RESEARCH PAPER:

Physico-chemical characteristics of leather tannery effluent- current scenario in Dindigul town (Tamil Nadu), India

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SUMMARY

Effluent of tannery samples were collected from leather tannery at dindigul town and analyzed bimonthly for a period of 6 months (October 2010 - March 2011) in order to understand various physical and chemical characteristics of the sample effluents. The parameters measured were temperature (26.95c), pH(6.7), turbidity (434 NTU), electrical conductivity (28935 µs/cm) , BOD (2600mg/l), COD(5083mg/l), DO(1.37mg/l), total hardness(2653mg/l, alkalinity(1330mg/lit), total dissolved solids(19713 mg/l), calcium(561 mg/l), magnesium(294mg/l), sodium(4388mg/l), potassium (901.7mg/l), iron (3.14mg/l), chromium (194mg/l), nitrate (47mg/l), chloride (8360mg/l), fluoride(1.45mg/l), sulphate (966mg/l) and phosphate (2.9mg/l). According to the permissible level suggested by Bureau of Indian standard, all the water quality parameters in the tannery effluents were found to be very high and well above the permissible limits. Ratios like sodium absorption ratio(SAR), Kelley's ratio KR, per cent sodium (PS), magnesium ratio(MR) and Wilcox ratio(WR) were well above the prescribed limits. It is concluded that tannery effluents was highly polluted as it exceeded the prescribed limits for irrigation and public use.

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Key Words :

Physico -chemical analysis, Biological oxygen demand, Chemical oxygen demand, Dissolved oxygen, Water, Tannery effluent

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The developed countries have used to exploit every bit of natural source to convert them into goods for their comforts to export them to needy developing countries. In doing this, the industrialized countries dump a lot of materials in their environment which become polluted (Dalela, 1985). Due to industrialization and urbanization, the availability and quality of drinking water resources is decreasing day by day. The requirement of water in all forms of lives, from micro-organisms to man, is a serious problem today because all water resources have reached to a point of crisis due to unplanned urbanization and industrialization (Singh *et al.,* 2002). Tanneries, oil refineries and metal industries are causing depletion of surface and water quality (Raj *et al.,* 1996). The discharge of various sub processes of tanneries like bathing, pickling, tanning, dyeing and fat liquoring may cause water pollution severely. The pollution of a particular water body can always be linked to an industry or sewage or agriculture(Subramanyam and Sambamurthy, 2006). The constituents that are present in raw waste water can be classified as physical, chemical, biological (Qasim, 1999) and toxic compounds. The problem of environmental pollution on account of essential industrial growth is the problem of disposal of industrial water, whether solid, liquid or gaseous. All three types of wastes have the potential of ultimately polluting water. Polluted water in addition to other effects, directly affects soil not only in industrial areas but also in agricultural fields, as well as the beds of rivers, creating secondary source of pollution (Kisku *et al.,* 2000 and Barman *et al.,* 2000).

The leather industry is an important foreign exchange earner for India. The states of Tamilnadu, West Bengal and Uttar Pradesh together have 88 per cent of the tannery units of the country. Tanners use a large number of chemicals during the process, discharging toxic wastes into the rivers and degrading agricultural land. All of the 68 tanneries in Dindigul, Tamilnadu are situated within a 5 km distance from the centre of the town. Several of them have been in existence for thirty to forty years. Effluents from the tanneries are discharged into streams which drain into ponds, thereby polluting the ground water sources and cultivable lands.

The present study has been undertaken with a view of document the water quality parameters of leather tannery effluents in dindigul to characterize and to find the extend of pollution. The name of the tannery is deliberately omitted to protect the privacy of the industry. The findings will provide a basis for the further extensive study.

EXPERIMENTAL METHODOLOGY

Study site:

The study area is located in the southern part of India, closed to Kodaganar river basin, mainly in hard rock terrain. The area is known for its leather industries. It lies between 10^0 12'44" – in 26'47" N Latitude and 77^0 55'08" - $78^0$01'24" E longitude and falls in survey of India Top sheet No. 58F/15 and J/3, in the state of Tamilnadu, India. The selected area is located in the central part of dindigul town and along Madurai, Batlagundu and Ponmandurai roads.

