

Akhand Pratap Singh^[a] and Devendra Pratap Rao^{[a]*}

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The tannery effluent collected at monthly interval from January 2011 to December 2011 and analyzed for its characteristics. Samples were collected from one of the tannery from Jajmau area of Kanpur city of India. Results of the analysis showed that presence of addition chemical load like iron, calcium, magnesium, carbonate, bicarbonate, chloride and BOD were found in the discharged effluent of the above stated tannery. The analysis of various physical and chemical characteristics of tannery effluents showed variations according to month and results reveals that these are certain relationships between physico-chemical characteristics of effluents both positive and negative.

* Corresponding Author

- E-Mail: devendraprataprao@yahoo.com [a] Department of Chemistry, D.A-V. P.G. College,
- Kanpur-208001, U.P., India.

Introduction

In global scenario, Kanpur is the top and famous for tannery industries. The Kanpur city is also known for their pollution in the world. The main reason of the pollution in Kanpur is due to the Tannery. Only about 20% of the chemicals used in the tanning process are absorbed by leather. Rest of these are released as waste, which is absorbed by bioaccumulation process in cultivated crops.^{1,2} The wastes from the tannery consist of tanned and untanned solids, waste effluents, and waste gases.3 Environmental pollution is one of the major problems of the world which increases day by day due to urbanization and industrialization. Over the last few decades, large scale usage of chemicals in various human activities has grown very fast, particularly in a country like India.⁴ Ground water is of great importance for potable water supply and also serves for the agricultural irrigation and industrial production. Ground water resources are experiencing an increasing threat of pollution coming from urbanization, industrial development and agricultural activities.⁵ The global water pollution due to the increase in number of industries is a serious problem faced by the modern world.⁶ Release of the effluents in the receiving water is the major reason for water pollution. These pollutants find their way to aquatic ecosystem such as rivers and ponds and lakes, which pose a risk to the health of human and ecosystem.⁷Almost all industries discharge water containing wastes in one stage or another during their manufacturing process. Industrial waste is not the same in every case. As a result the presence of pollutants in water alters different physico-chemical parameters from their normal prescribed levels.⁸ Negative impacts on water quality includes increase in turbidity, colour, nutrient load, addition of toxic and persistent compounds.9 The diversity in physical, chemical, and biological characteristics of tannery effluent is so much that each effluent habitat requires a separate study.

In the present study an attempt has been made to correlate chemical properties of polluted water discharged from tannery.

Materials and Experimental Methods

Samples and sampling sites

Samples were taken from one of the tannery from Jajmau area of Kanpur city of India. The study was conducted by a series of following tasks: (i) visit to tanneries and surrounding areas and (ii) on-site assessments and interviews with relevant personnel including workers, managers and other stakeholders.

The samples of effluent were collected from tannery for one month intervals from the spots fixed. The samples were collected in glass bottle (1.0 litre) and were corked immediately. All the samples were brought to the laboratory and stored at 4 °C temperatures in refrigerator till the analyses were completed. All chemical analyses were done in evening or the following days. All four or five samples of different sites were combined to get an integrated sample of the water. This sample was used for the tests given below. The sampling procedure was the same as described in Indian standard methods of sampling and test for water used in industries, I.S.I. New Delhi, India.

The physical and chemical characteristics analyzed for the effluents were colour, temperature, pH, carbonate, bicarbonate, chloride, total alkalinity, nitrite, total hardness, alkaline hardness, total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), dissolved oxygen (DO), oxygen consumed by potassium permanganate, BOD, calcium, chromium, potassium, magnesium, phosphorus, sulfur, nitrogen, iron, and manganese. The pH and temperature measurements were performed for each of the above given components were the same as described in IBH hand book No.-8,¹⁰ USDA hand book no.-60,¹¹ and Laboratory methods for blue green algae.¹² Standard methods for sampling and test for water used in industries,

ISI New Delhi is 2490¹³ and as earlier used by Mohan.¹⁴ The correlationships between various characteristics of effluent tested were worked out. The concentration of dissolved oxygen (DO) present in effluent samples was estimated by Winkler method. The alkalinity was analyzed by titrating against sodium thiosulfate using as indicator.¹⁵ The BOD, TDS, and TS determination of effluent samples were carried out using standard methods.¹⁶ The determination of COD was carried out according to Ademoroti.¹⁷

All data were statistically analyzed and tested for significance at 5% and 10% probability levels. For significant and highly significant 'r' values respectively one and two asterisks have been used.

