

Assessment of Chemically Treated Produced Water for Irrigation

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Abstract

This study investigates the effects of coagulation on the salinity, sodicity, and magnesium hazard of chemically treated produced water (PW). PW was treated with varying doses of aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) of analytical grade. Aluminium sulphate doses used were 0.1g, 0.2g, and 0.3g, and the samples were labeled T_1 , T_2 , and T_3 , respectively. A control sample without chemical treatment was labeled T_0 . The treatment process of the produced water followed a standardized jar test-style protocol using a magnetic stirrer. Salinity and sodicity were determined using electrical conductivity (EC), sodium adsorption ratio (SAR), Kelly's ratio (KR), and magnesium ratio (MR) values, while total petroleum hydrocarbon (TPH) toxicity was determined by ecological hazard quotient (EHQ). Results demonstrated a linear relationship between coagulant dosage and removal efficiency of both organic (TPH) and inorganic (EC, cations) pollutants. Coagulation treatment of the PW shifted PW from the C4-S1 category to the C1-S1 category, describing all treated samples as suitable for irrigation. However, with the toxicity test, only T_3 with a removal efficiency of 99.99% and $EHQ < 1$ was suitable for irrigation. T_1 and T_2 samples with 90.65% and 91.52% removal efficiencies, respectively, and $EHQ > 1$ were not suitable for irrigation. This implies that with treated PW, its suitability for irrigation should be assessed beyond salinity and sodicity hazards.

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I. INTRODUCTION

Over the past century, global water use has risen and continues to increase, fueled by population growth, economic progress, and shifting consumption habits. Agriculture remains the largest consumer of water, followed by the industrial and domestic sectors. Freshwater scarcity has become a critical concern, affecting billions of people living in water-stressed regions. As freshwater scarcity intensifies, there is growing interest in assessing other non-potable sources of water for agriculture, especially irrigation, which is reported as the highest water use sector (Ingrao et al., 2023).

One of the industrial wastewater streams is produced water (PW), which is the largest volume of waste stream generated during oil and gas extraction activities (Wei et al., 2019). It is a complex mixture of formation water and injected fluids that return to the surface during drilling, well stimulation, and production operations (Iggunnu & Chen, 2014). Its composition varies widely, containing dissolved salts, hydrocarbons, heavy metals, radionuclides, production chemicals (such as corrosion inhibitors and biocides), and suspended solids (Bhutani et al., 2024).

The management of produced water is a significant challenge for the oil and gas industry due to its volume, potential environmental impact, and cost of treatment. Advancements in chemical treatment methods, such as coagulation, flocculation, pH adjustment, oxidation, and chemical precipitation, have shown promise in removing key contaminants from produced water. However, the suitability of such treated water for safe discharge or agricultural use depends on compliance with environmental guidelines and irrigation water quality standards (Ibrahim et al., 2023).

Agriculture in Nigeria's Niger Delta region predominantly relies on rainfall, owing to the area's long wet season and short dry season. During the dry season, agricultural activity significantly declines, leading to food shortages (Amadi, 2013). However, the region has abundant sources of wastewater, such as produced water, which could potentially support year-round farming. Despite this potential, untreated or inadequately treated produced water poses environmental and health risks due to its content of hydrocarbons, heavy metals, and dissolved salts. Existing treatment approaches often focus primarily on removing total hydrocarbons, with limited attention given to dissolved salts, which can adversely impact soil salinity and sodicity (Daba, 2025). Consequently, there is a lack of reliable data on the quality of treated produced water and its suitability for

irrigation purposes. The aim of this study is to assess the quality of chemically treated produced water from oil and gas operations in Port Harcourt and determine its suitability for irrigation purposes.

This study is significant for multiple reasons. First, it provides data on the quality of a chemically treated PW, which is a critical need for environmental monitoring agencies, oil companies, and affected communities. Second, it evaluates the feasibility of repurposing treated water for irrigation, which could promote sustainable water use in agriculture. Third, it contributes to scientific literature and policy development on wastewater reuse in oil-producing environments. Fourthly, it provides knowledge about potential environmental and health risks associated with untreated or improperly treated produced water, and lastly, it supports the moral building both to the public and industry captains that properly treated produced water can be discharged into the environment or used for irrigation, which meets the acceptable quality standards and minimizes harm to ecosystems and human health. Assessing chemically treated produced water for irrigation is vital for environmental protection, public health, and sustainable resource management. It ensures that water resources are used responsibly and safely, minimizing potential harm to ecosystems and human populations.

