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Physico-Chemical Analyses to Assess the Quality of Distillery Effluents at Unnao

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Abstract: One of the distilleries in Unnao, India, was sampled for analysis in the laboratory to determine its physicochemical characteristics and pollution level. A fixed spot at the distillery was used for the collection of samples for a period of one year, from May 2021 to April 2022. Observations of high chemical loads in the effluent discharged from the above-stated distillery included carbonate, bicarbonate, iron, calcium, magnesium, chloride, and BOD and COD. Results showed that there are certain relationships between the physicochemical characteristics of positive and negative effluents every month.

Keywords: distillery, Pearson correlation, potassium permanganate, Regression equation, BOD.

1. Introduction

People had always lived near water sources, such as rivers, lakes, or groundwater springs when they first settled in one place and started growing crops [1-3]. In order to be able to drink, prepare food, bathe, clean, irrigate crops, and perform a variety of other tasks, it was essential to have easy access to water. However, a problem with the water sources used to supply water in the past and treating drinking water to make it better smelling, tasting, clearer, or eliminating disease-causing pathogens has occurred throughout recorded history in one form or another. Human well-being is directly linked to water quality, so its quality is a vital concern for humanity. Pollution occurs when water deviates from its natural condition, affecting its properties and functions [4]. Various biological, chemical, and physical interactions affect water quality and aquatic environment characteristics. With respect to their geological age and geochemical characteristics, estuaries, water bodies, lakes, and rivers are continuously changing. As a result of human activities disrupting this dynamic balance in the aquatic ecosystem, pollution manifests itself dramatically in fish kills offensive tastes, and odors. Industrial pollution is a type of pollution caused by effluents generated by industries [5].

Among the seventeen most polluting industries listed by the CPCB are distilleries. Distillery effluent is the liquid flow from the distilleries' wastewater treatment systems. India currently has 319 distilleries with a capacity of 3.29 billion liters of alcohol. Over 40% of the total installed capacity is in cane-growing states such as Uttar Pradesh and Maharashtra, followed by Madhya Pradesh (14.2%) and Tamil Nadu (9.5%). Distilleries using molasses frequently produce high amounts of BOD and COD wastewater per liter of alcohol produced [6,7]. The total amount of wastewater produced per liter of alcohol is between 40 and 50 liters [8]. Distilleries in India generate 40.72 million/m3 of spent water annually [9,10].

In the human body, blood is similar to water in our environment. As a result of urbanization and industrialization, humans pollute the Earth's blood, which is water, making it look like a sterile, desolate, grey hunk of rock orbiting the sun [11]. The nature of these industries may vary widely, but industrial processes primarily cause water pollution. Wastewater from industries includes wastewater from manufacturing units, employees' sanitary wastes, and water discharged for cleaning factory floors. It also includes relatively uncontaminated heating and cooling water [12].

Raw distillery effluent is commonly discharged into municipal sewage systems [13-15]. Environmental pollution has become a major problem worldwide because of urbanization and industrialization. Stringent regulations must be followed before effluents can be disposed of [16-18]. Water pollution is mainly caused by effluents released into receiving waters [19]. Humans and ecosystems are exposed to pollutants when contaminating aquatic ecosystems such as rivers, ponds, and lakes.

Increasing urbanization and industrialization have made environmental pollution one of the world's biggest problems. In recent decades, the use of chemicals in various human activities has increased rapidly, especially in nations like India [20]. Groundwater is crucial to delivering potable water, agricultural irrigation, and industrial production. Groundwater resources are threatened by urbanization, industrial development, and agricultural practices [21].

As a result of the expansion of industry in the modern world, global water contamination has become a major concern [22]. Water pollution is primarily caused by the discharge of effluents into bodies of water. These contaminants end up in aquatic ecosystems such as lakes, ponds, and rivers, posing a threat to human and ecosystem health. Every industry releases waste-containing water at some point in its production process. Industrial waste varies depending on the situation. As a result, water contaminants cause a number of physicochemical parameters to differ from those typically prescribed [23]. Water quality can be negatively impacted by increasing turbidity, color, nutrient load, and hazardous and persistent chemicals [24-26]. Tannery effluent has a wide range of physical, chemical, and biological characteristics that each effluent habitat requires its study.

Studying polluted water released from distilleries aims to compare its chemical characteristics.

