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Measurement of Corrosivity Index of Waste Water Using Langelier Saturation Index, Larson Skold Index, Ryznar Stability Index And Puckorius Scaling Index Adewole E^{1*}, Ojo A¹, Olagbemide P.T² and Peter O¹

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Waste water can be defined as water that has been greatly affected in quality as result of human uncontrolled activities. This can originate from a combination of industrial, commercial and agricultural activities. The high rate at which people in these sited location use the waste water for various purposes necessitated the analysis of the waste water in order to find out its degree of corrosivity.

Many parameters are being used in evaluating pollution and corrosivity index and this include Langelier Saturation Index, Larson Skold Index, Ryznar Stability Index and Puckorius Scaling Index [1].

METHODOLOGY

Collection of Sample

The waste water was collected from a nearby open channel in Warri metropolis and stored in sterilized bottle.

Waste Water Analysis

The following parameters were analyzed using standard procedure according to Furman [4]:

(a) Total Alkalinity

50 ml of the water sample was measured into a conical flask and 2 drops of mixed indicator (Bromocresol green-methyl red solution) was added. This was titrated with 0.02M HCl until colour change to pink. The volume of acid used was taken as V_t .

Total Alkalinity as mg/L CaCO₃ =

 $\frac{V_{t} \times M \times 100,000}{Volume of waste water of sample}$

(b) Hydrogen Carbonate and Carbonate

Fifty (50) ml of water sample was measured into conical flask and a slight excess of barium chloride was added to precipitate the carbonate. 2 drops of phenolphthalein indicator was added and titrated with 0.02M HCl until the solution becomes colourless and the titer value taken as V_1 . Two drops of mixed indicator was then added to the solution and titrated to end point with 0.02M HCl. The volume of acid used was taken as V_2 [5].

 $HCO_3^- = \underbrace{V_1 \times M \times 100,000}_{Volume waste water of sample}$

 $CO_3^{2-} = V_T - (V_1 - V_2) \times M \times 100,000$ Volume waste water of sample

(c) Sulphate

100ml of the water sample was measured into conical flask and 5ml conditioning reagent was added and stirred with the magnetic stirrer. A spoonful of barium chloride crystal was added and the solution further stirred for one minute. The absorbance of the sample was measured at 425nm using distilled water as blank. The corresponding sulphate concentration was extrapolated from sulphate calibration curve.

 $SO_4^{-2} = \frac{\text{Reading from curve} \times 1000}{\text{Volume waste water of sample}}$

(d) Chloride

25mL of the sample was measured into a conical flask and 1mL of potassium chromate indicator was added to the flask content. The mixture in the flask was titrated with standard 0.01N silver nitrate solution to a brick red end point. The titre value of the sample was recorded and also the reagent blank was also run and the titre value recorded.

Chloride, $(mg/L) = (A-B) \times N \times 35400$ V A = titre value for sample

B = titre value for blank N = Normality of silver nitrate

V = Volume of sample used

(e) Calcium

25mL of the sample was measured into a conical flask, 2mL of the 8N NaOH solution was added to give a pH of 12 and a pinch of the murexide indicator was also added to the flask content which gave a pink colour. The mixture in the conical flask was titrated immediately with standard 0.01M EDTA solution until a change in colour from pink to purple was observed which marked the end point [2].

Calculation

Calcium Hardness, (mgCaCO₃/L) = $\frac{V \times A \times 1000}{Vol. of sample}$

Where: V= Volume of EDTA used for sample $A = mg CaCO_3(mg)$ equivalent to 1.00mL EDTA

(f) Mineral Analysis

The following mineral contents; Lead, Cadmium, Magnesium, Iron, Nickel, Copper were determined using Atomic Absorption Spectrometer.

(g) The pH was determined using PH meter.

