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Comparative Analysis of Physico Chemical Parameters and Chromium Level of Untreated and Treated Effluent of Tannery Industries of Dindigul, Tamilnadu, India

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Abstract This study has been undertaken to investigate and evaluate the Physico-chemical parameters of tannery effluent. Dindigul is known for its Tanneries present in and around the district. Both untreated and treated effluent samples were collected from the discharge sites of industries for the analysis of various physical and chemical parameters. Various Physical and Chemical parameters such as Appearance, Temperature, Turbidity, and Electrical conductivity, Total Dissolved Solids, pH, Alkalinity, Acidity, Total Hardness, Salinity, Dissolved oxygen, Biological Oxygen Demand and concentration of Chromium were also analyzed. All the parameters were almost higher for untreated effluents when compared to the treated effluents. Higher ranges of values recorded also exceed the permissible level. Higher amount of hexavalent chromium was also recorded. From this investigation, it is concluded that untreated effluents were highly polluted and affects the environment when discharged without proper treatment.

Keywords: *physico-chemical parameters, tannery effluent, hexavalent chromium*

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1. Introduction

In last few decades, environmental pollution is the major issue faced throughout the world. Rapid Industrialization and urbanization is the cause for emergence of pollutants in to the environment. The natural flow of environment is due to the introduction of novel chemicals, release of organic compounds and heavy metals causing toxicity to plants and other biotic and abiotic components [1].

Thousands of Small and large scale industries release heavy metal containing effluents. Industries such as Metallurgy, battery, electroplating, Mine drainage, chemical manufacturing, oil refineries, Metal industries, leather tanning etc. Effluents are directly or indirectly into the water resources without proper treatment is a major treat to the environment [2,3,4]. Among the entire industrial waste tannery effluents are ranked as the highest pollutant [5].

More than 2500 Tanneries are present in urban centers of India. They Process about 500,000 tons of hides and 314 kg of skin per annum.100, 000 m^3 of water is wasted per day during leather processing [6].

Tanning industrial units in India are spread around Tamil Nadu, West Bengal, Uttar Pradesh, and Andhra Pradesh, Karnataka, Maharashtra, Rajasthan and Punjab. There are about 750 industries in Tamilnadu, (Dindigul, Trichy, Erode, Chennai, Ambur, Vaniyambadi and Ranipet) etc. All these industries discharge the tannery effluents without treatment into the aqueous system [7,8] which are considered toxic at certain levels of Concentration in Waste water. The Constituents present in waste water are Arsenic, Cadmium, Cobalt, Copper, Chromium, Nickel, Lead, Phenol, chloride, Sulphide, Tannins and Formaldehyde etc., [9]. These pollutants not only affect the soil and water in industrial areas but also the nearby agricultural fields, river beds and leads to the cause of secondary source of pollution [10,11].

In this present study, important water quality parameters were analyzed for effluents using Water Analysis Kit 371 and compared with the Standard values.

2. Materials and Methods

2.1. Description of Study Area

The study site is the Dindigul district which is known for its leather industries is shown in the (Figure 1). Nearly 80 tanning industries are present along Madurai, Vattalagundu and Ponmandurai roads [12,13]. Recently 49 tanneries are functioning. Effluents were collected from the Discharge site of the tannery industries that lies between 10.3520°N latitudes and 77.9491°E longitudes. Nearly 7 acres of land were used as the discharge site were shown in (Figure 2) and some of the salt tolerant short shrub *Suaeda maritima* were also grown in those areas as a bioremediation of the tannery effluents to reduce its deposition of salt were shown in the (Figure 3). The Residents living around these industrial area said that the treated effluents were collected and stored in deep well, which were used for the agricultural lands and toilet flush waters for corporate companies. They also gave as information that if their cattle feed on the untreated effluents mistakenly, it causes reduction of milk and leads to Udder diseases. By interacting with them, the seriousness of tannery effluent discharge can be realized. Therefore, the aim of the study was to investigate and evaluate the Physic chemical parameters of the effluents.