2. Materials and Methods

There were no chemicals other than AR grade used. MAC Digital Portable Kit (MSW-551) was used to measure pH, electrical conductivity, and turbidity. A flame photometer (Model Systronic 128) was utilized to determine metal ions Na^+, K^+, and Ca^{2+}. Chloride in water samples was estimated with the silver nitrate method. Using the turbidimetric method, sulfate was determined. Total hardness was calculated by complexometric titration with EDTA. The distillery effluent characterization has been carried out for parameters like pH, alkalinity, TDS, TH, Ca^{2+}, and Mg^{2+} as per the Bureau of Indian Standard 10500 (BIS-2012) [27].

2.1. Samples and sampling sites.

An analysis was conducted on samples taken from a distillery in Unnao, India, using the following methods:

(i) Visit the distillery and surrounding areas and

(ii) On-site assessments and interviews with relevant personnel, including workers, managers, and other stakeholders.

Immediately after sampling, the samples were corked in glass bottles (1.0 liters).All samples were stored at 4°C in refrigerators until they were analyzed. All chemical tests were completed the same day or the next evening. All four or five samples were merged for the experiments below to obtain a comprehensive water sample. This study collected samples in glass bottles (1 liter) and corked immediately after collection, according to the Indian Standard Methods for Sampling and Testing Water for Industries, I.S.I. New Delhi, India. All samples were stored at 4°C in refrigerators until they were analyzed. All chemical assays were completed the same day or the following evening. This sample was used in the experiments listed below. All four or five samples were blended to obtain a comprehensive water sample. As per the Indian Standard Methods of Sampling and Testing for Water Used in Industries, I.S.I. New Delhi, India, the sampling method was the same.

Using procedures outlined in IBH Handbook No. 8, a pH and temperature measurement was performed on color, temperature, pH, carbonate, bicarbonate, chloride, total alkalinity, nitrite, total hardness, total suspended solids (TSS), alkaline hardness, total solids (TS), total dissolved solids (TDS), BOD, dissolved oxygen (DO), oxygen consumed by potassium permanganate, calcium, chromium, potassium, magnesium, phosphorus, sulfur, nitrogen, iron, and manganese. According to IBH Handbook No. 8 [28], USDA Handbook No. 60 [29], and Laboratory Methods for Blue Green Algae, respectively [30], the pH and temperature of each component were measured. In water sampling and testing, the ISI New Delhi 2490 standard [31] is used, which was developed by Choubey [32,33]. In this study, various characteristics of wastewater testing were analyzed in relation to each other. In effluent samples, dissolved oxygen (DO) was assessed with the Winkler technique. As a means of measuring alkalinity, sodium thiosulfate was employed [34,35]. Effluent samples were measured for BOD, TDS, and TS using established techniques. According to Ademoroti, COD was calculated [36].

The significance of all data was assessed statistically using the 5% and 10% probability levels with one and two asterisks indicating significant and very significant 'r' values.

2.2. Statistical analysis.

Two parameters are required to describe the situation in a linear regression model for estimating water quality. A correlation analysis compares independent and dependent variables to determine how close they are to each other [37,38]. If the correlation coefficient approaches +1 or 1, it indicates a linear relationship between variables x and y.

In terms of correlation, the parameters are categorized as strong, moderate, and weak. Strong parameters lie between +0.8 and 1.0, moderate parameters lie between +0.5 and 0.8, weak parameters lie between +0.0 and 0.5, and weak parameters lie between −0.0 and −0.5 [39]. As a result of correlation analysis, forecasts and predictions can be made based on the relationship between variables [40]. The present study used Pearson correlation coefficients, commonly known as Pearson ‘r’ tests, to measure the strength of relationships between variables. The coefficient correlation value can be used to evaluate the strength of relationships between two variables:

$$r = \frac{\sum(x-\bar{x})(y-\bar{y})}{\sqrt{\sum(x-\bar{x})^2\sum(y-\bar{y})^2}}$$

where, x (x = values of x-variable, = average value of x) and y (y = values of y-variable, = average value of y) represent two different water quality parameters. There is a high degree of correlation between two variables X and Y, when their correlation coefficient 'r' is high. A straight line can be used to calculate linear regression using the following equation:

$$y = a + bx$$

The dependent variable in this equation is y, the independent variable is x, and the slope and intercept on the y axis are ‘a’ and ‘b’, respectively. For calculating the empirical parameters 'a' and 'b', here is the equation:

$$b = \frac{\sum(xy - \bar{x}\sum y)}{\sum x^2 - \overline{x\sum y}}$$

$$a = \bar{y} - b\bar{x}$$

In statistics, correlation measures the relationship between two variables. Relationships can be discovered through correlation studies in practical situations. In order to determine the significance of an association between two or more water quality parameters, its statistical significance can be measured [41]. For the purpose of studying the correlation between different water quality parameters, regression analysis has been conducted using the past-4 software versions.

