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CHARACTERIZATION OF INDUSTRIAL WASTEWATER PHYSICO-CHEMICAL PROPERTIES

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Abstract- Permanent Because the operations of industrial activity are aimed at gratifying consumers, industries, in general, utilize natural resources such as water to increase their production rate. However, in consideration of the paucity of these resources and the regulatory environment, these businesses are being urged to take steps to ensure long-term development and resource protection. In this study and Based on a practical investigation for an industrial site in the south of Morocco, we evaluated the variation of wastewater Physico-chemical parameters over one year. The results of analyzing the wastewater show a significant rise in Physico-chemical characteristics as a result of its storage. consequently, we are seeing an increase in water pollution. Using correlation statistical approaches, the significantly linked wastewater parameters were determined. The correlation method established in the study can be used to monitor wastewater quality parameters by evaluating the highest correlated metrics for the treatment purpose, as evidenced by a comparison of the recorded value of different wastewater characteristics. In certain cases, wastewater recycling is given as a control strategy to minimize significant environmental consequences.

Keywords: Industries, Environment, Wastewater, Physico-Chemical Parameters, Correlation.

1. INTRODUCTION

A broad in the 21st century, permanent loss of natural resources, mainly water, and deterioration of their quality remain key challenges.

The worldwide need for high-quality water, whether for consumption, sanitary, agriculture, or industrial use, has been steadily increasing over time, and there has been significant debate over water treatment and recycling, which requires the tightest requirements [1].

The majority of Morocco's water resources are traditional. Water recycling of wastewater is an example of non-conventional water resources that have recently been developed to reduce resource extraction and protect the environment [2].

Wastewater treatment to decrease pollution is a critical requirement in today's society to protect natural resources. This can be accomplished by employing a variety of ways to reduce contamination of water and eliminate the problem of wastewater disposal.

During the manufacturing system, several industries use a variety of chemical components, solvents, and solid water, and they discharge effluent water containing substantial chemicals, which is harmful to the environment, humans, and especially aquatic life [3].

Furthermore, due to tight requirements, the water used for industrial units in these businesses cannot be recycled, and thereby the toxic effects must be decreased to protect the environment [1].

Among the toxins and pollutants found in wastewater are:

• Dietary supplements (nitrogen, phosphorous, potassium)

• Microorganisms that cause diseases like bacteria and viruses.

• Heavies metals such as Zinc, Nickel Cadmium, Mercury Chromium.

• Organic pollutants like pesticides, and biodegradable organics (BOD and COD))

• Micropollutants are small particles that pollute the environment like cleaning agents.

These contaminants have a serious impact on the environment [4].

Heavy metal contamination, inflammation, and bacterial diseases, as well as nutrient enrichment, are some of the negative impacts. hazardous material release and nutrient enrichment are all outcomes of oxygen depletion. To avoid these undesirable and dangerous consequences, wastewater that is released into diverse water sources must be appropriately treated [5].

By examining the wastewater of an industrial site in the south of Morocco, we will highlight the inconvenience for all industrial sites that used to discharge their wastewater in the environment (water, soil. Etc). Physico-Chemical examination of the presence of water contaminants was carried out in this study. To link the physicochemical properties, statistical processing was used to define the most typical associations.

2. MATERIALS & METHODOLOGIES

2.1. Overview of the Research Area

An industrial facility with an internal water treatment system in the south of Morocco was chosen to collect wastewater samples from effluent during the year 2021 to cover all seasons of the year.

2.2. Sampling and Physicochemical Analysis

The sampling took place from January to December 2021, and a Sigma SD900 Portable Sampler was used to collect the data.

Standard procedures were used to conduct Physicochemical and bacteriological analyses of the wastewater in our Laboratory of Biotechnology, Materials, and Environment.

Samples were gathered in special containers attributed to the presence of oil residues in the effluent from the industrial site (Glass type).

The samples were taken from the industrial site and tested the same day.

The Standard Techniques for the Examination of Wastewater were used to follow standard protocols for the analysis of wastewater [6].

