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Research Paper :

Assessment of leather tannery effluent using multiple indicators

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ABSTRACT

In the present study physico chemical parameters such as Temperature, pH, Total dissolved solids, Total suspended solids, Electrical Conductivity, Calcium, Magnesium, Total Hardness, Chloride, Sulphate, Phosphate, Nitrate, Nitrite, Biological Oxygen Demand, Chemical Oxygen Demand and Dissolved oxygen were analyzed in the leather tannery of Dindigul, Tamil Nadu. All the parameters were found to be above the standard limit. The tannery effluent was alkaline with high BOD and COD, along with higher concentration of Total dissolved solids and Total Suspended solids, Sodium adsorption ratio and high amount of sodium having water quality class C3S1. A systematic statistical analysis showed correlation between water quality parameters. Water quality index minimum (WQI minimum) calculated using Temperature, pH, Electrical conductivity, DO and Total suspended solids which showed that effluent belonged to bad water class. Water quality index (WQI) calculated using all the 16 physico-chemical parameters showed that effluent belonged to very bad water class. The total dissolved solid present in the effluent is maximum hence effluent is unfit for irrigation and for any use. The discharge of leather tannery effluent is leading to the contamination of ground water to the surrounding area and highly polluting the environment. It can thus be concluded that waste effluent from leather tannery is unfit for agricultural use and it may have deleterious effect on soils when used for irrigation purposes causing salinity and sodicity problems unless proper management techniques are adopted.

KEY WORDS : Waste water effluents, Water quality index(WQI), Physico - chemical parameter, Tannery, Correlation, Water quality parameters, Sodium adsorption ratio (SAR), Water pollution limit, Threshold hazard of waste water and normalization factors

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Human civilization originated, developed and thrived in places within easy reach of fresh water sources. Amongst global resources, water is emerging as perhaps the most critical but misused natural resource (Saleemi, 1993). Water is the elixir of life without which no biota could survive in the biosphere. The industrial growth in Dindigul though solving economic problem, also add upto environmental pollution as waste water effluents from tanneries are discharged into water bodies deteriorating the water quality(Faisal and Husnain,2004; Qureshi and Barrett – lennard, 1998). The discharge of industrial effluents, besides increasing the dissolved residues,which increase the total amount of sediments, also bring about chemical transformation in soils continuously irrigated by polluted waters (Faisal and Husnain, 2004). As a result of this, serious biological and ecological instability may occur as more and more industrial wastes are thrown out into the bodies of water.

Industrial pollution is a global concern. Among the major different industries, the tanning industry is a notorious polluter of the environment. The tannery effluent pollutes soil and ground water if washed into the river. Tannery effluent is the untreated waste water of tanneries. It appears as dull grey colour with the odour of the hydrogen sulphide. It contains the preliminary hairs of animals. Pollutants are blood, fat, pieces of flesh, soil particles of other biological origin. In the tanning process, various inorganic and organic chemicals like Chloride,

Sulphides, Tanoloin (16 % Chromium), titanium dioxides are used (Manivasakam 1987). The tannery effluents contain high concentration of metallic ion like Chromium, Potassium, Sodium and Magnesium and organic pollutants like oil and grease, tannin and lignin (Manonmani *et al.*, 1991). Tannery is one of the major water consuming industrial responsible for water pollution problem of considerable magnitude, since most of the water discharged as waste water.

The most often affected natural resource is our water resources, which is used to dispose our industrial and domestic wastes (Sharma, 1975). Effluents discharged from leather tannery contains a number of chemical pollutants such as Carbonate, Bicarbonate, Nitrite, Phosphate, Oil and grease in addition to total suspended solids, volatile solids and score of other toxicants. These pollutants could bring about changes in temperature, humidity, oxygen supply, pesticide stress amounting to a partial or complete alteration in the physical, chemical and physiological spheres of the biota (Verma and Shukla, 1969). When the untreated effluents are discharged into the environment, they disrupt the ecosystem (Behera and Misra, 1985).

Water quality is the term widely used in multiple scientific publications and normative documents relating to the necessities of "sustainable" and "optimal" management of water resources. The water quality index (WQI) has been considered to give a criteria for surface water classification based on the use of standard parameters for water characterization (Pesce and Wunderlin, 2000; Swamee and Tyagi, 2000; Bordalo *et al.*, 2001; Cude, 2001; Nagel, 2001; Jonnalagadda and Mhere, 2011; Liou *et al.*, 2003; Hernandez Romero *et al.,* 2004). This index is a mathematical instrument used to transform large quantities of water characterization data into a single number, which represents the water quality level.