Results and Discussion

The physico-chemical characteristics of the tannery effluent were found to be highly variable monthly (Table 1). The following relationships between the characteristics were found (Table 2).

Table 1. The physico-chemical characteristics of the tannery effluent.

Positive correlation-ships

Positive correlation-ships were observed between temperature with nitrite; pH with each total solids, total chromium, dissolved oxygen and oxygen consumed by KMnO₄; carbonate with each bicarbonate, chloride, total hardness, alkaline hardness, total solids and total suspended solid; bicarbonate with each chloride, total hardness, alkaline hardness and total solids, total dissolved solids and total suspended solids; chloride with each nitrite, total hardness, alkaline hardness, total chromium, total solids and total suspended solid; total alkalinity with each nitrite, total chromium and total dissolved solids; total hardness with each alkaline hardness, total solids, total dissolved solids and total suspended solid; nitrite with each total chromium, total dissolved solids and BOD; alkaline hardness with total suspended solid, total solid, total dissolved solid; total solids with each total dissolved solids, total suspended solid, dissolved oxygen and BOD; J.C. Akan et al. have also been studies a positive correlation between these parameters¹⁸ total dissolved solids with total suspended solid; dissolved

Period of	Characteristics of effluent												
sample	Colour	Temp. (°C)	рН	Carbonate	Bicarbonate	Chloride	Total alkalinity as CaCO ₃	Total Cr	Total hardness as CaCO ₃	Alkaline hard- ness as CaCO ₃	TS	TDS	TSS
								m	eq. L ⁻¹				
Jan. 2011	Brown	23.7	5.2	3.1	2.0	277	1336	14.35	3500	710	1072	10460	625
Feb. 2011	Gray	24.0	4.6	2.3	1.5	341	1260	15.76	3400	670	741	10670	727
Mar. 2011	Brown	24.5	4.7	5.0	1.3	256	1372	13.70	2400	760	1062	10350	635
Apr. 2011	Light Brown	22.5	5.9	5.4	4.9	275	1436	15.35	2700	570	1970	10675	725
May. 2011	Brown	30.6	4.8	4.3	5.7	293	1251	16.65	2500	630	1862	10255	875
Jun. 2011	Brown	32.0	3.7	5.1	1.2	234	1382	13.75	2400	550	1859	10560	805
Jul. 2011	Brown	27.0	4.8	4.3	3.9	283	1347	14.25	2960	578	2065	10670	887
Aug. 2011	Brown	29.4	4.6	5.2	4.1	267	1293	16.65	3400	560	1852	10340	783
Sept. 2011	Brown	23.0	4.6	5.7	2.9	231	1380	12.76	2800	570	1870	10565	793
Oct. 2011	Brown	28.0	4.2	4.3	4.8	263	1140	16.35	2700	540	1472	10375	855
Nov. 2011	Gray	22.8	4.5	1.2	2.9	288	993	15.65	2600	630	769	10445	731
Dec. 2011	Deep Brown	20.7	4.9	1.7	5.7	267	1149	13.79	2630	576	842	10670	767

Table 1. (cont.)