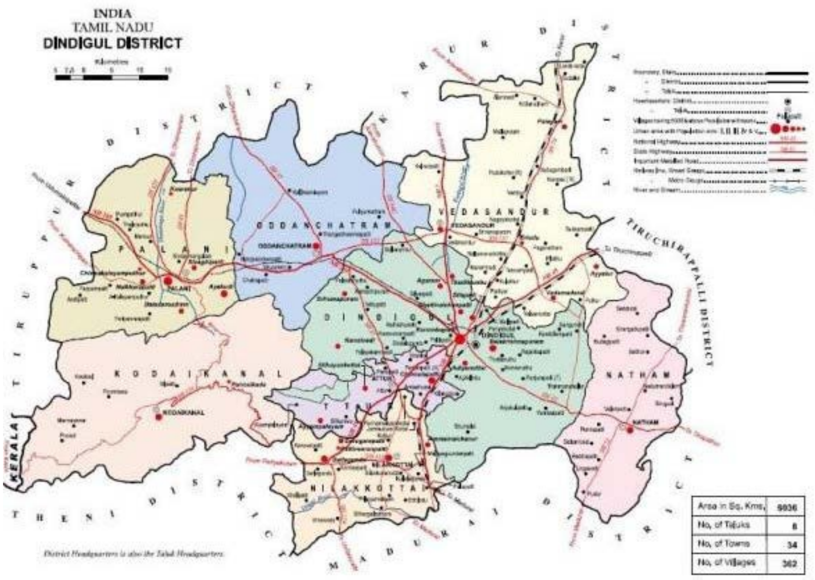

Figure 1. Study site of Dindigul district (Source: PCA of Dindigul District, Census of India, 2011)

Figure 2. Discharge sites of tannery industries

Figure 3. Salt tolerant Short shrubs *Suaeda maritime*

2.2. Collection of Samples

The untreated tannery effluents were collected from the discharge point using 5l capacity plastic containers. The Containers were sterilized with acid and distilled water thoroughly prior to the collection of sample to avoid any contamination. The treated tannery effluents were collected from the deep well stored at 4°C.In the present study, physicochemical parameters of the effluent were analyzed.

2.3. Physico-chemical Analysis of Effluent

The Physico-chemical properties such as appearance, odour, pH, Electrical conductivity, Dissolved Oxygen, Biological oxygen demand, Total dissolved solids, Total hardness, Total alkalinity, Total Acidity. Heavy metals such as chromium were also analyzed. Water Analysis kit -371 was used for the analysis of pH, Electrical conductivity, Salinity, Dissolved oxygen, Turbidity, TDS of the sample. The Analysis of parameters such as Acidity, Alkalinity, and Hardness were done using [14,15] methods. The Chromium determination was done using the Diphenylcarbazide method. Table 1 given below shows the abbreviation, and methods for the following parameters.

Abbreviations and Acronyms

Table 1. Abbreviations

S.No	Parameters	Abbrevation	Units
1.	Power of hydrogen	pH	pH unit
2.	Temperature	-	C
3..	Electrical conductivity	EC	µs/cm
4.	Salinity	-	ppt
5.	Dissolved oxygen	DO	mg/l
6.	Turbidity	-	NTU
7.	Total dissolved solids	TDS	mg/l
8.	Biological oxygen demand	BOD	mg/l
9.	Total Hardness	TH	mg/l
10.	Alkalinity	-	mg/l
11.	Acidity	-	mg/l
12.	Chromium	-	mg/l

2.3.1. Determination of pH

The pH is the Measurement of the hydrogen ion activity in a solution and is measured using specific electrode for accurate determination. pH is measured on a scale of 0 to 14 using the pH meter. The pH meter should be calibrated by using two buffers of standard pH.

2.3.2. Determination of Electrical Conductivity (EC):

The Electrical Conductivity of the water is the ability to conduct electric current. The conductivity depends on the concentration of ions present in the sample. The Salts or the chemicals dissolved in the effluents breaks down into the positively and negatively charged ions and these free ions conduct electricity.

2.3.3. Determination of Salinity

The Salinity of the sample is used to measure the amount of dissolved salts in the water. It is measured in terms of parts per thousand (ppt).

2.3.4. Determination of Dissolved Oxygen (DO)

The Dissolved Oxygen refers to the amount of oxygen dissolved in the water. It also indicates the total organic content of water oxygen that is necessary for the substance present in the sample.

2.3.5. Determination of Turbidity

The Turbidity measures the relative clarity of a liquid sample and the amount of light scattered by the materials present in the water sample. It also indicates the presence of dispersed and suspended solids.