The primary objectives of the present study are to assess the effluent from the leather tanneries to characterize and to find out the correlation co-efficient for all the possible correlation among water quality parameters. Analysis of any monitered parameter either in alone or group according to a common feature, provides partial information on the over all water quality. In this study a data matrix obtained during the monitoring period October 2010 - March 2011 is subjected to water quality index to assess and to classify water quality from multiple measured parameters.

EXPERIMENTAL METHODOLOGY

Study site:

The study area is located in the southern part of India, close to Kodaganar river basis, mainly in hard rock terrain. The area is known for its leather industries. It lies between $10^0$13'44" – $10^0$26'47" N latitude and $77^0$55'08" – $78^0$01'24" E longitude and falls in survey of India Top sheet No.58 F/15 and J/3, in the state of Tamil nadu, India. The selected area is located in the central part of Dindigul town and along Madurai, Batlagundu and Ponmadurai roads.

Analysis of waste water effluent:

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 liter 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 8M HNO_3 were used to wash the polythene bottles of 100ml capacity, which is 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) preservatives are essential for retarding, biological action, hydrolysis for chemical compounds and complexes and reduction of volatility of constituents for measuring COD, H_2SO_4 was added to bring pH to two and then preserved. For phosphates, 20mg 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 20^0 C.

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; Sanchez *et al.*, 2006). 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 1.

Water quality indices (WQI) calculation:

Water quality index was calculated using k = 1 in all the cases to account only for the variations due to measured parameters as

$$\mathbf{WQI = k \sum_{i=1}^{n} C_i P_i / \sum_{i=1}^{n} P_i} \quad (1)$$

The water quality classification system adopted here is proposed by kannel *et al.* (2007); Jonnalagadda and Mhere (2001); Dojlido *et al.* (1994). According to which, WQI in the range of 0 – 25 is very bad, 26- 50 is bad, 51 – 70 is medium, 71 – 90 is good and 91 – 100 is excellent.

Table 2 gives the different parameters that were used

Table 1 : Analytical method used during October 2010 to March 2011 for tannery effluents

Parameters	Abbreviation	units	Analytical methods	Instrument
Water temperature	Wtemp	^{0}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^{0}C	Winlker azide method
Chemical oxygen demand	COD	mg/L	Potassium dichromate oxidation (open reflux, titrimetric)	Dichromate method

Table 2 : Normalization factor

Variable	Units	Relative weight pi	Normalization factor (ci)										
			100	90	80	70	60	50	40	30	20	10	0
Wtemp	° C	1	21/16	22/15	24/14	26/12	28/10	30/5	32/0	36/"2	40/"4	45/"6	>45/<"6
pH	pH unit	1	7	7 - 8	7 - 8.5	7 - 9	6.5 - 7	6 - 9.5	5 - 10	4 - 11	3 - 12	2 - 13	1 - 14
EC	µS/cm	1	<750	<1000	<1250	<1500	<2000	<2500	<3000	<5000	<8000	<=12000	>12000
DO	mg/l	4	>=7.5	>7	>6.5	>6	>5	>4	>3.5	>3	>2	>=1	<1
TDS	mg/l	2	<100	<500	<750	<1000	<1500	<2000	<3000	<5000	<10000	<=20000	>20000
TSS	mg/l	4	<20	<40	<60	<80	<100	<120	< 160	<240	<320	<400	>400
Ca	mg/l	1	<10	<50	<100	<150	<200	<300	<400	<500	<600	<=1000	>1000
Mg	mg/l	1	<10	<25	<50	<75	<100	<150	<200	<250	<300	<=500	>500
Hardness	mg/l	1	<25	<100	<200	<300	<400	<500	<600	<800	<1000	<=1500	>1500
Cl	mg/l	1	<25	<50	<100	<150	<200	<300	<500	<700	<1000	<=1500	>1500
SO_4	mg/l	2	<25	<50	<75	<100	<150	<250	<400	<600	<1000	<=1500	>1500
PO_4P	mgP/l	1	<0.025	<0.05	<0.1	<0.2	<0.3	<0.5	<0.75	<1	<1.5	<=2	>2
NO_3	$mgNO_3$/l	2	<0.5	<2	< 4	<6	<8	<10	<15	<20	<50	<=100	>100
NO_2	$mgNO_2$/l	2	<0.005	<0.01	<0.03	<0.05	<0.1	<0.15	<0.2	<0.25	<0.5	<=1	>1
BOD	mg/l	3	<0.5	<2	< 3	<4	<5	<6	<8	<10	<12	<=15	>15
COD	mg/l	3	<5	<10	<20	<30	<40	<50	<60	<80	<100	<=150	>150

in the evaluation process, as well as their relative's weights and the normalization factor. These values ware adopted from various literatures : (Pesce and Wunderlin, 2000; Cude, 2001; Debels *et al.*, 2005; Sanchez *et al.*,2006; Kannel *et al.*, 2007).