Tannery effluent samples were collected from the discharged stream of tannery effluent situated in Dindigul town of India twice in a month from October, 2010 to March, 2011. During sampling, the samples were collected in a 2 litre polythene carbuoys and mixed in equal proportions to get uniform homogeneous samples (Rain water and Thatcher, 1960). Random selection procedure was adopted for the selection of both sampling unit and the sampling point in a given site (APHA, 1998), Tap water and 8MHNO_3 were used to wash the polythene bottles of 100 ml capacity, which was used for the sample preservation followed by washing it with distilled water and finally with double distilled water (Jeffery, 1996). Then, the bottles were rinsed thrice with effluent samples and the effluent samples were stored in a refrigerator at 4^0C, after adding the necessary preservatives (APHA, 1998). H_2SO_4 was added to bring pH to two and then preserved. For phosphates, 20 mg mercuric chloride was added and refrigerated. During analysis, the mixed, homogeneous effluents after reservation were taken out from the refrigerator. These samples were used for analysis of water quality parameters according to the standard methods reported in literature (Jeffery, 1996 and APHA, 1998). The other parameters such as temperature, pH and electrical conductivity were determined in the field itself (within 30 minutes). The other water quality parameters were determined within 82 hours except BOD, which was determined only after 5 days of incubation at 20^0C

The data set taken in this study is comprised of 24 parameters (period from October 2010 to March 2011) such as water temperature, pH, turbidity, TDS, electrical conductivity, alkalinity total as $CaCO_3$, total hardness as $CaCO_3$ calcium, magnesium, sodium, potassium, iron total free Ammonia, nitrite, nitrate, dissolved oxygen (DO), total chromium, biological oxygen demand, chemical oxygen demand, total suspended solids, chloride, fluoride, sulphate and phosphate. These parameters were chosen as they have verified weight factors for different ranges of the parameters to calculate water quality index in various literatures (Pesce and Wunderlin, 2000). Collection, stabilization, transportation, storage and analysis of the water quality samples were done in a local laboratory considering the standard methods described in APHA – AWWA (1998). The methods of analysis of water quality parameters are summarized in Table A.

Table A : Analytical method used during October 2010 to March 2011 for tannery effluents

Parameters	abbreviation	units	Analytical methods	Instrument
Water temperature	Wtemp	C	Instrumental	Oyster pH/conductivity/ temperature meter
pH	pH	pH unit	Instrumental	pH meter
Dissolved oxygen	DO	mg/l	Instrumental	Probe metod
Electrical conductivity	EC	µS/cm	Instrumental	Electrometric
Total dissolved solids	TDS	mg/l	Filtration and gravimetric	Temperature controlled oven
Total suspended solids	TSS	mg/l	Filtration and gravimetric	Temperature controlled oven
Calcium	Ca	mg/l	Digital titrimetric	Titration assembly
Magnesium	Mg	mg/l	Digital titrimetric	Titration assembly
Total hardness	Hardness	mg/l	Digital titrimetric	Titration assembly
Sulphate	SO_4	mg/l	Spectrophotometric (barium chloride)	UV spectrophtometer
Chloride	Cl	mg/l	Digital titrimetric (mercuric nitrate)	Titration assembly
Inorganic phosphorus	PO_4P	mg/l	Phosphomolybdate	UV spectrophotometer
Ammonia nitrogen	NH_4H	mg/l	Nesslerization	UV spectrophotometer
Nitrite nitrogen	NO_2N	mg/l	Diazotization	UV spectrophotometer
Nitrate nitrogen	NO_3N	mg/l	Cadmium reduction	HACH-DRE/2000, spectrophotometer
Biochemical oxygen demand	BOD	mg/l	5 -days incubation, 20?c	Winlker azide method
Chemical oxygen demand	COD	mg/l	Potassium dichromate oxidation (open reflux,titrimetric)	Dichromate method

A few important chemical parameters such as sodium absorption ratio (SAR), per cent sodium (PS), Kelley's ratio (KR) and magnesium ratio (MR) were determined to assess the general suitability of the industrial effluent for irrigation. These parameters were calculated by using the following relationships (Srinivasa Gowd, 1999):

$$PS = 100[(Na + K)/(Ca + Mg + Na + k)] \quad -- (2)$$

$$KR = [Na/(Ca + Mg)] \quad -- (3)$$

$$MR = 100[Mg/(Ca + Mg)] \quad -- (4)$$

$$WR = Na/(Na + Mg + Ca + K) \quad -- (5)$$

Where, the ionic concentration is expressed in milli equivalents per litre. The average values of SAR, PS, KR, MR and WR have been calculated from water quality parameters for the leather tannery effluent.