3. Results and Discussion

As shown in Table 1, the Bureau of Indian Standards (BIS 2012) and World Health Organization (WHO 2002) recommend acceptable and minimum limits for individual parameters for drinking water. Table 2 illustrates that tannery effluents differ significantly from month to month regarding their physical and chemical properties. The following correlations were found between traits in Table 3.

3.1. Positive correlation ships.

Positive correlation coefficients were found between temperature with each of the chloride, TA, chromium, TH, AH, TS, TDS, TSS, OC, P, S and Mn; pH with each of the carbonate, chloride, TA, chromium, AH, TS, TDS, TSS, OC, Ca, Mg, P, S and Mn; carbonate with each of the bicarbonate, chromium, DO, COD, K, N and Fe; bicarbonate with each of the chloride, chromium, DO, COD, K, Mg and P; chloride with each of the TA, chromium, TH, AH, TS, TDS, TSS, OC, P, S and Mn; total alkalinity with each of the TH, AH, TS, TDS, TSS, BOD, COD, OC, Ca, K, P and S; total chromium with each of the TH, AH, TS, TDS, TSS and Fe; total hardness with each of the AH, TS, TDS, TSS, OC, P and S; alkaline hardness with each of the TS, TDS, TSS, OC, S and Mn; total solids with each of the TDS, TSS, OC, P, S and Mn; total dissolved solids with each of the TSS, OC, Ca, P, Mg, P, S and Mn; total suspended solids with of the each OC, P, S and Mn; dissolved oxygen with each of the BOD, COD, P, K, Mg, S, N and Fe; biological oxygen demand with each of the COD, OC, Ca, K, P, N and Mn; chemical oxygen demand with each of the Ca, K, Mg, P, N and Fe; oxygen consumed with each of the Ca, S and Mn; calcium with each of the K, Mg, S, N and Mn; P with each of the Mg, N and Fe; Mg with each of the P, S, Fe and Mn; P with S and Mn; sulphur with Mn [42].

3.2. Negative correlation ships.

Negative correlation coefficients were found between temperature with each of the carbonate, bicarbonate, DO, BOD, COD, Ca, K, Mg, N and Fe; pH with each of the bicarbonate, TH, DO, COD, K, N, and Fe; carbonate with each of the chloride, TA, TH, AH, TS, TDS, TSS, BOD, OC, Ca, Mg, P, S and Mn; bicarbonate with each of the TA, TH, AH, TS, TDS, TSS, BOD, OC, Ca, P, S and Mn; ;chloride with each of the DO, BOD, COD, Ca, K, Mg, and Fe; total alkalinity with each of the total chromium, DO, N, Fe and Mn; total chromium with each of the DO, BOD, COD, OC, Ca, K, Mg, P, S, N and Mn; total hardness with each of the DO, BOD, COD, Ca, K, Mg, N, Fe and Mn; alkaline hardness with each of the DO, BOD, COD, Ca, K, Mg, P, N and Fe; total solids with each of the DO, BOD, COD, Ca, K, Mg, N and Fe; total dissolved solids with each of the DO, BOD, COD, K, N and Fe; total suspended solids with of the each DO, BOD, COD, Ca, K, Mg, N and Fe; dissolved oxygen with each of the OC, Mg, P and Mn; biological oxygen demand with each of the Mg, P and Mn; chemical oxygen demand with each of the OC, S and Mn; oxygen consumed with each of the K, Mg, P, N and Fe; calcium with the P and Fe; K with each of the P, S and Mn; Mg with N; P with N and Fe; sulphur with N and Fe; N with Fe and Mn; Fe with Mn [43].

Temp. = Temperature (ºC), TS = Total Solids (meq.L^{-1}), TDS = Total Dissolved Solids (meq.L^{-1}), pH = potentio Hydrogeni, carbonate = CO_3^{--}, bicarbonate = HCO_3^{--}, chloride = Cl^-, TSS = Total Suspended Solids (meq./L^{-1}), TA = Total Alkalinity as $CaCO_3$, TH = Total Hardness as $CaCO_3$, AH = Alkaline Hardness as $CaCO_3$, BOD = Biological Oxygen Demand (meq.L^{-1}), DO = Dissolved Oxygen (meq.L^{-1}), COD = Chemical Oxygen Demand (meq.L^{-1}), OC = Oxygen Consumed by $KMnO_4$ in 3 hrs.