To get the access of water quality using minimum number of parameters, Pesce and Wunderlin (2000) used Dissolved oxygen, Turbidity and conductivity and calculated the minimum water quality index. However, realizing the important parameters as temperature, pH, Dissolved oxygen, Total suspended solids and Electrical conductivity (weights are given equal to each parameter) to calculate the minimum water quality index (termed WQI min hereafter) as :

$$\mathbf{WQI\ min = k \sum_{i=1}^{5} C_i P_i / s} \quad (2)$$

EXPERIMENTAL FINDINGS AND ANALYSIS

The values of range and average of various water quality parameters of waste water generated from leather tannery collected from October 2010 - March 2011 have been summarized along with the permissible values prescribed by Bureau of Indian Standard (BIS, 1983) for drinking purpose, for industrial effluent discharge into on land surface water, on land for irrigation and into public sewers (BIS, 1983).

Further relation may be decide by the concerned agencies,** paper, dyestuff, pesticide and certain chemical and petrochemical industries, these values are relaxed; it shall be ensured that the effluent passes the test for lethal toxicity as given in IS : 6582 – 1972.*** If all these pollutants are present at the maximum permissible concentration, the effluent may lead to eutrophication. Therefore, data on eco – logical changes should be monitored, ++ IS : 2296, Standards Institution, New Delhi.1974.Ref: IS: 2490, IS : 3307;IS : 3360; IS : 2296 and IS :

The average temperature of leather tannery effluent is 26.95^0 C which is found to be ambient and almost equal to that of room temperature (30.5^0C ± 2^0C) observed on the day of sample collection. Hence tannery effluent is not thermally polluted. The parameter of temperature is basically important for its effects on physical and chemistry reaction in the water. The temperature ranged from 30 to 30.5^0C in the all stations and there is no wide fluctuation in temperature or with minimum variation at

Table 3 : Range and average values of water quality parameters of leather tanneryfluent, limit for drinking purpose and discharge of industrial effluents, prescribed by BIS in mg/L

Parameters	Limit prescribed by IS:10500, 1983				Limits prescribed by IS for industrial effluents discharges		
	Range	Average	Allowable missible	Max per- surface	Into inland water IS:2490-1974	Into land irrigation IS:3307-1977	Into public sewers IS:2490-1981
Parameters							
Temperature	25 - 35 ° C	30?C	-	-	shall not	- exceed 40°C 45?C at the	point of discharge
pH	6.4 - 9.5	8.1	6.5 - 8.5	6.5 - 8.5	5.5 - 9.0	5.5 - 9.0	5.5 - 9.0
Electrical conductivity	4920 – 6800	5530	-	-	-	3000++	5.5-9.0
Turbidity(NTU)	78.5 - 99.6	84.7	-	-	-	-	-
Alkalinity	120 - 398	254	-	-	-	-	-
BOD	5630 - 7015	6856	-	-	30	100+	350+
COD	6763 - 8840	7432	-	-	250**	-	-
Calcium	281 - 476	364	75	200	-	-	-
Magnesium	99.8 - 272	151	30	100	-	-	-
Chloride	1692 - 1907	1894	250	1000	1000	600	1000
Sulphates	498-608.5	540	150	400	1000	1000	1000
Phosphates	182 – 310	224	-	-	5***	-	-
Total hardness	270 – 465	342	300	600	-	-	-
Total acidity	35 – 55	45	-	-	-	-	-
Total solids	1070 – 4610	3070.1	-	-	-	-	-
Total dissolved solids	914 – 3698	2516	500	1500	2100	2100	2100
Dissolved oxygen	0-10	0.5	-	-	-	-	-