Results of the waste water

Appearance: Clear Liquid Odour: Hydrocarbon odour

STATISTICAL ANALYSIS

Descriptive method of analysis was used for the Statistical Analysis

Table-1.0 showing the statistical analysis results of Chemical properties of the waste water

Descriptive Statistics					
	Ν	Minimum	Maximum	Mean	Std. Deviation
pH	2	6.62	6.63	6.6250	0.00707
Conductivity(µscm ⁻¹)	2	122.00	122.20	122.1000	0.14142
Total_dissolved solid (mg/L)	2	73.30	73.40	73.3500	0.07071
Alkalinity(mg/L)	2	73.80	74.10	73.9500	0.21213
$HC0_3^{-}$ (mg/L)	2	73.80	74.10	73.9500	0.21213
$C0_3^{2-}$ (mg/L)	0				
Valid N (listwise)	0				

Table-1.2: showing the statistical analysis results of chemical properties of the waste water

	Ν	Minimum	Maximum	Mean	Std. Deviation
Sulphate(mg/L)	2	5.60	5.70	5.6500	0.07071
Chloride(mg/L)	2	45.10	45.20	45.1500	0.07071
Manganese(mg/L)	2	0.04	0.04	0.0400	0.00000
Cadmium(mg/L)	0				
Lead (mg/L)	2	0.08	0.08	0.800	0.00000
Magnessium(mg/L)	2	0.67	0.69	0.6800	0.01414
Valid N (listwise)	0				

Table1.3: showing the result of chemical properties of waste water

	Ν	Minimum	Maximum	Mean	Std. Deviation
Zinc(mg/L)	2	0.10	0.11	0.1050	0.00707
Iron(mg/L)	2	0.31	0.33	0.3200	0.01414
Nickel(mg/L)	2	0.04	0.05	0.0450	0.00707
Copper(mg/L)	2	0.01	0.01	0.0100	0.00000
Chromium(mg/L)	2	0.03	0.03	0.0300	0.00000
Calcium(mg/L)	2	10.14	10.28	10.2100	0.09899
Valid N (listwise)	2				

EVALUATION OF POLLUTION/CORROSION PARAMETERS

(1) Langelier Saturation Index (LSI)

 $LSI = pH - pH_{(s)}$ (where TDS < 10,000mg/L)

$$A = \frac{\log_{10} [TDS] - 1}{100} = \frac{\log_{10} (73.35) - 1}{100} = 0.00865 \approx 0.009$$

$$B = -13.12 \log_{10} \left[{}^{0}C + 273 \right] + 34.55 \qquad Temp = 24.7 {}^{0}C$$
$$= -13.12 \log \left[24.7 + 273 \right] + 34.55 = 2.09$$

$$pH_{(s)} = (9.5 + A + B) - (C + D)C = \log_{10} \left[Ca^{+2} \ as \ CaCO_3\right] - 0.4$$
$$= \log_{10} \left[10.21\right] - 0.4 = 0.6$$
$$D = \log_{10} \left[Alkalinity \ as \ CaCO_3\right]$$

$$= \log_{10} (73.95) = 1.87$$

$$pH_{(s)} = (9.5 + A + B) - (C + D)$$

= (9.5 + 0.009 + 2.09) - (0.6 + 1.87) = 9.13
$$\therefore LSI = pH - pH_{(s)}$$

= 6.63 - 9.13
$$LSI = -2.5$$

(2) Ryznor Stability Index (RSI)

$$\begin{split} &RSI = 2 \ (pH_s) - pH \\ &Where: pH \text{ is the measured water pH} \\ &pH_{(s)} = \text{ is the pH at saturation in calcite/CaCO}_3 \\ &RSI = 2 \ (9.13) - 6.625 \\ &RSI = 11.635. \end{split}$$

(3) Puckorius Scaling Index (PSI) $PSI = 2 (pH_s) - pH_{equilibrium}$ $pH_{equilibrium} = 1.465 \log_{10} (Alkalinity) + 4.54$ $= 1.465 \log_{10} (73.95) + 4.54$ = 7.28 PSI = 2(9.13) - 7.28PSI = 10.98

(4) Larson-Skold Index (LSI) =
$$\frac{epmCl^{-} + epm504^{-2}}{epmHc_{3}^{-} + epmCo_{3}^{-2}}$$