Period of	Characteristics of effluent													
sample	Colour	DO	BOD	COD	[a]	Ca	Κ	Mg	Р	S	Ν	Fe	Mn	
		meq. L^{-1}				mg L^{-1} effluent								
Jan. 2011	Brown	0.4	876	4435	2.3	575	489	385	375	240	2031	6.80	1.58	
Feb. 2011	Gray	1.5	965	4485	3.2	595	665	380	145	162	1167	7.52	1.76	
Mar. 2011	Brown	1.7	886	4815	1.6	535	940	364	276	292	1074	5.85	0.50	
Apr. 2011	Light Brown	0.2	835	4515	1.6	575	689	362	256	264	1068	6.75	2.85	
May. 2011	Brown	0.5	935	4456	2.2	650	849	385	194	83	1167	5.30	1.90	
Jun. 2011	Brown	0.7	856	4845	2.7	535	972	364	183	635	1179	6.50	3.82	
Jul. 2011	Brown	1.5	945	4879	2.3	570	764	352	62	84	1176	7.75	0.87	
Aug. 2011	Brown	1.8	985	4750	3.2	556	872	379	182	182	1085	6.45	2.45	
Sept. 2011	Brown	0.3	1125	4625	2.5	575	870	355	169	172	1065	5.70	1.40	
Oct. 2011	Brown	0.6	945	4435	2.2	535	962	352	132	175	1165	7.30	0.80	
Nov. 2011	Gray	1.2	958	4345	3.6	680	582	372	143	162	1056	5.45	2.30	
Dec. 2011	Deep Brown	1.8	923	4390	2.1	570	868	342	147	252	1345	6.50	0.75	

^a Oxygen consumed by KMnO₄ in 3 hrs.

Table 2. Correlation coefficients.

Variables	Нq	CO ₃ ^{2–}	HCO3 ⁻	CI⁻	Total Alkalinity	NO_2^-	Total Cr	Total Hardness	Alkaline Hardness	TS	TDS	TSS
Temp.	-0.88*	+0.79	+0.919*	+0.034	-0.256	+0.856*	+0.866*	-0.185	+0.133	+0.053	+0.034	-0.042
pН		-0.78	-0.693**	-0.577*	-0.357**	-0.542	+0.578	-0.764*	-0.978**	+0.787	-0.497	-0.878*
CO3 ²⁻			+0.882*	+0.877*	+0.166	+0.442	+0.645*	+0.787*	+0.977*	+0.844*	+0.388	+0.822*
HCO_3^-				+0.683*	+0.353	+0.387	+0.432	+0.876	+0.958*	+0.833*	-0.598	+0.897*
Cl⁻					-0.022	+0.863*	+0.654*	+0.565	+0.787	+0.643*	+0.186	+0.586
Total Alkalinity						+0.577	+0.675	-0.553*	+0.296	+0.415*	+0.765	+0.544*
NO_2^-							+0.234	+0.528*	-0.615*	+0.966*	+0.616	+0.397
Total Cr								+0.342	+0.543	+0.675	+0.342	+0.345
Total									+0.822*	+0.875*	+0.565	+0.833*
Hardness												
Alkaline										+0.323	+0.434	+0.866*
TS											+0.612	+0.844*
TDS												+0.686*