all times, A rise in temperature of the water leads to the speeding up of the chemical reactions in water, reduces the solubility of gases and amplifies the taste and odour (Trivedy and Goel, 1986). Hydrogen ion concentration provides a good estimate of acidity and alkalinity of water. Hydrogen ion concentration of the sample analyzed was found to range between 6.3 and 7.56 of the tannery effluent. The pollutant present in the effluent alters the acidity of the effluent in natural waters. Dissolved solids are composed mainly of carbonates, Bicarbonates, Chloride, Sulphates, Phosphates and nitrate of calcium, Magnesium, Sodium, Potassium, iron and manganese. Among the samples analyzed for total dissolved salt ranged from 10,100 to 27,444 mg/l. Total suspended solid range from 2100 to 2500 mg/l. The increased level of solids in the effluent may be due to the secondary pollution due to leakage and storage. The total dissolved solid is an important parameter in the water quality standards. Chloride concentration depends on the characteristics of sediments and the pollution load. The concentration of chloride was in the range of 1360 mg/l to 11133 mg/l. Sulphate ion concentration is found to be from 500 mg/l to 1299 mg/l. Fluxuations in this values and Concentration of sulphates linked to the status in and around environment.

The Electrical conductivity of the tannery effluent is in the range of 14533 mg/l to 40359 mg/l which is well above the permissible limits. The total dissolved salts are very high. Since mostly the ionic substances such as acids and bases are responsible for the higher electrical conductivity (EC). Alkalinity causes corrosion and influences the chemical and biochemical reactions. The value of average alkalinity of leather tannery effluent sample is 1772 mg/l. Hardness of water is due to the presence of dissolved chloride, Sulphate, Carbonate and bicarbonates of calcium, Magnesium ions. The average and range of total hardness are 1170 mg/l and 2230 mg/l to 3400 mg/l, respectively. The total hardness well above the prescribed limit. Industrial effluents have more phosphate ion with an average 5.5 mg/l than the permissible limit prescribed by BIS standards. Biochemical oxygen demand(BOD) is a measure of biologically degrable organic matter. Chemical oxygen demand (COD) is a measure of chemically oxidisable organic matter. High load of organic compounds in the effluent may cause an increase in BOD and COD load and simultaneous depletion of DO concentration. The observed values of BOD (average = 2600 mg/l, range = 2000 – 3200 mg/l), COD (average = 5083 mg/l, range = 4000 – 6000 mg/l) and Dissolved oxygen (average = 1.37 mg/l, range = 1.10 – 1.63 mg/l) are found to be very high and well above the limit prescribed by BIS, indicating as heavy load of organic compounds in the leather tannery effluents. The average levels of calcium and magnesium ions varied 561 mg/l and 294 mg/l, respectively. These cations exceeded the permissible limit as prescribed by BIS Standards.

Amidst the various cations analyzed sodium content is very high and well above the toxic level. Sodium represents in the range 1900 – 6200 mg/l, Potassium 179 mg/l – 1600 mg/l, Iron 3 mg/l – 3.8 mg/l, Total chromium 154 mg/l – 233 mg/l, respectively. The turbidity of effluent ranged from 400 – 480 NTU above its prescribed limit. The high turbidity may ascribed to the living and non living suspended matter. Fluoride level range from 1.1 – 2.4 mg/l. The level of fluoride recorded was found to be above the prescribed limit. The nitrate and nitrite present in the tannery varied between 0.29 to 0.31 mg/l and 45 to 48 mg/l, respectively. They are found to be above the prescribed limit. It is observed that all the physical and chemical parameters are well above the permissible limits.

The mean physical and chemical parameters of the tannery effluent along with minimum – maximum, range, medium and standard deviation are represented in the Table 4.

Correlation among water quality parameters of leather effluents:

The correlation co-efficient(r values) for all the possible correlation among water quality parameters are presented in the form of a correlation matrix in Table 5.

In order to establish the relationship of various physico chemical parameters, correlation analysis was undertaken. In leather tannery effluent analysis significant positive correlation was observed between different pairs of other parameters such as temperature and free ammonia(r = 0.84) ,Temperature and nitrite (r = 0.75). With temperature, other parameters showed Positive and insignificant correlation to one another. The parameter pH is found to have positive and significant correlation such as pH and Iron(r = 0.81), pH and Phosphate(r = 0.86) pH and chromium(r=0.87).pH and BOD(r = 0.71) and pH and COD(r = 0.83). It is interesting to know that pH had significant and negative correlation with pH and Turbidity (r = -0.72); pH and TDS (r = -0.85), pH and EC(r = -0.85), pH and Alkalinity (r = -0.83),pH and Total hardness (r = -0.73), pH and calcium (r = -0.83), pH and magnesium(r = -0.766), pH and sodium (r = -0.85),pH and potassium(r = -0.85),pH and fluoride(r = -0.82),pH and SO_4^{-2} (r = -0.85),pH and DO (r = -0.87).

