarez-Bernal *et al.*, 2006).

Sharma and Malaviya (2013) also reported alkaline pH, high colour intensity, and high values of physicochemical parameters such as COD, TDS, TSS, chloride, sodium and nitrate of untreated tannery waste water. In the present study, the nitrate and nitrite values of untreated effluent were 11 mg/L & 17.9 mg/L and 1.3 mg/L & 0.5 mg/L for first year and second year respectively, whereas for treated effluent, the values were 9 mg/L & 11.2 mg/L and 0.9 mg/L & 0.3 mg/L.

Table.1 Physicochemical parameters of untreated and treated tannery effluent during May 2009- April 2011

S.No.	Parameters	2009-2010		2010-2011	
		Untreated	Treated	Untreated	Treated
1.	Turbidity NTU	28.9	17.8	3.6	14.8
2.	Total Solids (mg/L)	6867.3	5457.4	6640.7	5627.9
3.	Total Suspended solids (mg/L)	492	135.3	357.8	84.08
4.	Total Dissolved solids (mg/L)	6375.3	5322.2	6282.8	5543.8
5.	Electrical conductivity (μ mho/cm)	9070.3	7561.5	8924.4	7889.08
6.	pH	7.08	7.76	7.07	7.52
7.	Alkalinity pH (as CaCO ₃) (mg/L)	0	3.33	0	0
8.	Alkalinity Total (as CaCO ₃) (mg/L)	1021.5	516.8	1187.2	665.5
9.	Total Hardness (as CaCO ₃) (mg/L)	1512.5	1129.2	1320.8	1245.8
10.	Calcium (as Ca) (mg/L)	312.7	259.3	314.2	300.8
11.	Magnesium (as Mg) (mg/L)	140.2	102.5	128.5	118.5
12.	Sodium (as Na) (mg/L)	2087.9	1760.7	1367.5	1120.8
13.	Potassium (as K) (mg/L)	318.5	270.8	240.4	212.5
14.	Iron (as Fe) (mg/L)	16.2	8.67	11.20	4.8
15.	Manganese (as Mn) (mg/L)	0	0	0	0
16.	Free Ammonia (as NH ₃) (mg/L)	126.56	32.1	35.7	35
17.	Nitrite (as NO ₂) (mg/L)	1.3	0.9	0.5	0.3
18.	Nitrate (as NO ₃) (mg/L)	11	9	17.9	11.2
19.	Chloride (as Cl) (mg/L)	1026.8	842.2	1523.7	1147.6
20.	Fluoride (as F) (mg/L)	0.3	0.3	0.3	0.3
21.	Sulphate (as SO ₄) (mg/L)	1517	1271.5	1056.9	1091.4
22.	Phosphate (as PO ₄) (mg/L)	2.5	2.7	1.5	0.7
23.	Tidy's test (as O) (mg/L)	434.3	239.9	292.1	231.6
24.	Silica (as SiO ₂) (mg/L)	50.02	32.2	102	23.1
25.	COD (mg/L)	2749.8	2260.9	3420.3	2281.8
26.	BOD (mg/L)	1099.2	856.3	1130.4	736.8
27.	Total Kjeldhal Nitrogen (as N) (mg/L)	572.9	41.44	64	75.4
28.	Oil and grease (mg/L)	0.03	0.02	0.01	0.01

Fig.1a Heavy metal [Chromium (Cr), Copper (Cu) and Zinc (Zn)] concentration in untreated tannery effluent during May 2009-April 2010

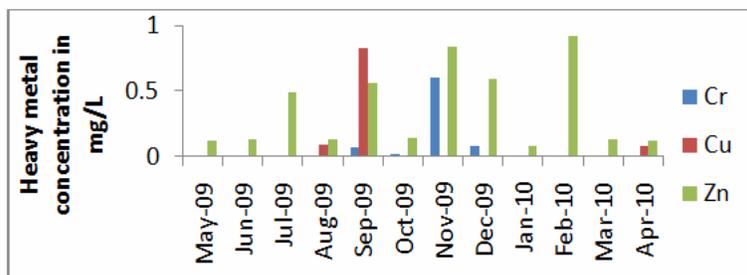


Fig.1b Heavy metal [Chromium (Cr), Copper (Cu) and Zinc (Zn)] concentration in treated tannery effluent during May 2009-April 2010

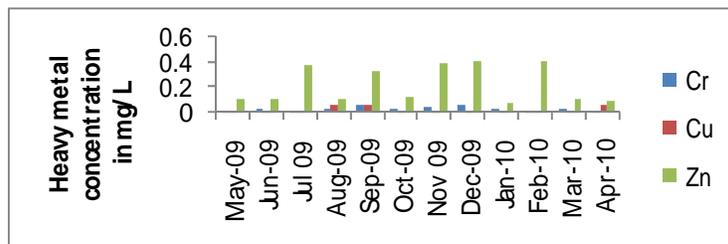


Fig.2a Heavy metal [Chromium (Cr), Copper (Cu) and Zinc (Zn)] concentration in untreated tannery effluent during May 2010 to April 2011