$Table \; 2 \mathrel{.} (cont.)$

ariables	0	SOD	COD	D ₂ consu- ned by XMnO ₄	à		Ag			7	ė	Лп
>	н 0.122	Щ 0.155*	0.070		0.070**	A 412**	Z	LL 0.101	0.142	4	Щ 10.125	A 471**
Temp.	-0.133	-0.155*	-0.078	-0.168	-0.2/9**	-0.412**	+0.292	-0.191	-0.143	+0.317	+0.435	-0.4/1**
pН	+0.858*	-0.038	-0.086	+0.953*	+0.257	+0.286*	+0.270	-0.313**	+0.032	+0.238	+0.317*	-0.196*
CO_{3}^{2-}	-0.978**	+0.044	+0.136	-0.957**	-0.375	-0.033	-0.191	+0.066	+0.062	-0.146	-0.456**	+0.126*
HCO_3^-	-0.986**	+0.231*	+0.326*	-0.945**	+0.355*	-0.434*	-0.218*	+0.171	+0.091	-0.383**	-0.494*	+0.124*
Cl⁻	-0.822*	-0.066	-0.147	-0.202	+0.322*	-0.355**	-0.236*	-0.029	+0.031	-0.169	-0.459*	+0.178*
Total Alkalinity	-0.055	+0.244*	+0.068*	-0.076	+0.244	+0.075	+0.281	+0.328	+0.298*	-0.189*	-0.329*	+0.046
NO_2^-	+0.545*	+0.775*	+0.871*	-0.964**	-0.658**	-0.566**	-0.860**	-0.524**	-0.115	+0.139*	-0.937**	-0.581**
Total Cr	-0.678*	+0.256*	+0.045*	-0.784**	-0.765*	-0.756**	-0.645**	-0.657**	+0.432*	+0.875*	+0.835*	+0.463*
Total	-0.646	+0.075	+0.189	-0.724*	-0.197	-0.168*	-0.089	+0.143	+0.163	-0.211	-0.538**	+0.289*
Hardness Alkaline Hardness	-0.966*	+0.233*	+0.742*	-0.928**	-0.357**	-0.484**	+0.323*	+0.170	+0.071	-0.313*	-0.465**	+0.132
TS	+0.864*	+0.119	+0.267	-0.946*	-0.353**	-0.168	-0.260*	+0.152	+0.034	-0.150	-0.398**	-0.054
TDS	-0.478	+0.232*	+0.063*	-0.313	-0.256	-0.298*	+0.093	+0.459*	+0.169	+0.139	-0.186	-0.186*
TSS	-0.877*	+0.143*	+0.647*	-0.778**	-0.364**	-0.321*	-0.355*	+0.143	-0.093	+0.049	-0.511**	+0.128
DO		+0.044	-0.180	+0.957**	+0.357*	+0.313*	+0.244*	-0.094	-0.136*	+0.228*	+0.486*	+0.045
BOD			+0.357*	-0.132	-0.063	+0.068	+0.051	+0.112	+0.029	+0.061	+0.262	+0.126
COD				+0.243	+0.087	+0.352*	+0.675*	+0.142*	-0.812**	+0.087	+0.176*	+0.064
O ₂ cons. ^a					+0.322*	+0.290*	+0.280*	-0.022	+0.032	+0.384*	-0.378*	-0.197
Ca						+0.592*	+0.568*	+0.186	+0.651*	+0.271*	+0.025	+0.434*
К							-0.134*	-0.061	+0.184	+0.255	+0.183	+0.126
Mg								+0.514*	+0.759*	+0.275	+0.358*	+0.386*
Р									+0.487*	+0.219*	+0.296*	+0.519*
S										-0.071	-0.290**	+0.433*
N											-0.045	-0.097
Fe												+0.079

 $^{a}\,O_{2}$ consumed by $KMnO_{4}.$

oxygen with oxygen consumed by $KMnO_4$; calcium with each potassium, phosphorus, nitrogen, iron, magnesium and sulfur; magnesium with sulfur, nitrogen, iron and manganese.

Negative correlation-ships

Negative correlation-ships were observed between pH with each carbonate, bicarbonate, chloride, total hardness, alkaline hardness, total dissolved solids and total suspended particles; carbonate with dissolved oxygen calcium potassium, magnesium, nitrogen, iron and oxygen consumed by KMnO₄; chloride with potassium, magnesium, phosphorus, dissolved oxygen, oxygen consumed by KMnO₄, and BOD; nitrite with each oxygen consumed by KMnO₄, potassium, magnesium, phosphorus, sulfur, iron and manganese; total solids with oxygen consumed by KMnO₄, calcium, potassium, magnesium, nitrogen, iron and manganese. Similar results have also observed by Piyush et al. during their study of impact of distillery effluent on seed germination behaviour.¹⁹