Table 1. Water quality standards set by the BIS and WHO.

S. no.	Parameters	BIS standards (BIS 10500:2012)		World Health Organization (WHO) (2002)
		Acceptable limit	Permissible limit	
1	pH	6.5–8.5	No relaxation	6.5–9.2
2	Chloride	250	1000	200
3	Magnesium	30	100	200
4	Total alkalinity	200	600	500
5	Total hardness	200	600	300
6	Calcium	75	200	150
7	Total dissolved solids	500	2000	250

Note: All values are in mg.L^{-1}, except pH

Table 2. An analysis of tannery effluent's physico-chemical characteristics.

Color	Sample No.	Temp.	pH	Carbonate	Bicarbonate	Chloride	TA	Total Cr	TH	AH	TS
Yellow	May 21	27.5	7.2	1.4	0.5	520	1250	00	1450	810	1884
Yellow	June 21	30.2	7.4	1.0	0.7	505	1290	00	1685	840	1805
Light Brown	July 21	30.0	4.9	6.4	1.1	545	1365	0.05	2208	830	1994
Brown	Aug. 21	28.0	5.2	5.0	3.9	490	1215	0.03	1565	690	1850
Brown	Sept. 21	30.6	6.2	5.0	4.2	530	1220	1.00	2350	825	1935
Light Brown	Oct. 21	28.4	5.8	5.1	3.8	60	1085	0.05	1245	880	1508
Light Brown	Nov. 21	23.5	5.5	4.9	1.9	72	1005	00	650	450	880
Yellowish	Dec. 21	21.3	5.6	5.5	3.0	55	1160	00	810	400	865

Color	Sample No.	Temp.	pH	Carbonate	Bicarbonate	Chloride	TA	Total Cr	TH	AH	TS
Light Brown	Jan. 22	21.5	5.2	5.6	2.8	67	1200	00	830	230	996
Brown	Feb. 22	23.3	6.2	5.2	2.7	89	1310	0.02	880	310	702
Brown	Mar. 22	26.5	6.0	1.6	1.2	45	1320	00	2325	350	1104
Yellowish	Apr. 22	27.0	7.3	1.6	1.2	530	1295	00	810	784	2035

Table 2. continued….

Color	TDS	TSS	DO	BOD	COD	OC	Ca	K	Mg	P	S	N	Fe	Mn
Yellow	1410	887	00	4200	5944	2.7	210	75	15.5	130	172	1055	3.90	1.25
Yellow	1415	965	00	3750	5245	2.2	350	60	25.7	132	630	1110	3.05	1.66
Light Brown	1364	980	00	4005	5575	1.6	195	78	14.5	155	164	1165	2.80	0.65
Brown	1506	840	0.6	3890	6347	1.2	94	50	32.7	165	178	1030	4.25	1.34
Brown	1320	925	00	3630	5884	1.5	90	65	23.4	140	175	1020	4.35	0.83
Light Brown	1095	765	00	3415	5320	1.6	95	68	26.7	116	164	1120	4.05	0.85
Light Brown	934	684	1.6	3965	5755	1.3	190	82	26.5	120	175	1110	4.65	1.36
Yellowish	935	656	2.3	4405	6340	1.5	244	145	22.4	160	214	1350	3.85	0.78
Light Brown	1160	790	2.2	4300	6465	1.5	230	124	26.7	126	235	1170	4.15	0.76
Brown	1454	764	2.4	3850	6325	1.3	385	170	33.0	120	190	1165	4.85	0.64
Brown	1510	776	1.9	3950	5812	1.4	204	74	33.4	235	260	1155	4.55	0.82
Yellowish	1220	890	00	4295	6304	1.8	208	86	35.3	255	282	1045	3.76	1.82

Table 3. Linear correlation coefficients 'r' (Pearson) and statistics table correlation coefficients.