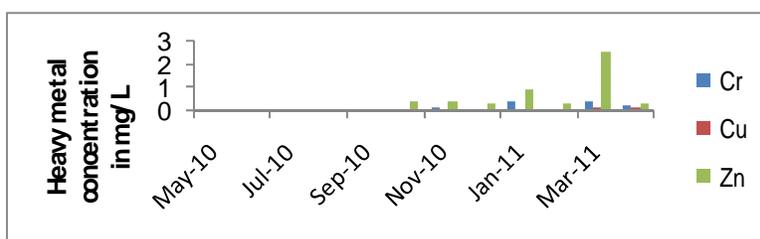
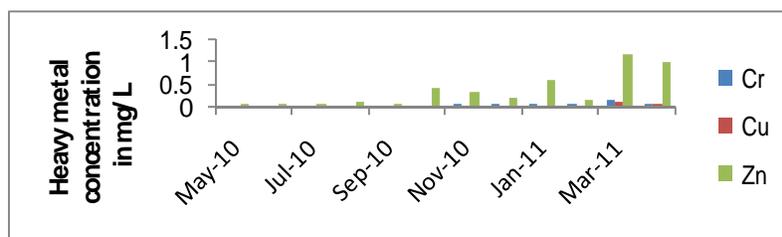


Fig.2b Heavy metal [Chromium (Cr), Copper (Cu) and Zinc (Zn)] concentration in treated tannery effluent during May 2010-April 2011



Salim *et al.* (2013) reported nitrate content fluctuating from 0.141 mg/L in July to 0.649 mg/L in February. High level of Total kjeldhal nitrogen (572.9 mg/L) and free ammonia (126.56 mg/L) was observed in the untreated effluent in I yr. Several components in tannery effluent contain nitrogen as part of their chemical structure. The most common chemicals are ammonia (from deliming materials) and the nitrogen contained in proteinaceous materials (from liming/unhairing operations). High level of

N₂ in aquatic system leads to eutrophication (Bosnic *et al.*, 2000). The effluent under study contained 0.03 mg/L and 0.01 mg/L (untreated) and 0.02 mg/L and 0.01 mg/L (treated) oil and grease in first year and second year respectively. During leather manufacture, natural oils and grease are released from within the skin structure. Floating grease and fatty particles aggregate to form 'mats' which then bind other materials, thus causing a potential blockage problem especially in effluent treatment

systems. If the surface waters are contaminated with grease or thin layers of oil, oxygen transfer from the atmosphere is reduced. If these fatty substances emulgate, they create a very high oxygen demand on account of their biodegradability (Bosnic *et al.*, 2000).

The physicochemical properties and heavy metals concentration of the effluent varies depending on the process of tanning adopted in various industries (Vidya and Usha, 2007). The tannery waste water is being contaminated with higher levels of metals (iron, nickel, chromium, zinc, cadmium, manganese and copper) and these metals contaminate the agricultural soil. The crops and vegetables, which when consumed cause serious health hazards to the consumer (Mohanta *et al.*, 2010). Higher value of chromium (0.6 mg/L) was found in the untreated effluent during Nov. 2009 whereas, higher value of copper (0.8 mg/L) was found in the untreated effluent during Sep. 2009. Maximum level of zinc (2.6 mg/L) in untreated effluent was reported in March 2011 in the present study (Fig 1a, 1b, 2a & 2b).

Rabah and Ibrahim (2010) reported 0.26 mg/L of chromium content in soil contaminated with tannery effluent. Continuous discharge of chromium in low concentration has been reported to be toxic to aquatic life and has been shown to disrupt the aquatic food chain (Fent, 2004). Deepali and Gangwar (2010) reported copper content (0.022 mg/L) in waste water samples of tannery industry. Copper is an essential element in mammalian nutrition as a component of metallo-enzymes in which it acts as an electron donor or acceptor. Conversely, exposure to high levels of copper can result in a number of adverse health effects (Bremner, 1998). Acute toxicity of zinc may result in sweet taste, throat dryness, cough, weakness,

generalized aching, chills, fever, nausea and vomiting (Kanawade and Gaikwad, 2011). Thus the analysis of physicochemical parameters of untreated effluent for the period of May 2009-April 2011 confirms that the waste water released from the tannery industry has higher concentration of EC, BOD, COD, TSS, TDS etc. which exceeded the permissible limits prescribed by CPCB (1995) for discharge of industrial effluent into inland surface water as well as on land for irrigation than the treated effluent. From the result of physicochemical analysis of untreated and treated tannery effluents, it has been concluded that EC, TDS, chlorides, sulphates, BOD, COD, Sodium and Calcium etc. are very high in concentration compared to the treated effluent. pH is lower in untreated effluent than the treated. The parameters of untreated effluent and treated effluent in some instance exceed the standards prescribed by CPCB. Heavy metal concentration also shows great variability. Such effluents should not be discharged into the nearby water body or soil without proper treatment. They are unfit for irrigation. The effluents containing noxious pollutants lead to environmental problems which will affect plant, animal and even human life.

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