Conclusion

The assessment of the tannery industry effluent is carried out and observed that the tannery industry effluent was brown, turbid, and had an offensive odour. The pH of the effluent was found to be in acidic range. The physical parameters studied in the effluent namely total hardness, total suspended and dissolved solids were at higher level. The chemical parameters namely COD, BOD, carbonate, bicarbonate, calcium, magnesium, chloride, potassium, nitrite, sulfur, and chromium, is found to be much above the permissible limits prescribed by the Bureau of Indian Standards (2009). Tanneries pollution readily accelerates to cause deterioration in ground water quality. The poor quality of water resists its use for our daily life and also for aquatic life. This study will helpful for developing new techniques for the treatment of effluent.

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References

- ¹Sahu, R. K., Katiyar, S., Yadav, A. K., Kumar, N., Srivastava, J., *CLEAN Soil Air Water*, **2008**, *36*, 517.
- ²United Nations Industrial Development Organization, UNIDO, *Cost of Tanned Waste Treatment*, 15th Session of the Leather and Leather Products Industry Panel Leon, Mexico, 2005.
- ³Ogbonna, J. O., Lawal, F. A., Owoeye, L. D., Udeh, M. U. "Chemical Characteristics and Fertilizing value of Primary Sludge from Tannery Effluent Treatment Plant", 6th Ann. Natl. Conf. Nigerian Inst. Sci.Technol. Univ.Ibadan, 24-27th, 2008.
- ⁴Mustafa, S., Ahmad, T., Naum, A., Shah, K. H., Wassum, M., Water, Air and Soil Pollution, 2010, 210, 43.
- ⁵Hema, S., Subramani, T., Elango, L., *I. J. Inv. Sci.*, **2010**, *1*, 1.
- ⁶Ganesh, S., Baskaran, L., *Iranian J. Environmental Health Sci.* Eng., **2009**, *6*, 17.
- ⁷Rehman, A., Anjum, M. S., *Water, Air and Soil Pollution*, **2010**, 205, 149.
- ⁸Shamoune, M. N., Louhab, K., Boukhiar, A., *I. J. Environmental Res.*, **2008**, *3*, 229.
- ⁹Ahmed, W. A., Zakaria, Z. A., Razali, F., Samin, J., Water, Air and Soil Pollution, 2009, 204, 195.
- ¹⁰IBH Hand Book No. 8, "Method for Physical and chemical analysis of fresh waters," Blackwell Scientific Publications Oxford Edinburgh London Melbourne, **1978**.
- ¹¹Richards, L. A., "Diagnosis and improvement of saline and alkali soils," U. S. Salinity Laboratory Staff USDA Handbook No. 60, **1954**.
- ¹²Kaushik, B. D., *Proc. A.I.A.P.C.* Kanpur, **1987**, 60.
- ¹³Indian standard institution, New Delhi, "Tolerance limit for industrial effluents discharged into inland surface waters," IS: 2490 part-I, 1964.
- ¹⁴Mohan, N., "Influence of water pollutants on algal flora," UGC, MRP 3-33/86 (SR-II), **1989**, 1.
- ¹⁵Trivedy, R. K., Goel, P. K., "Chemical and biological methods for water pollution studies," Environmental Publications, Kara", **1986**.
- ¹⁶APHA-AWWA-WPCF In: Standard methods for the examination of water and waste water. American Public Health Association, Washington, D. C 20th ed., New York, 2005.
- ¹⁷Ademoroti C. M. A., "Standard method for water and effluents analysis," Foludex press Ltd, Ibadan, **1996**, 111.
- ¹⁸Akan, J. C., Ogugbuaja, V. O., Abdulrahman, F. I., Ayodele, J. T., *Global J. Pure and Applied Sci.*, **2009**, *15*, 343.
- ¹⁹Malviya, P., Sharma, A., J. Environmental Biology, 2011, 32, 91.

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