The following physical, chemical, and bacteriological analyses were carried out using the methods described in Table 1.

Table 1. The sampling analysis method used for wastewater

Parameter	Methods
Temperature (T°)	NM 03-7-008 v 1989
pH	NM ISO 10523 v 2012
Electrical conductivity (EC)	NM ISO 7888 v 2001
Total suspended solids (TSS)	NM EN 872 v 2013
Chemical Oxygen Demand (COD)	NM 03.7.054 v 2013
Biochemical Oxygen Demand (BOD ₅)	NM 03.7.056 v 1998
Sodium (Na)	NF T 90-019
Aluminium (Al)	NF-T 90-138
Nitrates (NO ₃)	NM ISO 7890-3 v 2012
Total suspended solids (TDS)	NM ISO 7888 v 2001
Iron (Fe)	NF 90-112
Zinc (Zn)	NF 90-112
Chrome total (Cr)	NF 90-133
Sulfate (SO ₄)	NF-T 90-040
Nickel (Ni)	NF 90-112
Copper (Cu)	NF 90-112
Mercury (Hg)	NM 03.7.028
Cadmium (Cd)	NF 90-134
Lead (Pb)	NF 90-112
Arsenic (As)	NM 03.7.238
Selenium (Se)	NM 03.7.234
Manganese (Mn)	NF 90-112
Cobalt (Co)	NF 90-112
Cyanide (CN)	Colorimetric method
Fluorine (F)	Colorimetric method
Phenol index (C_6H_6O)	NF 90 - 109
Salmonella	NM ISO 1925 v 2012
Vibrio cholerae	NM 03.7.051 v 1996
Escherichia coli	NM ISO 9308-1 v 2007

3. STATISTICAL ANALYSIS

3.1. Correlation

As Correlation statistical analysis helps determine the quality of wastewater. Correlational analyses were carried out by using statistical tools. The Pearson correlation type was used to calculate the correlation coefficient (r) for industrial wastewater Physico-chemical parameters in this study. The most common types of correlations used in statistics are Pearson, Spearman, Point-Biserial, and Kendall rank correlations. Pearson correlation, on the other hand, is the most often used method for determining the degree of linearly connected variables' association. The formula described in Equation (1) is used to compute the Pearson coefficient (r) correlation [7].

$$r = \frac{N\sum xy - \sum x\sum y}{\sqrt{\left[N\sum x^2 - (\sum x)^2\right]\left[N\sum y^2 - (\sum y)^2\right]}}$$
(1)

where,

r= correlation coefficient of Pearson

N = value in each data set number

 $\sum x = x$ scores' sum

 $\sum y = y$ scores' sum

 $\sum x^2$ = scores multiplied by x square

 $\sum xy$ = the product of two paired scores

 $\sum y^2$ = scores multiplied by *y* square

The goal of statistical analysis is to determine how Physico-Chemical characteristics in wastewater are related to each other. Correlation is a bivariate analysis that evaluates the strength of correlation between variables including the significance of the relationship [8].

To determine correlation coefficients, the correlation matrix was formed by calculating the coefficients of different pairs of those parameters.

A correlation coefficient (r) of -1 or +1 specifies the important negative or positive association between two different parameters; when this value is near to 1, the degree of relationship between the two parameters is highly significant. If the correlation value approaches zero, the relationship between those two variables will become less significant. [9].

The p-value was then used to determine the correlation's significance. In this situation, the correlation is significant if the value of p is less than 0.05 or less than 0.01. The correlation is non-significant if the value of p is 0.05 or more. At the 0.01 & 0.05 levels, significance is determined (2-tailed analysis) [10].

4. RESULTS AND DISCUSSION

4.1. Results of Wastewater Physico-Chemical and Bacteriological Analysis

Table 2 summarized the result obtained during one year for the Physico-chemical and bacteriological analysis of the wastewater.