2.3.6. Determination of Total Dissolved Solids

The Total dissolved solids measure the total inorganic salts and other substances that are completely dissolved in water and used to determine the water capability for domestic purposes.

2.3.7. Determination of Biological Oxygen Demand (Winkler's Method)

50ml of the untreated and treated sample was taken in glass stopper bottles and fully filled with the sample adjusted to pH using 1N acid or 1N alkali and temperature to 20°C. Allow it to stand as such for 15 min to avoid air bubbles. Initial DO was taken and the sample bottles were kept in dark in the BOD incubator for 5 days at 20°C and determine the dissolved oxygen. From this BOD was calculated.

Calculation:

$$BOD\ (mg/l) = \frac{Initial\ D\ O - Final\ D\ O}{Volume\ of\ the\ Sample\ (ml)}$$

2.3.8. Determination of Hardness

Hardness is the presence of minerals dissolved in the sample, which makes the water unfit for domestic purposes. The hardness of the samples were determined using the APHA Methods., 2012.

Procedure:

A known sample volume is take in a conical flask→ 5ml of buffer solution and a pinch of Erichrome T black was added → Titrate against 0.01N EDTA until wed red colour changes to blue→ Note down the titrant value.

Calculation:

$$Acidity = \frac{Vol\ of\ NaOH \times Strength\ of\ NaOH}{Volume\ of\ Sample(ml)} \times 1000$$

2.3.9. Determination of Alkalinity

Alkalinity is the acid neutralizing capability of the water. By measuring the alkalinity of the effluent, the acidic pollution of the tannery industry can be determined. The Alkalinity of the effluents was analysed using APHA (2012) methods.

Procedure:

A known sample volume is take in a conical flask →Add few drops of Phenolphthalein indicator → If colour pink colour appears titrate it against acid titrant (0.1N H2SO4) → Titrant value was noted → If the pink colour doesn't appear, add few drops of Methyl orange and continue titration until the colour change from yellow to orange (end point) → Note the titrant Value.

Calculation:

$$Alkalinity\ (mg/l) = \frac{A + B \times N}{Sample\ Vol\ (ml)} \times 1000$$

Where, A = ml of H_2SO_4 required with Phenolphthalein indicator

B = ml of H_2SO_4 required with methyl orange indicator

N = Normality of H_2SO_4.

2.3.10. Determination of Acidity

Acidity in the water contributes to the corrosiveness and increases the chemical reaction in the sample. The Acidity of the effluents was analysed using APHA (2012) methods.

Procedure:

A known sample volume is take in a conical flask →Add few drops of phenolphthalein indicator →Titrate against (0.02N of NaOH) → End point is the appearance of faint permanent pink colour.

Calculation:

$$Acidity = \frac{Vol\ of\ NaOH \times Strength\ of\ NaOH}{Volume\ of\ Sample(ml)} \times 1000$$

2.3.11. Estimation of Chromium

The Chromium content in the effluents was determined using the Diphenlycarbazide method proposed by APHA, 2012.

Procedure:

2.3.11.1. Preparation of Calibration curve

Potassium dichromate is used as the stock solution and the volumes ranging from 2 to 20ml was taken in each beaker respectively → Adjust the pH of the solution to 1.0+0.3 → The solution is transferred to 100ml volumetric flask→ Add 2ml of Diphenlcarbazide solution in all the flask and wait for 5 to 10 minutes for full colour development → Prepare blank with water → OD taken at 540nm → Plot calibration curve for absorbance against micrograms of chromium in 100ml of the final volume.

2.3.11.2. Determination of Hexavalent Chromium

The filtered sample containing 10 to 100 µg of Cr into a 100ml beaker →Make up the volume up to 50ml with water → Adjust the pH to 1.0 + 0.3 using 0.2 N H_2SO_4 → Transfer it to a volumetric flask and add 2ml of Diphenylcarbazide solution → Make up the volume to 100ml and mix well and wait for 5 to 10 Min → OD taken at 540nm → From the absorbance data determine the micrograms of Chromium in 100ml of the final solution using the calibration curve.

Calculation:

$$Hexavalent\ Cr = \frac{\mu g\ of\ Cr\ (100ml\ of\ final\ Solution)}{V}$$

Where, V is ml of Sample used.