Turbidity hadPositive and significant correlation with TDS, EC, Alkalinity, Total hardness, Calcium, Magnesium, Sodium, Potassium, Fluoride, Sulphate and dissolved

Table 4 : Statistical values of water quality parameters of leather tannery effluents

Sr. No.	Name of the parameters	Mini	Max	Range	mean	medium	Std.deviation
1.	Temp	26.2	28.3	2.1	26.95	26.55	0.8139
2.	pH	6.3	7.56	1.26	6.7	6.59	0.4411
3.	Turbidity	400	480	80	434	430	27.45
4.	TDS	10100	27444	17344	19713	21975.5	4949.68
5.	TSS	2100	2500	400	2244	2199	125.64
6.	EC	14533	40359	25826	28935	45558	11049.87
7.	Alkalinity total of $CaCO_3$	308	2080	1772	1330	1610	1464.25
8.	Total hardness	2230	3400	1170	2653	2474	407.67
9.	Calcium	504	640	136	561	554.5	47.84
10.	Magnesium	233	432	199	294	257.5	71.99
11.	Sodium	1900	6200	4300	4388	5081	1890.95
12.	Potassium	179	1600	1421	901.7	1004	535.57
13.	Iron	3	3.83	0.83	3.41	3.355	0.3073
14.	Free ammonia	1.79	1.82	0.03	1.8	1.795	0.0122
15.	Nitrite	0.29	0.31	0.02	0.3	0.305	0.0135
16.	Nitrate	45	48	3	47.5	47.5	1.08
17.	Chloride	1360	11133	9773	8360	6176	3946.14
18.	Fluoride	1.1	2.4	0.3	1.45	2	0.55
19.	Sulphate	500	1299	799	966	1096.5	353.29
20.	Phosphate	0.45	6.25	5.8	2.9	2.07	2.5247
21.	Total chromium	154	233	79	194	194.5	32.3084
22.	BOD	2000	3200	1200	2600	2650	458.26
23.	COD	4000	6000	2000	5083	5200	837.49
24.	DO	1.1	1.63	0.53	1.37	1.4	0.2067

oxygen. It is evident from the table that turbidity is due to the presence of dissolved ions. Turbidity has negative and significant correlation with iron, phosphate, chromium, BOD and COD. Total dissolved solids have positive and significant correlation with EC, Alkalinity, Total hardness, Ca, Mg, Na and chloride. It has negative but significant correlation with iron, NH_3, nitrate and nitrite. Total suspended solids have insignificant positive and negative correlation with other parameters. Water quality parameters such as electrical conductivity have Positive correlation with Alkalinity, Total hardness, Ca, Mg, Na, K, F, SO_4^{2-} and Dissolved oxygen. It have significant negative correlation with iron, nitrite, PO_4^{3-}, Total chromium, BOD and COD. Alkalinity have Positive correlation with total hardness , Ca, Mg, Na, K, F and Sulphate. It has negative correlation with iron, PO_4^{3-}, Cr, BOD, COD and DO. Total hardness has Positive and significant correlation with Ca, Mg, Na, K, F, S and DO but negative significant correlation, Fe, PO_4^{3-}, Cr, BOD and COD. Calcium have Positive correlation with Mg, Na, K, NH_3, F, SO_4^{2-} and DO. But negative correlation with Iron, phosphate, Cr, BOD and COD. Magnesium have Positive correlation with Na, K, NH_3, F, SO_4^{2-} and DO. But negative significant correlation with PO_4^{3-}, Cr, BOD and COD. Sodium have positive correlation with K, F, SO_4^{2-}; and DO but negative correlation with Iron, PO_4^{3-}, Cr, BOD and COD. Potassium have positive significant correlation with F, SO_4^{2-} and DO but negative correlation with Iron, PO^{3-}, Cr, BOD and COD. Iron have Positive significant correlation with PO^{3-}, Cr, BOD and COD. But negative significant correlation with nitrate, Cl, F and DO. Nitrite and nitrate have significant and negative correlation with chloride alone. Fluoride have significant correlation with sulphate and DO and negative significant correlation with PO^{3-}, Cr, BOD and COD. Sulphate have Positive significant correlation with Do oxygen. But negative significant correlation with PO^{3-}, Cr, BOD and COD. Phosphate have Positive significant correlation with Cr, BOD and COD and COD and negative significant correlation with DO. Chromium have Positive significant correlation with BOD and COD and negative significant correlation with DO. BOD have Positive significant correlation with COD and negative significant correlation with DO. COD have negative significant correlation with DO. The study revealed that all the physico chemical parameters are either positively or negatively significantly correlated with each other.