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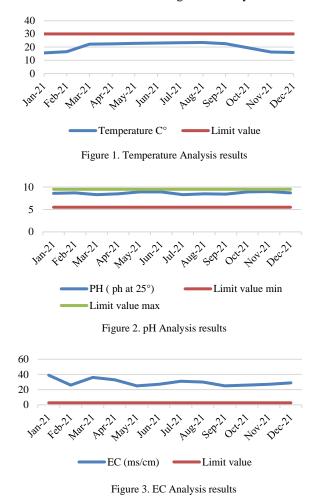
Chemical and bacteriological analysis of the wastewater											
Parameter	Jan-21	Feb-21	Mar-21	Apr-21	May-21	Jun-21	Jul-21	Aug-21	Sep-21	Oct-21	Nov-21
$^{\circ}\mathrm{T}$	15.6	16.5	22.3	22.5	22.8	23.1	23.3	23.5	22.6	19.5	16.3
Ηd	8.6	8.7	8.3	8.5	8.9	8.9	8.3	8.5	8.4	8.9	9.0
EC (ms/cm)	39.0	26.0	36.0	33.0	25.0	27.0	31.0	30.0	25.0	26.0	27.0
TSS	55.0	56.0	72.0	84.0	31.0	30.0	27.0	29.0	25.0	65.0	54.0
DCO	810.0	715.0	700.0	615.0	569.0	512.0	426.0	548.0	622.0 25.0	315.0	355.0 54.0
DBO5	312.0	287.0	216.0	205.0	200.0	198.0	156.0	142.0	170.0	165.0	98.0
Na	6000.0	5600.0	5200.0	4300.0	1800.0	2100.0	4500.0	3650.0	5120.0	5002.0	3689.0
AI	10	0.9	0.56	0.3	0.4	0.1	0.15	0.36	0.45	0.1	0.2
NO_3	1.3	0.15	0.21	0.19	0.25	1.56	1.63	1.8	0.96	0.85	0.45
TDS	21000	19000	16000	15500	12300	26000	22000	19000	15420	14633	22000
Fe	0.02	0.19	0.08	0.23	0.1	0.1	0.15	0.23	0.09	0.08	0.14
Zn	0.02	0.68	0.24	0.01	0.02	0.09	0.08	0.15	0.16	0.23	0.14
Cr	0.01	0.015	11000 0.019	0.005	0.01	0.005	0.009	0.008	0.009	0.15	0.09
SO_4	8000	5200		8500	2500	5100	7800	6300	4200	3600	7500
Ni	0.011	0.17	0.02	0.005	0.01	0.004	0.008	0.005	0.02	0.005	0.01
Cu	0.09	0.18	0.015	005 0.008 0.005	0.01	0.03	0.01	0.02	0.18	0.002 0.015	001 0.008
Hg	0.001	0.001	0.001	0.	0.001	0.001	0.001	0.001	0.002	0.002	0.001
Cd	0.012	0.01	0.01	0.005	0.01	0.05 0.005 0.005 0.005 0.002 0.001	0.002	0.002	0.01	0.01	0.07 0.003 0.004 0.005 0.005 0.
Pb	0.017	0.18	0.26	0.005	0.014	0.005	0.005	0.005	0.17	0.23	0.005
As	0.012	0.013	0.019	0.025	0.01	0.005	0.008	0.006	0.01	0.005	0.004
Se	0.05 0.011 0.012 0.017	0.03 0.012 0.013	0.01	0.004	0.01	0.005	0.009	0.008	0.05 0.002 0.01	0.01	0.003
Mn			0.12	0.019	0.01		0.01	0.08	0.05	0.06	0.07
Co	0.012	0.012 0.012	0.013	0.018 0.005 0.019 0.004 0.025 0.005 0.005	0.011	0.005	0.017 0.005 0.01 0.009 0.008 0.005 0.002 0.001	0.01 0.005 0.08 0.008 0.006 0.005 0.002 0.	0.011	0.02 0.005	0.004
CN	0.01	0.012	0.01	0.018	0.015 0.011	0.01	0.017		0.017 0.011		1.69 0.017 0.004
F	0.05	0.04	0.065 0.01	0.45	0.65	1.33	2.15	3.15	2.18	2.14	1.69
C ₆ H ₆ O	0.02	0.025	0.01	0.018	0.014	1.69	1.9	0.67	0.52	0.014	0.13