3. Results and Discussion

3.1. Results of Physico-chemical Parameters

The Physico chemical parameters of the untreated and treated tannery effluents were given along with the WHO 2012 exceeding limit in the (Table 2).

3.1.1. Colour & Appearance

The Colour of the collected untreated sample was found to be Pale-Yellowish brown with offensive odour. Similar results were reported by [16,17].

Brown colour of the effluents was reported by [18]. The colour and the odour of the effluent might be due to the presence of the pollutant, biodegradable, non-biodegradable, high molecular weight organic compound and high amount of organic chemicals consumed during the processing of leather and the offensive odour due the putrefaction of the organic residues from processed skin and hides [19].

In case of treated sample it was found to be colorless and this show that the chemical load has been reduced and sent out for irrigation and domestic purposes

3.1.2. Temperature

The average temperature of the untreated effluent from leather industry was found to be 29.4°C and treated effluent was 28.6°C, which was less than that of the temperature of Dindigul district (33.4°C) on the day of sample collection. Similar range of values of temperature was reported by [20] effluents in Dindigul district and [21] in the tannery effluents in Bangladesh.

Table 2. Physico-chemical parameters of the Untreated and Treated effluents

Parameters	Untreated	Treated	Reduced percentage	WHO Limit
Colour & Appearance	Pale yellowish brown	Colourless	-	-
Temperature	29.4°C	28.6°c	-	-
pH	6.59	7.13	-	6.5-9.2
Turbidity(NTU)	4.9 (100%)	2.3 (46.9%)	53.1%	10
EC(µs/cm)	9340 (100%)	3860 (41.3%)	58.6%	-
TDS (mg/l)	5400 (100%)	2080 (38.5%)	61.5%	2000
Total hardness	7.9 (100%)	2.5 (31.6%)	68.3%	600
Acidity (mg/l)	2.6 (100%)	1 (38.4%)	61.5%	-
Salinity(ppt)	21.9 (100%)	1.89 (8.6%)	91.3%	-
Alkalinity(mg/l)	1300 (100%)	400 (30.7%)	69.3%	-
BOD(mg/l)	5.3 (100%)	3.4 (64.1%)	35.8%	-
Total hexavalent Chromium(µg/l)	24 (100%)	1.4 (5.8%)	94.1%	0.1

3.1.3. pH

The average pH of the untreated effluent was 6.59 with a slight acidic pH which was within the desirable range reported by [22,23]. These similar range of pH was reported by [24,25]. The average range of pH in treated effluent was 7.13 which were slightly alkaline and so can be used for irrigation purpose. The results obtained were shown in Table 2 and Figure 4.

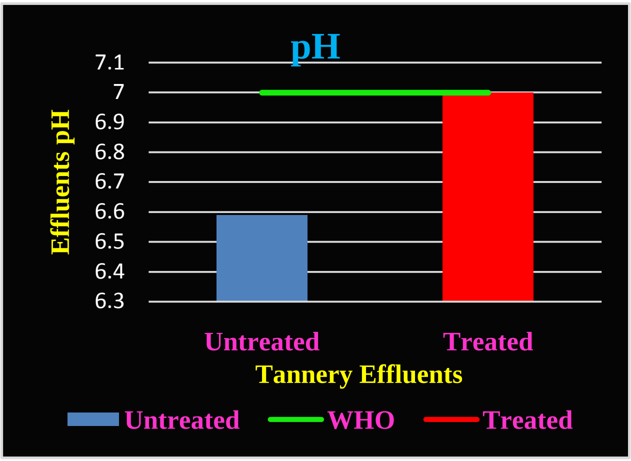

Figure 4. pH of untreated and Treated Tannery effluents

3.1.4. Turbidity

The turbidity of the untreated effluent was 4.9 NTU and treated effluent was 2.3 NTU is shown in the Table.2 and compared with the WHO Permissible limit in Figure 5. The absorbed turbidity was considerably less than that of the WHO. The solid impurities present in the effluents might be due to the hides and skin processed in the tannery industry [25].