EXPERIMENTAL FINDINGS AND DISCUSSION

Physico-chemical characteristics of tannery effluents Table 1.

Data of the physico-chemical analysis of leather tannery effluent are found to be very high and well above the permissible limits chemicals (ICMR, 1975 BISIS; 10500, 1983; MWH 1975).

The parameters show the maximum variation in the analyzed samples with respective of their chemical composition. The average temperature of leather tannery effluent was 26.95^{0}C and the value of range 26.2^{0}C-28.3^{0}C.

The average value of temperature of the effluent sample was found to be ambient and almost equal to that of room temperature (30^{0}C±2^{0}C) observed on the day of sample collection. Hence, the effluent was not thermally polluted. The pH value of effluent fluctuated from 6.3 to 7.56 with an average 6.7 which was with in the desirable range 6.5 - 8.5 (BIS, 2003). The effluent from the tannery was found to be slightly acidic with average pH 6.7.Electrical conductivity is an excellent indicator of ionic forms of total dissolved salts which was a measure of salinity which affects the taste of portable water (WHO, 1994). The electrical conductivity of the effluent was the range of the 14533 micromohos and the average electrical conductance was 28935 micromohos which was very much above the permissible limit. The tolerance limit of

Table 1 : Physico – chemical characteristics of tannery effluents

Parameters	Oct. 2010	Nov.2010	Dec. 10	Jan. 2011	Feb. 2011	Mar. 2011
Temperature	27.8	26.3	26.2	26.8	26.3	28.3
pH	6.36	6.3	6.38	6.9	7.56	6.8
Turbidity	480	455	440	420	410	400
TDS	27444	26680	25933	18018	10106	10100
Electrical conductivity	40359	39230	38136	26490	14862	14533
Alkalinity total $CaCo_3$	2080	2057	2040	1180	320	308
Total hardness	3400	2973	2560	2388	2230	2372
Calcium	640	597	576	533	504	517
Magnesium	432	345	269	246	233	241
Sodium	6100	6120	6200	4062	1950	1900
Potassium	1600	1435	1280	728	188	179
Iron metal	3.31	3.15	3	3.4	3.83	3.79
Free ammonia	1.82	1.8	1.8	1.79	1.8	1.82
Nitrite	0.31	0.29	0.31	0.3	0.3	0.33
Nitrate	48	45	48	47	48	47
Chloride	11360	11133	10920	7752	4600	4400
fluoride	2.4	2.3	2.4	1.7	1.2	1.1
Sulphate	1292	1290	1299	903	513	500
Phosphate	0.45	0.561	0.68	3.46	6.25	6.11
Dissolved oxygen	1.63	1.55	1.51	1.29	1.1	1.13
Total chromium	160	154	175	214	233	229
BOD	2100	2400	2000	3200	214	3000
COD	4200	4000	4600	5800	5900	6000
TSS	2281	2200	2189	2500	2100	2198

EC is 3000m mohs/cm as suggested by BIS (1983). The value of turbidity range from 400NTU to 480NTU and the average turbidity was 434 NT above the prescribed limit. The high turbidity may be ascribed to the living and the non-living suspended matters. The values of average and range of total dissolved solid was 19713 mg/l and 10100 mg/l and 27444 mg/l total dissolved solids was found to be well above the tolerance limit prescribed by BIS for the discharge of tannery effluent and hence they are to be necessary to be removed by primary and secondary effluent treatment which before discharging the effluent in order to safeguard the environment .