Conversion from mg/c (ppm) to epm

 $epm = \frac{mg/L}{equivalent \ weight}$ Equivalent weight of $Cp^- = 35.5$, $So_4^{-2} = 48$, $HCo_3^- = 61$ and $Co_3^{-2} = 30$

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$$epmCl^{-} = \frac{45.15}{35.5} = 1.272$$
$$epmSo_{4}^{-2} = \frac{5.65}{48} = 0.118$$
$$epmHCo_{3}^{-} = \frac{73.95}{61} = 1.212$$
$$epmCo_{3}^{-2} = \frac{10.21}{30} = 0.340$$

$$LSI = \frac{1.272 + 0.118}{1.212 + 0.340} = \frac{1.39}{1.552} = 0.896 \approx 0.90$$

(5) Potential Soil Salinity (PSS)

$$PSS = Cp^{1}(epm) + \frac{1}{2}So_{4}^{-2}(epm)$$

$$= 1.272 + \frac{1}{2} \times 0.118$$

Table-1.4: showing the summary of pollution/ corrosivity parameters

Parameters	Values	Reference Std.
(1) Langelier Saturation Index (LSI) -2.50	-2.50	$-2 \leq LSI \leq -3$ (moderate corrosion)
		and treatment may be needed
(2) Ryznar Stability Index (RSI)	11.64	Index >> 8
(3) Puckorius Scalilng Index (PSI)	10.98	
(4) Larson-Skold Index (LSI)	0.90	0.8 < < Index < < 1.2
Potential Soil Salinity (PSS)	1.331	

DISCUSSIONS

From the results of tables, it has shown that the waste water is corrosive, the odour showed presence of hydrocarbon, the pH was 6.62 at 24.7° C, alkalinity values was 73.95Mg/L ±0.21, conductivity (122.10±0.14) was high and Calcium was 10.21mg/L ±0.10. Corrosive index has been regarded as a measure of the tendency for lime (calcium carbonate) to precipitate (form and scale out) from water and it is calculated from PH, alkalinity, Calcium hardness and conductivity data [1]. The Langelier Saturation Index (LSI) (-2.50) was lower than the reference standard (-2≤LSI≤-3) and this shows that the waste water is moderately corrosive and treatment may be needed. Also the negative LSI suggests that the water would be undersaturated with respect to carbonate equilibrium and the water may be more likely to have a greater corrosive potential. Corrosive water can react with household plumbing and metal fixtures resulting in the deterioration of the pipes and increased metal content of the water and this has shown from the results of mineral analysis; Mg 0.68mg/L ±0.01, Mn 0.04mg/L±0.00, Zn 0.11mg/L ±0.01, Fe 0.32 mg/L±0.01, Ni 0.04mg/L±0.01, Cu 0.01mg/L ±0.00, Cr 0.03mg/L±0.00 and Ca 10.21mg/L ±0.10. This reaction could result in aesthetic problems such as stains around basins, bitter water [1]. The Ryznar Stability Index (RSI) (11.64) was greater than the reference standard (RSI>>8) and this means that mild steel corrosion becomes an increasing problem. The RSI attempts to correlate an empirical database of scale thickness that is always observed in municipal water system to water chemistry [6]. The Larson –Skold index (0.90) this value fall in the range of 0.8 <<index << 1.2 indicating that sulphates and chlorides may

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interfere with natural film forming and higher than desired corrosion might be anticipated [1,3]. Puckorius Scaling Index (PSI) value indicated 10.98. The PSI attempts to quantify the relationship between the saturation state and scale formation. The high Calcium ion (10.21mg/L \pm 0.10) increases the ion activity product. The Potential Soil Salinity (PSS) was 1.331.

CONCLUSION

The high values recorded in Langelier Saturation Index (LSI), The Ryznar Stability Index (RSI), Larson –Skold index, Puckorius Scaling Index (PSI) and The Potential Soil Salinity (PSS) have shown that the waste water is polluted and mildly corrosive and may not be desirable for human activities and aquatic life around the areas.

RECOMMENDATION

Further treatment of the waste water is strongly recommended.

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