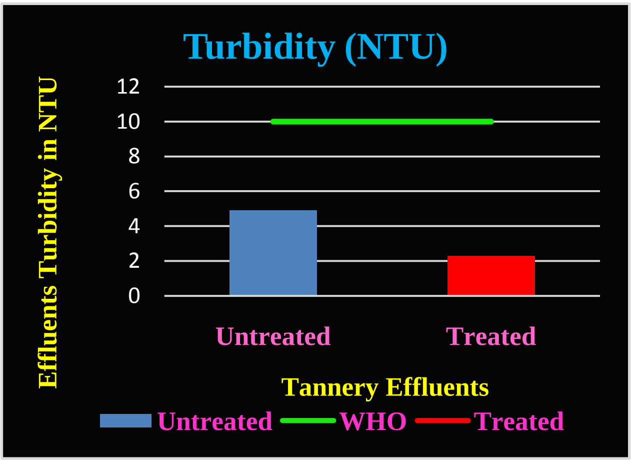

Figure 5. Turbidity of Untreated and Treated tannery effluents compared with WHO permissible limit

3.1.5. Electrical Conductivity

The electrical conductivity was reported higher in case of untreated effluents 9340µs /cm in Table 2, which considerably exceeds WHO standards (1400µs/cm). Similar range of electrical conductivity was also reported by [21,26,27]. According to [28] higher electrical conductivity alters the chelating properties of the water bodies and create imbalance of free metal availability for flora and fauna. Treated effluents also shows higher electrical conductivity 3860 µs/cm is shown in Table 1. Similar high electrical conductivity in treated effluent was also reported by [27]. This indicates that the discharge of chemicals as cations and anions in the waste water is higher [28]. Electrical Conductivity of untreated and treated effluents was compared with the WHO permissible limit in Figure 6.

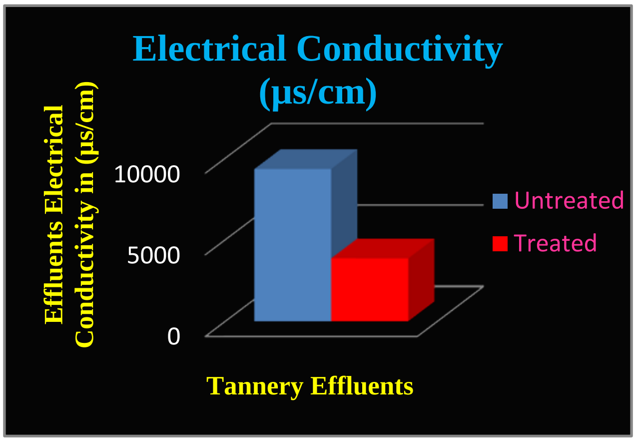

Figure 6. Electrical Conductivity of untreated and Treated Tannery Effluent

3.1.6. Total Dissolved Solids

Total dissolved solids of the untreated effluents were found to be 5400 mg/l and it exceeds the tolerance limit of WHO standards (2000mg/l) in Table 2. Similar range of TDS was also reported by [27]. According to [29,30] TDS of the effluents are mainly due to the presence of insoluble organic and inorganic compounds present in the effluents. In the present study TDS of the treated effluent was reported as 2080 mg/l is shown in the Table- 1 was also slightly more than WHO standards. The untreated and treated effluent's TDS were compared with the WHO Standards in Figure 7.

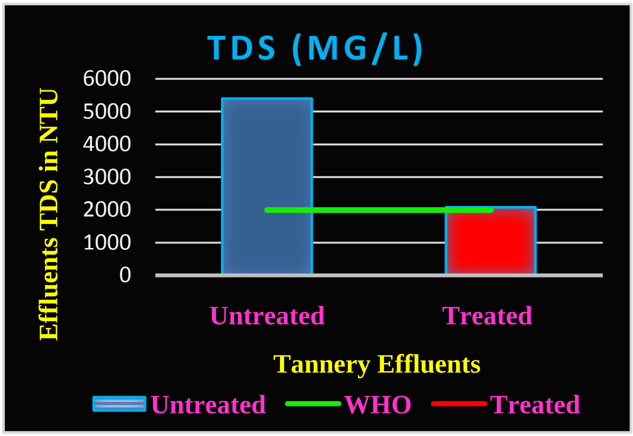

Figure 7. TDS of Untreated and Treated tannery effluents Compared with WHO permissible limit

3.1.7. Total Hardness

Total hardness of the untreated effluent and treated effluent in present study was reported as 7.9mg/l and 2.5mg/l in Table 2 was less than the permissible limit of WHO (600mg/l) similar results were reported by [31]. Both the untreated and treated effluents were compared with WHO permissible limit in Figure 8.