Amidst the various cations analyzed sodium content was very high which ranged from 1900mg/l to 6200 mg/l and the average sodium found in the tannery effluent was 4388mg/l which exceeded the desirable limit of 1000-1500mg/l. Calcium contents ranged from 504mg/l to 640mg/l which exceeded the desirable limit 50mg/l. The tannery effluent showed the magnesium content ranged from 233mg/l to 432 mg/l which was above the prescribed limit 50 to 1mg/l. Similarly, potassium content ranged from 179 mg/l to 1600 mg/lit which was above the prescribed limit. The values of average and range of sulphate and chloride ion (in mg/lit) were 966 mg/l and 500 mg/l to1299 mg/l and 8360 mg/l and 4600 mg/l to 11360 mg/l, respectively. The high content of these ions was responsible for high hardness and it increased the degree of eutrophication. Besides, the tannery effluent has more phosphate ion which ranged from 0.45 mg/l to 6.25 mg/l with an average 2.9 mg/l. Phosphate was noticed comparatively higher. For phosphates, the U.S. Environments Protection Agency (1976) suggested that 0.08 ppm was the critical level for the occurrence of eutrophication in lakes and reservoirs. The amount of phosphate was found out to be much higher than the acceptable limit.

The iron content of all the analyzed samples were found to have 3.41mg/l concentration which was found to be above the desirable limit of 0.3mg/l. BOD ranged from 2100 mg/l to 3200 mg/l with an average 2600 mg/l of the tannery effluent. Biochemical oxygen demand is the measure of the biodegrable organic material present in water sample .The higher values of the BOD has direct correlation with the increase in nutrient level of the lake due to immersion activity (Mccoy and Olson, 1986). The BOD is directly linked with decomposition of dead organic matter present in the lake and hence the higher values of BOD can be directly correlated with pollution status of the lake (WQM,1999).An inverse relation was found between the dissolved oxygen concentration and biochemical of oxygen demand values (Coscun and Gurol,1987). Dissolved oxygen ranged from 1.10 mg/l to 1.63 mg/l in the tannery effluent. Dissolved oxygen depends on physical, chemical and biological activities of the water body. It is very important parameter to check the pollution level in water. For drinking water, limit is 6.0 mg/l (WHO, 1968).

Dissolved oxygen is an index of the total organic content of water oxygen demanding substance in water. It means amount of oxygen required for oxidation of oxidizable organic matter. The COD is more realistic parameter, which indicates the pollution status of water body as it is related with the allocthonous matter present in the lake (WQM, 1999). The COD ranged from 4200mg/l to 6000mg/l. It was noticed comparatively higher COD in the tannery effluent against the prescribed limit 250 mg/l.

Nitrate ranged from 45 mg/l to 48 mg/l which was comparatively higher in the tannery effluent. The raw sewage is the source of nitrate and phosphate in the water (Agarwal and Gupta, 2000). The standard drinking water quality guideline for nitrates is 40 mg/l (American Public Health Associations, 1985). The total suspended solids of tannery effluent samples were 2100 mg/l to 2500 mg/l which was very above the permissible limit 100 to 600 mg/l. It was observed that the fluoride content in the sample ranged from 1.1 mg/l to 2.4 mg/l, most of which exceeded the desirable limited of 1.0 mg/l to the maximum permissible limit of 1.5 mg/l for drinking purpose. It may be inferred that the fluoride was endemic in this area and it is due to the geochemical contamination. The range of chromium level was found to be 154 mg/l to 233 mg/l. It exceeded the permissible limit 0.05 mg/l. They are very high and above the tolerance level. The water from the source need to be treated before use to avoid its carsenogenic effect. Total hardness ranged from 2230 mg/l to 3400 mg/l against the permissible limit 500 mg/l. Total hardness as calcium carbonate was noticed comparatively higher (Vyas *et al.,* 2006). The hardness of water is not a pollution parameter but indicates water quality. The alkalinity of the samples was in the range of 320 mg/l -208 mg/l which was well above the permissible limit 200 mg/lit. The effluent samples were having high salinity which is hazardous to human health (Bockris , 1977).

The values of few important chemical parameters such as sodium absorption ratio (SAR), per cent sodium(PS), Kelley's ratio (KR) magnesium ratio (MR)and Wilcox ratio are tabulated in Table 2.