Table 2. Results were obtained during one year for the Physico-Chemical and bacteriological analysis of the wastewater

Escherichia coli	Vibrion Colerique	Salmonella
<1	Absence	Absence

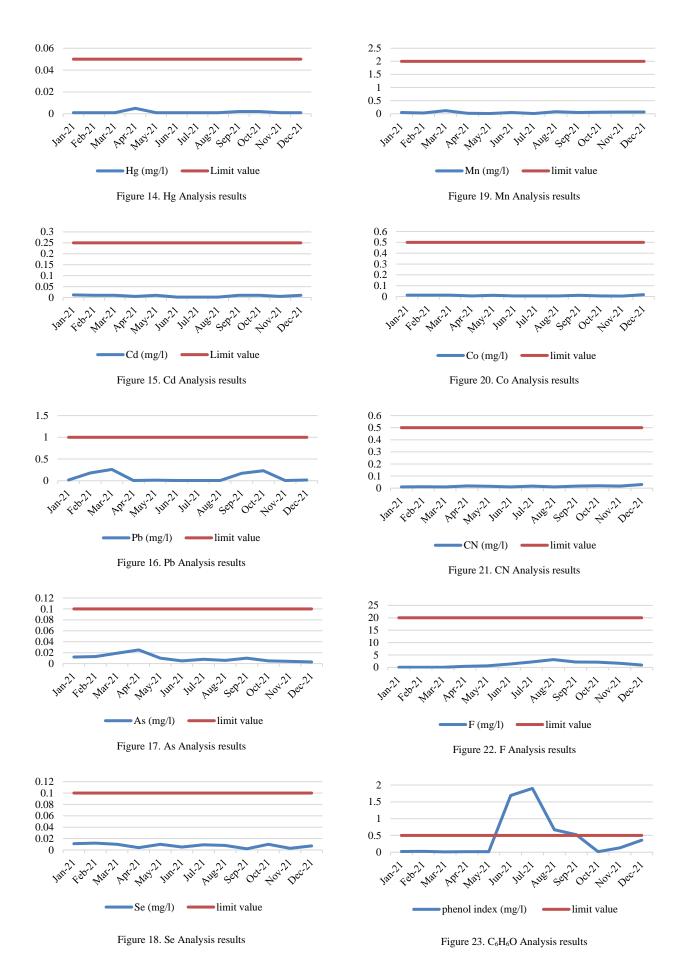
Based on Table 2, twenty-six wastewater parameters were analyzed, five parameters (EC, COD, BOD₅, SO₄, phenol index) exceed the limit levels fixed by Moroccan standards for wastewater discharge into surface or subsurface waters [11].

The bacteriological analysis shows that this industrial wastewater is free from Microorganisms. The following graphs (Figures 1 to 23) show the evolution of the wastewater Physico-Chemical parameters compared with the limit standards values during the whole year.





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The following parameters, according to the wastewater physicochemical analysis results, exceed the Moroccan regulations for wastewater discharge into surface or subterranean waters:

- The EC averages 29.5 ms/cm, which is more than the limit of 2.7 ms/cm.

- The average BOD5 value of 187.5 mg O_2/l is higher than the limit value of 100 mg O2/l.

- The COD has a median value of 544 mgO₂/ l, which is higher than the limit value of 500 mg O₂/l.

The Na level is quite high, with a median of 3800 mg/l. TDS has a median value of 18487 mg/l, which is above recommended irrigation limit of 7680 mg/l.

 SO_4 has an average value of 6260 mg/cm, which is above the limit value of 600 mg/l.

During June, July, August, and September, the phenol index surpasses the 0.5 mg/l limits.

Also, the results show that the parameters of the industrial water discharge changed between summer and winter seasons, namely:

When comparing the value of pH at 25° during the winter season to the value during the summer season, there is a small increase in winter.

The strongest EC values were seen in March and April, while the lowest values were seen in September.

The TSS values decreased during the summer period.