Variables	Temp.	pH	Carbonate	Bicarbonate	Chloride	TA	Total Cr	TH	AH	TS	TDS	TSS	DO
Temp.		0.29	-0.291	-0.117	0.749	0.353	0.419	0.750	0.873	0.856	0.520	0.820	-0.888
pH			0.855	-0.489	0.392	0.270	0.024	-0.024	0.376	0.344	0.247	0.360	-0.394
Carbonate				0.661	-0.303	-0.319	0.192	-0.145	-0.244	-0.315	-0.376	-0.309	0.305
Bicarbonate					0.259	-0.444	0.490	-0.071	-0.096	-0.176	-0.224	-0.340	0.159
Chloride						0.476	0.321	0.446	0.760	0.917	0.471	0.881	-0.804
TA							-0.015	0.509	0.111	0.365	0.768	0.647	-0.158
Total Cr								0.491	0.295	0.308	0.075	0.309	-0.297
TH									0.409	0.513	0.630	0.613	-0.435
AH										0.891	0.184	0.698	-0.979
TS											0.392	0.855	-0.938
TDS												0.604	-0.244
TSS													-0.770
DO													
BOD													
COD													
OC													
Ca													
K													
Mg													
P													
S													
N													
Fe													
Mn													

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Table 3. continued….

Variables	BOD	COD	OC	Ca	K	Mg	P	S	N	Fe	Mn
Temp.	-0.594	-0.642	0.339	-0.355	-0.790	-0.224	0.093	0.240	-0.636	-0.479	0.258
pH	00	-0.181	0.723	0.365	-0.143	0.119	0.225	0.565	-0.363	-0.140	0.626
carbonate	-0.091	0.222	-0.655	-0.260	0.354	-0.205	-0.461	-0.599	0.348	0.131	-0.659
bicarbonate	-0.380	0.274	-0.624	-0.503	0.107	0.228	-0.301	-0.441	00	0.452	-0.394
chloride	-0.030	-0.145	0.487	-0.171	-0.557	-0.299	0.176	0.220	-0.622	-0.572	0.479
TA	0.154	0.071	0.235	0.387	0.046	00	0.444	0.278	-0.065	-0.392	-0.068
Total Cr	-0.403	-0.067	-0.116	-0.428	-0.225	-0.149	-0.117	-0.175	-0.372	0.155	-0.207
TH	-0.421	-0.449	0.087	-0.310	-0.569	-0.263	0.185	0.080	-0.293	-0.272	-0.223
AH	-0.432	-0.579	0.505	-0.399	-0.709	-0.359	-0.004	0.156	-0.558	-0.583	0.406
TS	-0.182	-0.313	0.481	-0.416	-0.734	-0.272	0.244	0.159	-0.658	-0.604	0.449
TDS	-0.237	-0.042	0.176	0.142	-0.272	0.148	0.219	0.203	-0.449	-0.059	0.0208
TSS	-0.200	-0.349	0.485	-0.034	-0.528	-0.303	0.115	0.362	-0.563	-0.647	0.273
DO	0.388	0.546	-0.529	0.421	0.767	0.324	-0.054	-0.169	0.663	0.572	-0.456
BOD		0.659	0.156	0.276	0.430	-0.096	0.361	-0.067	0.399	-0.118	0.114
COD			-0.317	0.080	0.569	0.346	0.242	-0.375	0.156	0.432	-0.100
OC				0.212	-0.254	-0.501	-0.075	0.383	-0.222	-0.499	0.405
Ca					0.615	0.093	-0.100	0.536	0.410	-0.097	0.035
K						0.115	-0.163	-0.181	0.677	0.309	-0.472
Mg							0.467	0.148	-0.167	0.546	0.271
P								0.090	-0.083	-0.058	0.316
S									-0.007	-0.452	0.523
N										-0.090	-0.514
Fe											-0.219
Mn											

Nevertheless, Table 4 lists some parameters with correlation coefficients of r > 0.05. For tannery effluent parameters, linear regression analysis has been performed, and it has been found that their correlation coefficient (r > 0.50) has a higher level of significance [44].

We substituted the dependent parameters' values for the independent parameters in the regression equation to determine the various tannery effluent quality characteristics [45]. These correlations revealed that physical parameters were interrelated with cations, anions, and physicochemical parameters in the Unnao area [46]. There is a positive correlation between. Ca^{2+}, Mg^{2+}, CO_3^{--}, HCO_3^{--}, Cl^- with the majority of water parameters. Most water parameters have a negative correlation with pH. Highly negative correlation coefficients are found between DO and AH (r = −0.979) and DO and TS (r = −0.938). There are no differences in correlation coefficients between regression and correlation relations [47,48].

Table 4. The linear correlation coefficient 'r' and regression equation have been calculated for some physicochemical parameters with significant correlations.