Table 2 :Values of SAR, PS, KR ,MR and WR of leather tannery effluent

Parameters	Average
SAR	147.55
PS	102.11
KR	4.97
MR	33.97
WR	0.714

Kelley (1951) first pointed out the importance of considering the concentration of sodium in assessing the suitability of water for irrigation. According to him excess sodium in irrigation water reacts with soil to reduce its permeability as a result of cogging of particles. The parameter that is commonly used to determine whether or not the amount of sodium in a waste water is excessive is the sodium adsorption ratio or SAR (Ferguson, 1976). This concept is based in equilibrium theory and is defined as:

$$SAR = Na/\sqrt{Ca + Mg}$$

Where, the concentration of the metal ions are also expressed as milli moles per litre. According to the U.S salinity laboratory, the SAR predicts reasonably well the degree to which irrigation water tends to enter cation exchange reactions in soil. High values for SAR imply a hazard of sodium replacing adsorbed calcium and magnesium, a situation ultimately damaging soil structure. Therefore, the SAR is used for adjudicating the irrigation waters. Irrigation waters are classified by Richards (1954) based on SAR. If the SAR is between 0 and 10, the water is excellent and it is good if the value is 10 to 18, the quality is fair if the SAR ranges from 18 to 28,while it is poor beyond 28 based on the above classification. The value of SAR of tannery effluent 147.55 indicated that the effluent was unsuitable for irrigation. per cent sodium value less than 50 are suitable for irrigation (Wilcox, 1948) and therefore that tannery effluent has more than 75 per cent sodium. per cent sodium found for tannery effluent was 102.11 which is unsuitable for irrigation. Excess level of sodium in water is indicated by having the value of Kelley's ratio (KR) more than one. The KR value for the tannery effluent sample was found to be 4.97 which was more than one and unsuitable for irrigation. Calcium and magnesium maintain a state of equilibrium generally in most of the water. In equilibrium with more magnesium being present in waters, it will adversely affect the soil quality converting it to alkaline. This inturn affects the crop yields. MR values must be 50 per cent for a water sample for irrigation. Since MR value of the tannery effluent sample is 33.97 which is suitable for irrigation. But, when the effluents are properly treated, probably they will be more suitable for irrigation.

The critical valve for the Wilcox ratio was 0.8. The value of Wilcox ratio calculated from the tannery effluent was found to be 0.741 which was below the critical value. It is inferred that the amount of sodium present relative to the concentration of other divalent ion present in the tannery effluent is below the critical value.

Conclusion:

The result of physico-chemical analysis of tannery effluent are compared with recommended (WHO 1984) standards like mean values of water quality parameter such as temperature, pH, turbidity, total dissolved solids. Total suspended solid, EC, alkalinity, total hardness, calcium, magnesium, sodium, potassium, iron, nitrate, nitrite, chloride, fluoride, sulphate, phosphate, chromium, dissolved oxygen, BOD and COD values of tannery effluents were in the higher limit than the permissible standards. It is confirmed that the effluents are in the polluted nature which indicate heavy load of pollutants which are present well above the toxic level(De, 1987).Tannery effluent contains appreciable amount of heavy metals which can pollute the water and soil(Koe *et al.* 1976; Chandra, 1988). Heavy metals not only cause phyto-toxicity (Sharma and Bisht, 1990) but also enter into the food chain resulting in toxicity in animals and carcinogency in human beings (Kjellstrom *et al.,* 1979).Tannery effluent in soil can eliminate most of the rhizosphere fungi and can lead to soil fertility problem. Tannery effluent having high pH and EC has a negative influence on germination, root growth, absorption of water and nutrients (Solaimalai and Saravana Kumar, 2004). Sulphate concentration in the samples exceeded the permissible limit of 200 mg/lit water having sulphate level less than 200 mg/lit, is excellent for irrigation (Rajkumar *et al.,* 2003). Therefore, as far as sulphate is concerned, the irrigation water quality in the present study area is affected. The application of SAR, PS, KR, MR and WR to assess the suitability of water for irrigation has been mostly tested with fresh water system, however this has also been extended to the industrial effluent as reported by Venkateswara Rao *et al.*(1996). Tannery effluents are highly polluted and it exceeds all the five values (SAR, PS, KR, MR and WR) and which is not at all suitable for irrigation purpose. Hence, these effluent from tannery industry are not at all suitable for any use for human activities without any further waste water treatment. It is concluded that physico-chemical analysis for leather tannery effluent will certainly affect the environment and leads to severe water pollution. We are reminded of the words of Mahatma Gandhi. "Your laboratories are devil's workshops unless they serve the rural poor.

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