The highest values of the COD and BOD_5 were shown during the winter season.

The highest Na values were seen in January and February, while the lowest values were seen during May and June.

When comparing the value of Al during the winter season to the one during the summer season, there is a small increase in winter.

Increase of NO_3 and TDS values during the summer seasons compared to the winter.

The strongest phenol index values were seen in June, July, and August, while the lowest values were seen in March, April and May.

Because most of the heavy metal values are widely below the limit values, there is no discernible difference between the summer and winter periods for heavy metals.

The results of the wastewater assessment demonstrate that radiation from the sun has a negative impact on industrial effluents, as indicated by a large increase in numerous wastewater characteristics, according to Physico-Chemical criteria discarded by industrial facilities. This phenomenon has the potential to have significant environmental and ecological consequences.

The high value of EC, which is associated to the increase of several physiochemical properties, could be explained by biodegradation in the wastewater; EC is raised when there is a lot of organic pollutants.

Finally, based on the findings, we advocate repurposing wastewater collected by industrial sites using conservatory techniques like greenhouses technology, particularly in dry and sunny places.

Because some organic molecules are tiny or nonbiodegradable, bacteria will need to adapt for a long time before they can modify the organic substances, the presence of oxidant resilience of organic compounds in wastewater, as well as the presence of salt, could explain the high COD values [12].

Table 3 summarize the correlation results during the whole year (both winter and summer seasons), the interpretations of correlation results are as follow:

Table 3. Correlation matrices for wastewater parameters for one year

	BOD5	Al	NO_3	SO_4	Cr	Ni	Cu	Cd	Pb	\mathbf{As}	Co	CN	F	C ₆ H ₆ O
EC				0.814^{**}										
TSS			-0.614*							0.669^{*}				-0.625*
COD	0.858**	0.822**			-0.683*					0.659*		-0.672*	-0.578*	
BOD5		0.777**										-0.602*	-0.671*	
Na		0.581^{*}												
AI						0.577*	0.627^{*}	0.623^{*}			0.621^{*}		0623*	
NO_3													0.647^{*}	0.650* 0.734**
TDS														0.650*
Zn						0.919^{**}	0.590^{*}		0.614^{*}					
Ni							0.683^{*}							
Hg										0.652*				
Cd											0.756**			-0.727**
\mathbf{As}													-0.588*	
** So, at 0.01 level, the correlation is significant (2-tailed).														
* So, at 0.05 level, the correlation is significant (2-tailed).														

• T°: Table 3 shows the statistical analytical results, which indicate that the temperature of wastewater has a negative correlation with pH, Na, and Al; and a positive correlation with the phenol index, however, the Temperature has a very weak correlation with COD, BOD₅, SO₄, Pb and Mn.

• pH: pH has a positive association between Cr, and a negative moderate association with EC, NA, SO₄, and As, pH shows its weak correlation with TSS, Zn, Ni, Cd, Se, and F.

The effect of pH showed that when the wastewater was alkaline, the generation of NO₃, Al, Zn, and Se increased.

• EC: The EC has a positive association with TSS, COD, BOD5, Na, Al, and As and a negative correlation with F, however, a weak association has been observed with NO₃, Hg, Cd, Pb, and phenol index.

The high EC value, which correlates with increases in TSS, BOD₅, COD, Na, and Al, could be explained by organic matter breakdown in the wastewater. When there is a lot of organic pollution, conductivity rises.

• TTSS: TSS have a positive association with Na, SO₄, Hg; a negative association with F; TSS shows its weak correlation with Zn, Cu, Co, CN and Se.

Total suspended particles in industrial wastewater can also rise due to the oxidation of iron complexes with oxygen.

• COD: COD has a positive correlation with Cu and Cd and shows its weak correlation with NO₃, TDS, Hg, Pb, and Mn.

The presence of oxidative resistance of organic compounds, particularly in wastewater, and the presence of sodium could explain the high COD readings [12].

• BOD₅: BOD₅ has a positive correlation with Na, Ni, Cu, Cd, As, Se and a negative correlation with Cr, however, BOD₅ has a very weak correlation with NO₃, SO₄, and Hg.