Table 5 : Co-efficient of correlation among water quality parameters leather tannery effluent

Parameters	Temp	pH	Turb	TDS	TSS	EC	Alk	T.H.	Ca	Mg	Na	K	Iron	F.A.	Nitrite	Nitrate	Cl	F	SO_4^{2}	PO_4^{2}	T.Cr.	BOD	COD	DO
Temp	1	0.19	0.02	0.18	0.15	0.18	0.22	0.29	0.61	0.3	0.24	0.12	0.41	0.84	0.75	0.18	0.75	0.24	0.23	0.19	0.13	0.13	0.09	0.07
pH		1	0.72	0.85	0.16	0.85	0.85	0.73	0.83	0.66	0.85	0.85	0.81	0.24	0.008	0.34	0.33	0.82	0.85	0.86	0.87	0.71	0.83	0.87
Turbidity			1	0.91	0.09	0.91	0.89	0.95	0.98	0.94	0.87	0.94	0.69	0.2	0.34	0.08	0.22	0.89	0.88	0.89	0.92	0.79	0.92	0.94
TDS				1	0.18	0.99	0.99	0.8	0.92	0.75	0.42	0.2	0.63	0.66	0.45	0.53	0.99	0.37	0.41	0.39	0.33	0.18	0.3	0.24
TSS					1	0.18	0.18	0.08	0.09	0.05	0.18	0.16	0.2	0.32	0.12	0.09	0.01	0.14	0.18	0.18	0.22	0.33	0.1	0.15
EC						1	0.998	0.8	0.92	0.76	0.997	0.993	0.93	0.47	0.4	0.19	0.35	0.995	0.998	0.99	0.97	0.81	0.94	0.98
Alkalinity							1	0.773	0.9	0.73	0.999	0.988	0.95	0.08	0.398	0.2	0.389	0.996	0.999	0.999	0.96	0.81	0.93	0.95
Tot. Hardness								1	0.83	0.995	0.75	0.86	0.53	0.44	0.17	0.16	0.195	0.76	0.76	0.783	0.86	0.695	0.86	0.87
Calcium									1	0.94	0.888	0.955	0.72	0.72	0.2	0.11	0.007	0.9	0.89	0.9	0.94	0.81	0.92	0.97
Magnesium										1	0.7	0.82	0.47	0.5	0.08	0.11	0.27	0.72	0.711	0.73	0.82	0.669	0.82	0.94
Sodium											1	0.98	0.96	0.09	0.4	0.196	0.411	0.996	0.999	0.998	0.96	0.81	0.92	0.977
Potassium												1	0.866	0.043	0.39	0.21	0.24	0.97	0.97	0.98	0.98	0.798	0.95	0.996
Iron													1	0.271	0.389	0.22	0.62	0.9	0.95	0.94	0.86	0.73	0.81	0.88
Free Ammonia														1	0.71	0.21	0.68	0.07	0.09	0.053	0.08	0.26	0.115	0.09
Nitrite															1	0.42	0.46	0.38	0.4	0.38	0.378	0.09	0.39	0.32
Nitrate																1	0.53	0.13	0.196	0.21	0.32	0.14	0.3	0.17
Chloride																	1	0.37	0.4	0.37	0.31	0.17	0.29	0.23
Fluroide																		1	0.996	0.995	0.95	0.85	0.92	0.98
Sulphate																			1	0.998	0.96	0.8	0.93	0.988
Pohsphate																				1	0.97	0.81	0.93	0.99
T. Cr.																					1	0.83	0.991	0.98
B.O.D.																						1	0.86	0.84
C.O.D.																							1	0.95
D.O.																								1

Assessing the water quality using water quality index:

Water quality indices appeared in the literature as early as 1965 (Horton, 1965). The general WQI was developed by Bordalo *et al.* (2001). WQI is a mathematical instrument used to transform large quantities of water quality data into a single number (Stambuk-giljanovic, 1999) which provides a simple and understandable tool for managers and decision makers on the quality and possible uses of a given water body (Bordalp *et al.*, 2001). It serves the purpose to improve understanding of water quality status and evaluate water quality trends, to the public and policy makers that are important in terms of increased support for water resources improvement efforts (Cude, 2001). WQI also permits the assessment of changes in water quality and to identify water trends (Chapman, 1992).