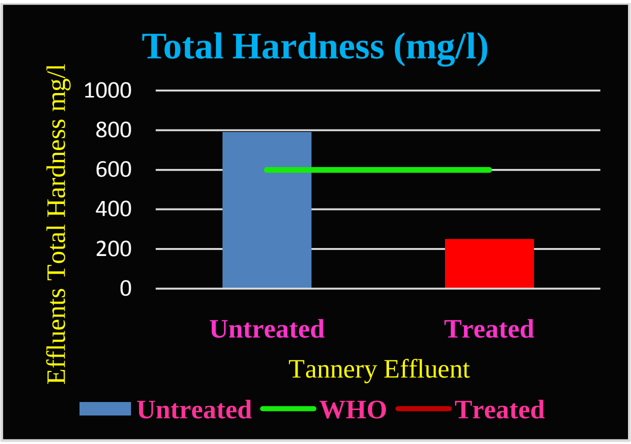

Figure 8. Total Hardness of untreated and treated tannery effluents compared with WHO Permissible limit

3.1.8. Acidity

Acidity of the untreated effluent in the present investigation was found to be 2.6mg/l and and treated effluent contain 1 mg/l were shown in Table 2 and Figure 9.

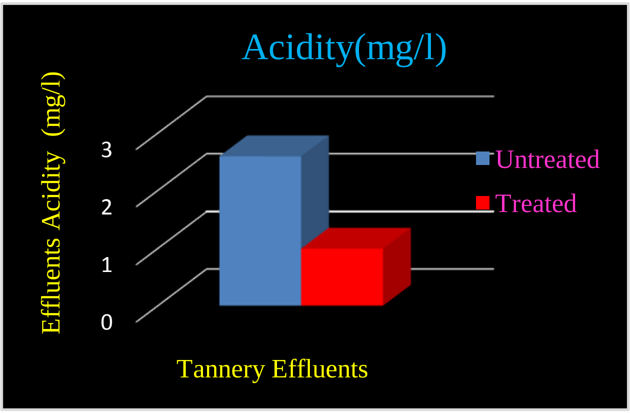

Figure 9. Acidity of untreated and treated tannery effluents

3.1.9. Salinity

Salinity is the total concentration of dissolved salts in the effluents. The salinity of the untreated effluent was reported as 21.9 ppt and treated as 1.89ppt was given in Table 2 and Figure 10. The enormous reduction in the salinity level of the treated effluent might be due to the growth of *Suaeda maritima*, which has the ability to absorb the salt from the waste land.

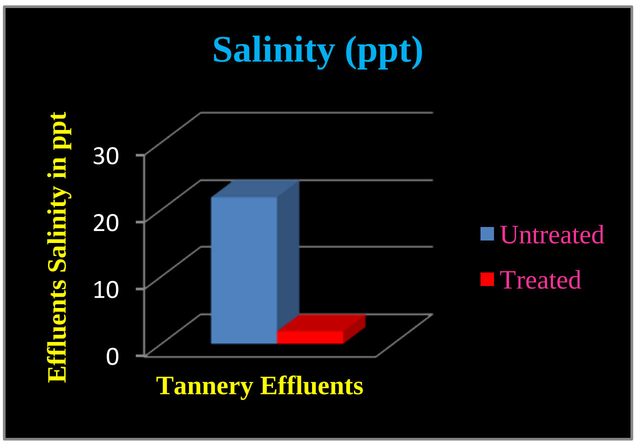

Figure 10. Salinity of untreated and treated tannery effluents

3.1.10. Alkalinity

Total Alkalinity of the untreated effluent was higher (1300mg/l) when compared to the treated effluent (400 mg/l) were given in Table 2 and Figure 11. According to [32] the alkalinity of the effluent may be due to presence of carbonate and bicarbonate.