This association could be regarded as the DBO₅ result being under-evaluated if the wastewater is lacking in nutrients. Nitrification happens if the nutrient concentration is too high, and the DBO is overrated.

- Na: Na has a positive correlation with Zn, Cu, Cd, Pb and a very weak correlation with NO₃, TDS, Cr, Hg, and CN. This is an example of the contact between fresh and saltwater.
- Aluminum (Al): Al has a positive correlation with Se, Zn, and a negative correlation with phenol index, however, Al shows its weak correlation with TDS, Hg, and Mn.
- NO₃: NO₃ has a positive association with TDS, a negative association with Cd, As, and a very weak correlation with SO₄, Cr, Cu, Se, and Mn.
- SO₄: SO₄ has a positive association with As, Mn; a very weak association with Zn, Ni, Hg, Cd, Pb, Se, Co and phenol index.

Sulphates are commonly measured. A high sulphate level could indicate industrial wastewater pollution.

• Zn: Zn has a positive correlation with Se, however, Zn shows its weak correlation with Cr, As, Mn, Co, CN, and F.

Zn continues to be the most harmful material released into wastewater.

- Cr: Cr has a positive correlation with CN, and a negative correlation with As, however, Cr shows its weak correlation with Hg, Ni, and Se.
- Ni: Ni has a positive association with Se; a negative association with F, however, Cr shows its weak correlation with Hg, As, and Mn.
- Cu: Cu has a positive association with Cd, Pb, Co and a moderate association with Hg, As, Se, F, Phenol index and Mn.

Cu has a remarkable affinity for soluble organic ligands, and the creation of these complexes can greatly improve copper's mobility in wastewater.

• Hg: Hg has a negative association with Se and a weak association with Cd, Pb, and F.

The Hg is a transition metal from the third series of elements. The Hg is a chalcophile metal that forms strong covalent connections with chalcogenide ions like Se (II). • Cd: Cd has a positive association with Pb; a negative association with F and a weak correlation with As, Mn, and CN.

This could be explained by Cd being a chalcophile element that is commonly linked to lead. Ionic structures and electronegativity are similar in both elements.

• Pb: Pb has a positive association with Mn and a weak association with CN and F.

Lead concentrations in wastewater are limited in some circumstances under reducing conditions by metallic lead, which has high stability under reducing conditions.

- As: As has a negative association with phenol index and a weak association with Se, Mn, and Co.
- Se: Se has a positive association with Co, a negative association with F, and a weak association with pH, Mn, and phenol index.

Iron oxides rapidly bond to Se. The loss of Se in the presence of iron oxides increased with lowering pH, according to [13].

This research not only shows how pH affects selenite adsorption but also how concentration affects it.

- Mn: Mn has a moderate association with CN and F. this could be explained that Most clay minerals, carbonates, and iron or manganese hydroxides can absorb cadmium.
- Co: Co has a negative association with F and phenol index.

The degree of inorganic cobalt complexation rises with increasing pH and water hardness, according to data from these models. Similarly, as the quantity of dissolved organic carbon rises, proportion of cobalt linked to organic matter, such as humic acids and fulvic acids, rises (DOC).

• CN and F: CN has a moderate association with F and phenol index. F has a positive association with the phenol index.

The statistical analysis results showed the major significative correlation of the wastewater parameters as follow:

The EC of wastewater has an important positive association with SO₄ (r= 0.814, p< 0.01).

TSS has an important negative association with NO₃ (r= -0.614, p< 0.05), phenol index (r= -0.625, p< 0.05), however TSS showed an important positive association with as (r= 0.699, p< 0.05).

The COD showed an important positive association with BOD₅ (r=0.858, p<0.01), Al (r=0.822, p<0.01), As (r=0.659, p<0.05), and an important negative association with Cr (r=-0.683, p<0.05), CN (r=-0.672, p<0.05) and F (r=-0.578, p<0.05).