Realizing the importance of parameters such as pH, Temp, EC, TSS and DO minimum water quality index was calculated. It is documented in Table 6.

Table 6 : WQI for leather tannery effluent using minimum number of parameters

Sampling period	WQI	Water class
Oct.-10	30	Bad
Nov.-10	40	Bad
Dec.-10	40	Bad
Jan.-11	36	Bad
Feb.-11	38	Bad
Mar.-11	34	Bad

Table 6. Clearly showed that WQI characterized the tannery effluent as bad water class.

WQI is also calculated using all the parameters and using the formula:

$$\mathbf{WQI = k \sum_{i=1}^{n} C_i P_i / \sum_{i=1}^{n} P_i}$$

WQI is tabulated in Table 7

Table 7 revealed that leather tannery belonged to the very bad water class.

To understand the status of industrial waste water better, some categories have been considered. These

Table 7 : Revealed that leather tannery belonged to the very bad water class.

Sampling period	WQI(16)	Water class
Oct.-10	10.67	Very bad
Nov.-10	13	Very bad
Dec.-10	11.33	Very bad
Jan.-11	12	Very bad
Feb.-11	13.33	Very bad
Mar.-11	12.33	Very bad

categories showed hazard of waste water low, moderate and severe. These classes have been showed that suggested base on limit threshold of pollutants it given Table 8.

Table 8 : Class of hazards of effluents waste water based on limit threshold

Parameter	low (mg/lit)	moderate (mg/lit)	severe
Fe	< 3	3	> 3
Nitrate	0	50 - 10	> 50
pH	6 - 6.5	6.5 - 9	> 9
COD	< 60	6 - 200	> 200

The values of parameters such as Fe, nitrate, pH and COD of the effluent of leather tannery has been reported in Table 9.

Iron and COD parameters of tannery effluent showed that effluent are in the severe class. The quality of tannery effluent showed that pH and nitrate are low and moderate class. The quality of waste water is not suitable for irrigation.

According to Davis and Dewiest (1966), water can be classified based on the concentration of TDS as given in Table 10.

Total dissolved solids 10,100 mg/l – 27,444 mg/l and is more likely to be increased in the tannery effluents. Total dissolved solids during the sampling period are more than the permissible limits and the table clearly showed that tannery effluent is neither useful for irrigation nor allowing them into the land. Sodium adsorption ratio for the tannery effluent was calculated using the formula:

Table 9 : Physico-chemical parameters and class of hazards of tannery effluent

Sampling period	Fe mg/lit	Class	Nitrate	Class	pH	Class	COD (mg/lit)	Class of hazard
Oct.-10	3.31	Severe	48	Moderate	6.36	Low	4200	Severe
Nov.-10	3.158	Severe	45	Moderate	6.3	Low	4000	Severe
Dec.-10	3	Moderate	48	Moderate	6.38	Low	4600	Severe
Jan.-11	3.409	Severe	47	Moderate	6.9	Moderate	5800	Severe
Feb.-11	3.83	Severe	48	Moderate	7.56	Moderate	5900	Severe
Mar.-11	3.79	Severe	47	Moderate	6.8	Moderate	6000	Severe

Table 10 : Classification of water based on concentration of total dissolves solids

TDS	Water type
Up to 500	Desirable for drinking
500 - 1000	Permissible for drinking
< 3000	Useful for irrigation
> 3000	Unfit for drinking and irrigation

Table 11 :

Parameters	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Average
Na	6100	6120	6200	4062	1950	1900	4388
Ca	640	597	576	533	504	517	561
Mg	432	345	269	246	233	241	294
SAR	186.3	199.4	213.3	145.5	71.82	69.01	147.55

$$\mathbf{SAR = Na / \sqrt{[Ca + Mg]/2}} \qquad (4)$$

Since the SAR (Sodium adsorption ratio) tannery effluent is higher. It means that it cannot be used for irrigation purpose.

Conclusion:

The assessment of tannery effluent for various parameters gave the following conclusion.

– The physico – chemical parameters such as Temp, pH, Turbidity, TDS, EC, Alkalinity, Total hardness, Calcium, Magnesium, Sodium, Potassium, Fluoride, Free ammonia, Nitrate, Nitrite, Chloride, Phosphate, Sulphate, Iron, Dissolved oxygen, Biological oxygen demand, Chemical oxygen demand and Total suspended solids were found to be very high and well above the permissible limit and cannot be used into in land and into land for irrigation and into public sewers.