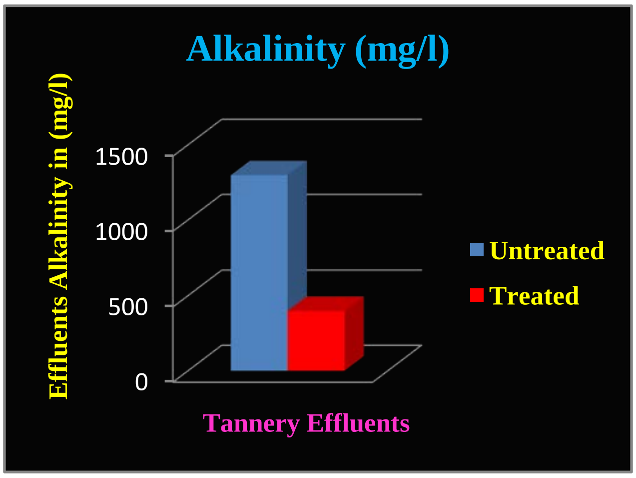

Figure 11. Alkalinity of untreated and treated tannery effluents

3.1.11. Dissolved Oxygen and BOD

BOD observed in the untreated effluent (5.3mg/l) was higher when compared with treated effluent (3.4mg/l) given in Table-2 and Figure 12. Similar results were reported by [26,33]. The higher BOD in the effluent were due to the presence of considerable organic matter

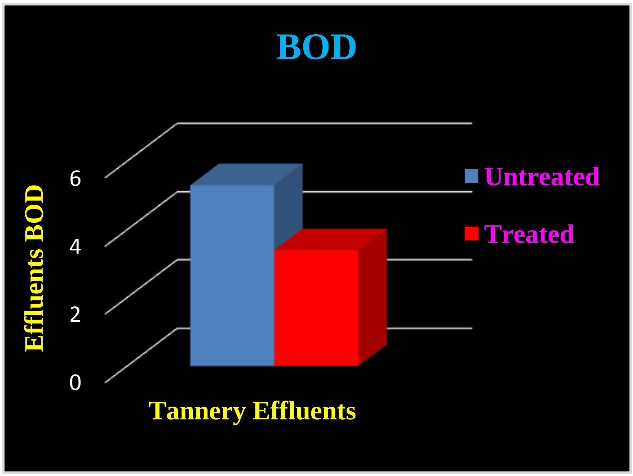

Figure 12. BOD of untreated and treated tannery effluents

3.1.12. Total Hexavalent Chromium

The effluents generated by the tanneries are the major source of chromium pollutants. In the present study, the untreated effluent contains 24µg/l exceeding than the permissible limit of WHO (0.1 µg/l) and Even the treated effluent contains 1.64µg/ml of chromium higher than the permissible limit were shown in Table 2 and Figure 13. The chrome tanning process generates toxic metals and so that regular treatment methods cannot eliminate chromium from it hence the treated effluents also contains minor chromium load in it [34,35].

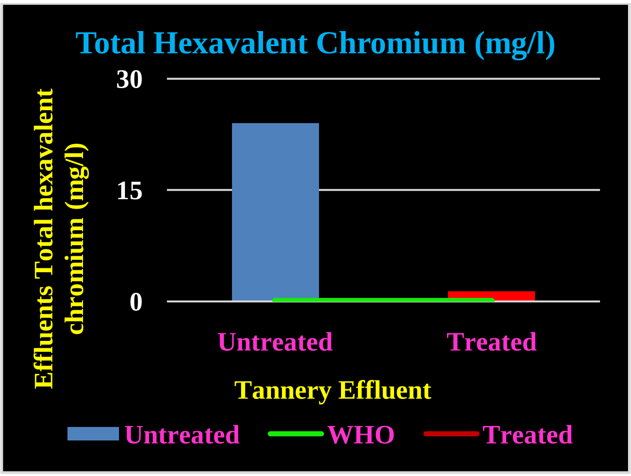

Figure 13. Total Hexavalent Chromium Content of Untreated and Treated Tannery effluents compared with WHO

4. Conclusion

In the present study, the untreated and treated effluents physico chemical parameters were analyzed and compared with the WHO standards. Treated effluents values were low for turbidity (53.1%), EC (58.6%), TDS (61.5%), Total hardness (68.3%), Acidity (61.5%), Salinity (91.3%), Alkalinity (69.3%), BOD (35.8%) and Total hexavalent chromium (94.1%) compared to untreated effluents.

Though, the tannery effluents are treated before discharge 100% reduction of toxic pollutant and chromium is not possible so that alternate methods can be adopted. In the further study, steps were taken to reduce the chromium in the form of nanoparticles using green synthesis.

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