The BOD₅ showed an important positive association with A1 (r=0.777, p< 0.01) and an important negative association with CN (r= -0.602, p< 0.05) and F (r= -0.671, p< 0.05).

Al showed an important positive association with Ni (r=0.577, p<0.05), Cu (r=0.627, p<0.05), Cd (r=0.623, p<0.05), Co (r=0.621, p<0.05) and an important negative association with F (r=-0.623, p<0.05).

NO₃ showed an important positive association with F (r=0.647, p<0.05) and phenol index (r=0.734, p<0.01). TDS showed an important positive association with phenol index (r=0.650, p<0.05).

Zn showed an important positive association with Ni (r= 0.919, p< 0.01), Cu (r= 0.590, p< 0.05), Pb (r= 0.614, p< 0.05).

Ni showed an important positive association with Cu (r=0.683, p<0.05).

As showed an important positive association with Hg (r= 0.652, p< 0.05) and an important negative association with F (r= - 0.588, p< 0.05).

Cd showed an important positive association with Co (r= 0.756, p < 0.01) and important negative association with phenol index (r= -0.727, p < 0.01).

The above heavy metal correlation results (Table 3) show that wastewater is not a high pollutant because most heavy metal values are below the limit value. As a result, this wastewater could be treated and recycled using normal wastewater treatment methods.

Industrial sludge is commonly detected heavy metals in wastewater. As a result, reusing sludge is regarded as a method of contaminating the environment.

Throughout the study period, zinc levels were below the limit values. When the pH is mildly acidic and the environment is already well, dissolved zinc is plentiful, but when the pH is basic, it's much less soluble, stationary, and bioactive [14].

Furthermore, wastewater must be adequately treated to keep pollutants below harmful levels before irrigation can be considered as a safe way of disposing of [15], [16].

Heavy metals and some other wastewater pollutants are more likely to accumulate in ground and crops watered with inadequately treated or transformed wastewater effluent was documented by [17].

5. CONCLUSION

The outcomes of evaluating the Physico-Chemical parameters of wastewater discharged by industrial sites show that wastewater stagnated or stored in dedicated ponds hurts the wastewater quality. As a result, wastewater storage causes a significant increase in several Physico-chemical parameters, such as electrical conductivity, sulfates, phenol index, suspended particles, chemical, and biological oxygen demand COD, BOD₅ etc.

Accordingly, we're talking about a rise in water contamination [18]. Based on wastewater quality measurements taken from an industrial facility for a year, this study found the most significant connections between BOD₅, COD, EC, SO₄, NO₃, phenol index, Cd and Al.

According to the results of the correlation analysis, the chemical oxygen demand COD of industrial wastewater generated by industrial operations shows a substantial association with most of the other wastewater parameters. The wastewater, on the other hand, shows the strongest significant correlations between zinc and nickel, as well as between COD and BOD₅.

All the physicochemical characteristics of industrial effluent are linked in some way, according to this study. The electrical conductivity, chemical and biological oxygen needs, sodium, Total Dissolved Solids, total chrome, sulphates, and phenol index, on the other hand, exceed the permitted limits for wastewater quality characteristics in the research region.

To prevent potential environmental and ecological concerns, wastewater reuse or recycling using different technical procedures is offered as a method of control. Because most levels of heavy metals are below the limit level, the results of heavy metal correlation data analysis suggest that wastewater is not a high contaminant.

As a result, using standard wastewater treatment technologies, this effluent might be treated and recycled

NOMENCLATURES

1. Symbols / Parameters

 T° : Temperature *pH*: Potential of hydrogen EC: Electrical conductivity TSS: Total suspended solids COD: Chemical Oxygen Demand BOD₅: Biochemical Oxygen Demand Na: Sodium Al: Aluminum NO₃: Nitrates TDS: Total suspended solids Fe: Iron Zinc: (Zn) Cr: Chrome total SO₄: Sulphate Ni: Nickel Cu: Copper Hg: Mercury Cd: Cadmium Pb: Lead As: Arsenic Se: Selenium Mn: Manganese Co: Cobalt CN: Cyanide F: Fluorine C₆H₆O: Phenol index

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