– The correlation co-efficient for all the possible correlation among the water quality showed significant correlation and linearly related to each other.

– Water quality index integrates the result of the environment parameters into a single score in time and space which allows water quality to be viewed in terms of numerically values that qualifies possible water uses. WQI minimum reflects water quality because it takes into consideration 5 key parameters which present in same environmental importance to described water quality. WQI minimum for leather tannery shows that the tannery effluent belong to bad water class.

WQI index considering 16 parameters of waste water leather effluent were used in the evaluation on the basis of relative weight and normalization factors. Water quality classification lies in the range 0 - 25 which is said to be very bad water class. Hence leather tannery effluent comes under the very bad class water.

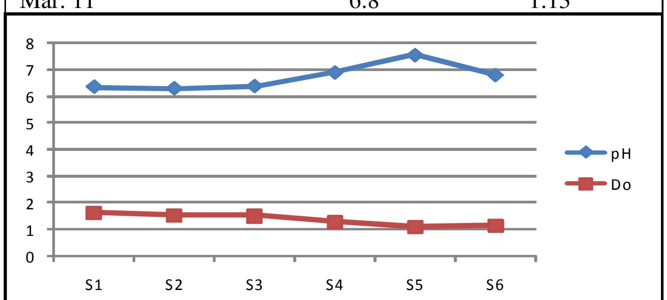
– Class of hazards tannery effluent waste water based on limit threshold of Iron, Nitrate, pH and COD showed that the water belonged to severe class and not suitable for irrigation. The quality of effluent does not have proper quality to agricultural usages.

– Total dissolved solids for the tannery effluent was in the range of 10,100 mg/l – 27,444 mg/l. Tannery effluent was highly saline because the total dissolved solids lies with in the range of 10,000 mg/l – 1,00,000 mg/l. Since the effluent contains total dissolved solids more than 3000 mg/l, it is unsafe to use.

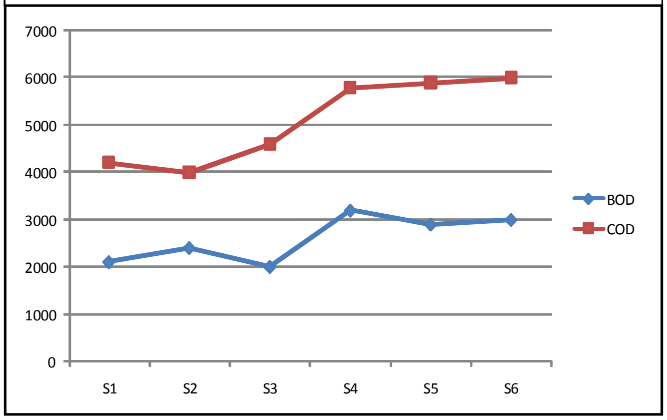
– For irrigation purposes the pH value of tannery effluent water highly basic. BOD and COD were very high showing that no life sign could be present in the effluents. Effluent was very rich in Calcium, Magnesium, Sodium, Chloride and suspended solids. Hardness was also very strong rendering it unfit for domestic use. For irrigation purposes, water is usually classified for its quality on the basis of electrical conductivity and sodium adsorption criteria. According to these categories, full

Correlation between pH and dissolved oxygen

Sampling month	pH	DO
Oct. 10	6.36	1.63
Nov. 10	6.3	1.55
Dec. 10	6.38	1.51
Jan. 11	6.9	1.29
Feb. 11	7.56	1.1
Mar. 11	6.8	1.13



Correlation between BOD and COD		
Sampling month	BOD	COD
Oct. 10	2100	4200
Nov. 10	2400	4000
Dec. 10	2000	4600
Jan. 10	3200	5800
Feb. 10	2900	5900
Mar. 10	3000	6000



strength waste was very high in salts and placed in C3 – S1 category that is, highly saline and low sodium water. Effluent contained much higher amount of total dissolved solids, Suspended solids, BOD, COD, Calcium, Magnesium, Sodium, Chloride, Electrical Conductivity, Sodium adsorption ratio, pH, Total cations and anions as compared to control. The results of effluent analysis at the source are in conformity with the studies of sever workers (Algur *et al.*, 1995, Chatterjee and Chatterjee, 2000; Sillen and Wartell, 1989; Wahid *et al.*, 1999, 2000).It can be concluded that physical and chemical parameters of well above the permissible limit prescribed by ISI and WHO for any purpose. It is also concluded that analysis of effluent from leather tannery will certainly simplify the task of rapid monitoring and control of water pollution.

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