S. No.	Parameter	r value	Correlation coefficient		Regression equation
			a	b	
1	pH–TH	-0.024	1509.06439	-17.94169	TH = -17.94169 (Ph) + 1509.06439
2	TA–Ca^{2+}	0.387	-213.5296	0.34369	Ca^{2+} = 0.34369(TA) – 213.5296
3	TA–Cl^-	0.476	-1048.55802	1.09349	Cl^- = 1.09349(TA) – 1048.55802
4	Ca^{2+}–Mg^{2+}	0.093	24.9013	0.00681	Mg^{2+} = 0.00681(Ca^{2+}) + 24.9013
5	Ca^{2+}–Cl^-	-0.171	384.62343	-0.44388	Cl^- = -0.44388(Ca^{2+}) + 384.62343
6	Mg^{2+}–Cl^-	-0.299	571.27487	-10.59943	Cl^- = -10.59943(Mg^{2+}) + 571.27487
7.	DO-AH	-0.979	825.63213	-228.05323	AH= -228.05323(DO) + 825.63213

The correlation coefficients between various physicochemical parameters are plotted which are given in fig.1. Stacked bar charts of various physicochemical parameters in percentage are given in fig. 2. Matrix of various physico-chemical parameters can be seen in fig. 3. Auto correlations of various physico-chemical parameters can be seen in fig. 4. Fig. In fig. 5, there is a significant negative correlation between DO and AH.

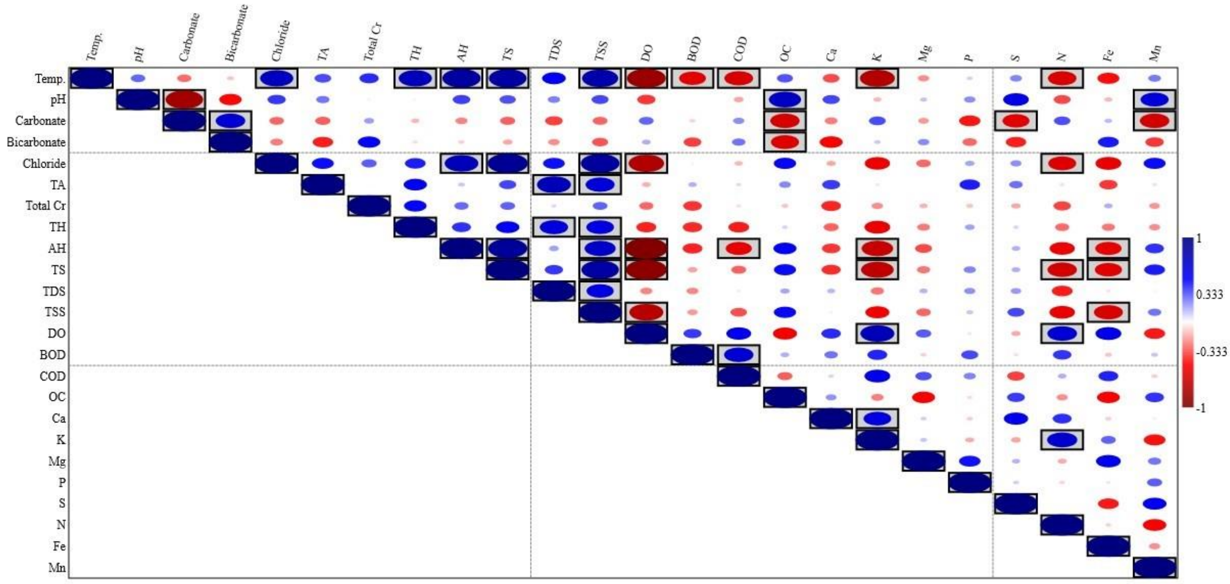

Figure 1. Plot of Correlation coefficients between various physico-chemical parameters.

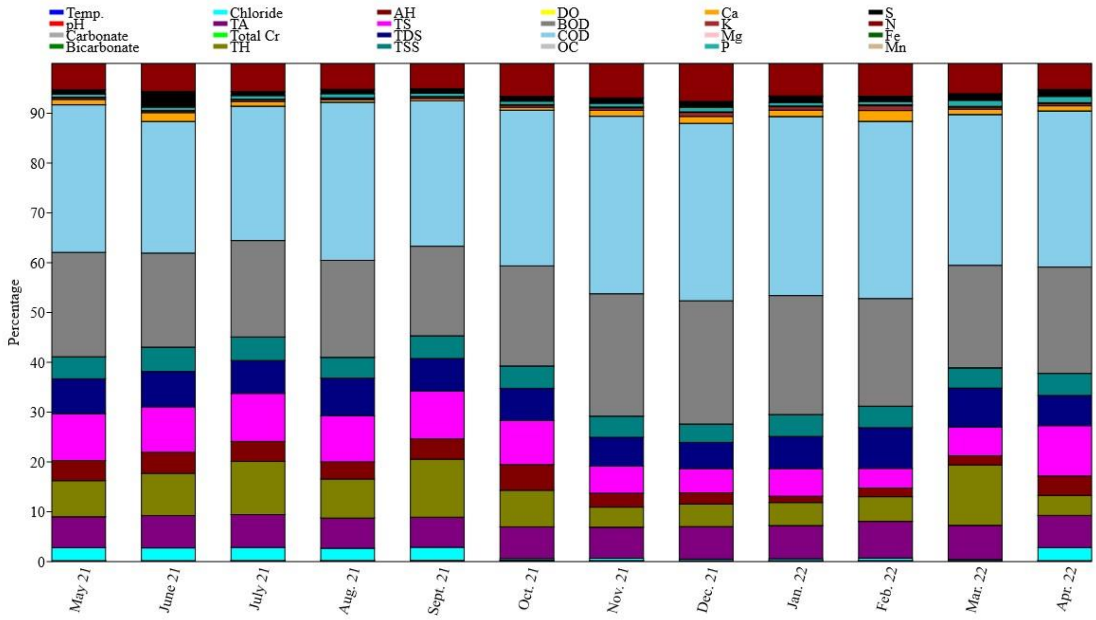

Figure 2. Stacked bar charts of various physico-chemical parameters in percentage.

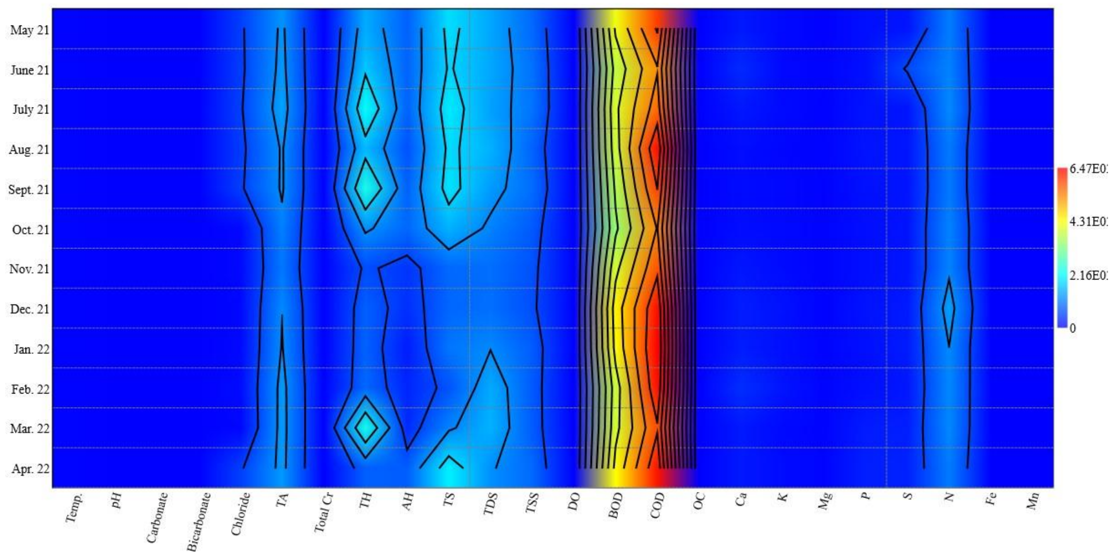

Figure 3. Matrix of various physico-chemical parameters.

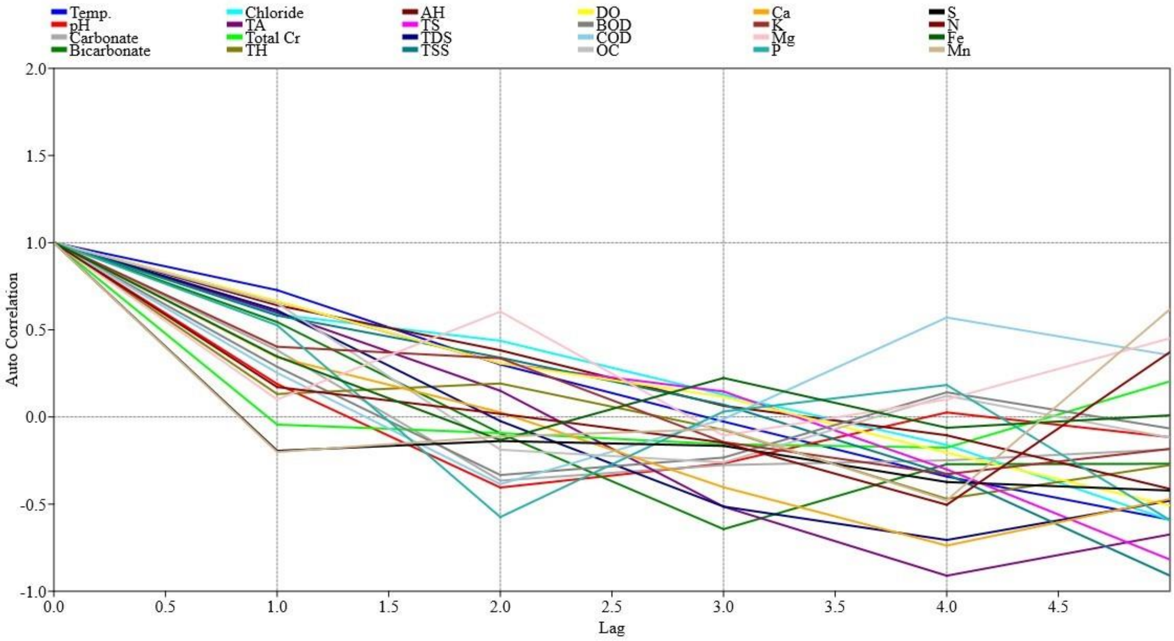

Figure 4. Autocorrelation various of physico-chemical parameters.

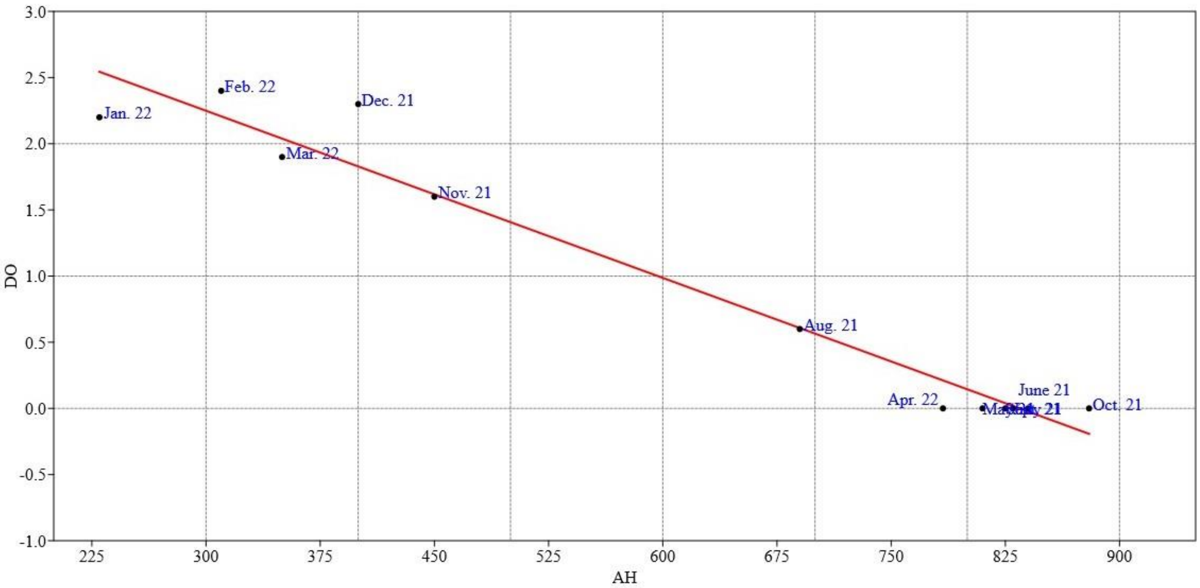

Figure 5. Strong negative correlation between DO and AH (r = -0.979).

4. Conclusion

In addition to being brown, turbid, and having an offensive odor, the distillery effluent was also assessed and found to have a pH in the near acidic range. The effluent had a high level of total hardness, total suspended solids, and dissolved solids. According to the Bureau of Indian Standards (2012), the chemical parameters COD, BOD, carbonate, bicarbonate, calcium, magnesium, chloride, potassium, nitrite, sulfur, and chrome are higher than the permissible limits. As distillery pollution rapidly accelerates to cause groundwater pollution, the degradation of water quality threatens our daily lives as well as aquatic life. New techniques for effluent treatment can be developed with the help of this study.

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Conflicts of Interest

The authors declare no conflict of interest.

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