II. MATERIALS AND METHODS

2.1 Description of Study Area

The Niger Delta is one of the world's largest wetlands, located in Southern Nigeria (Short & Stauble, 1967). Figure 1 shows the map of the region as a vast "bird-foot-shape". Geographically, it is defined by the area where the River Niger bifurcates at Aboh and extends to the Atlantic Ocean with an area coverage of approximately 70,000 square kilometers across nine states, including Abia, Akwa Ibom, Bayelsa, Cross River, Delta, Edo, Imo, Ondo, and Rivers (ERML, 1997). The topography is predominantly low-lying, with elevations rarely exceeding 45 meters above sea level, making it a complex basin of meandering rivers, creeks, and estuaries (Abam, 1999).

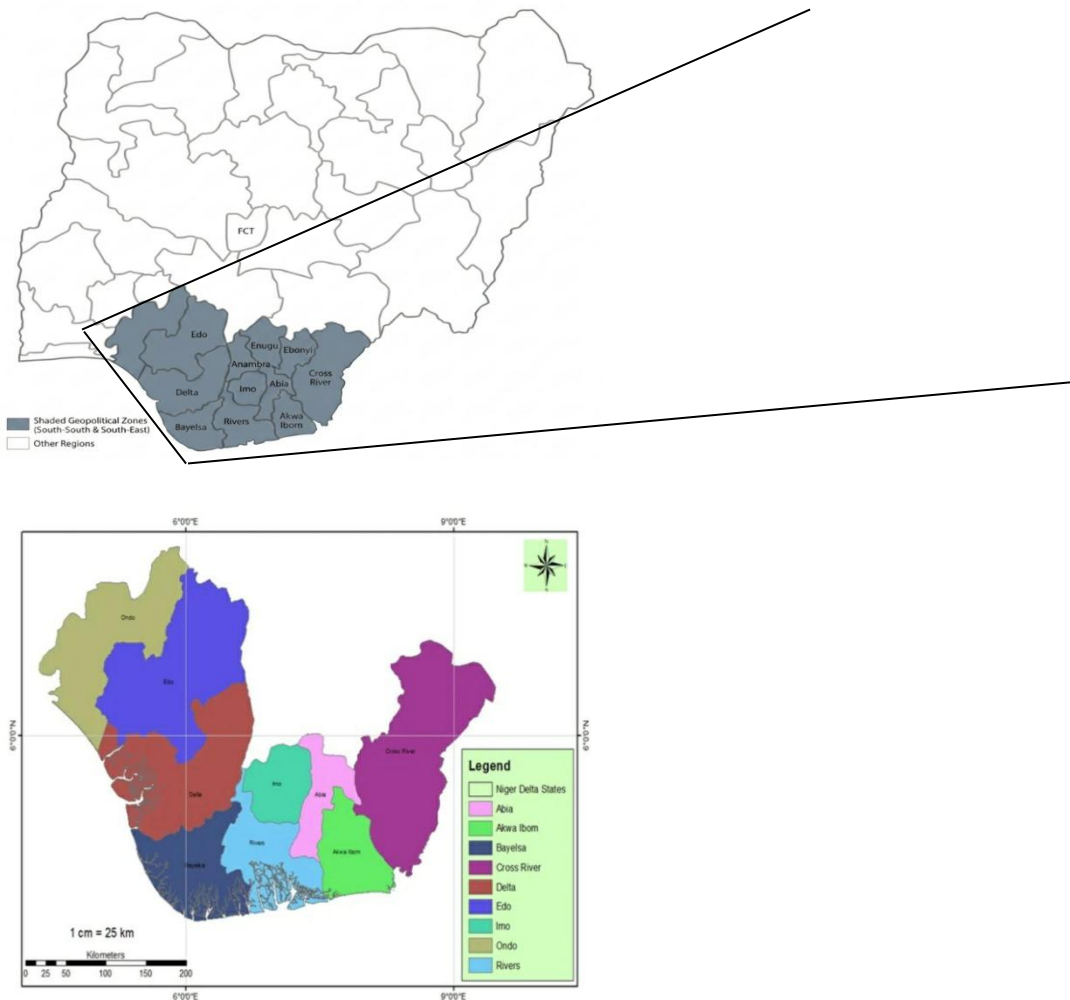


Figure 1: A Map of Nigeria Numerically Showing States Typically Considered Part of the Niger Delta Region (National Bureau of Statistics, 2024).

2.2 Materials and Equipment used.

The primary materials used in this research include produced water samples, glass beakers, coagulant, magnetic stirrer (Thomas Scientific, USA), and weighing balance (Adam Equipment LBK 12a, USA). The produced water was obtained from an oil field in the Niger Delta region, while the coagulant (Aluminum Sulfate - $Al_2(SO_4)_3 \cdot 18H_2O$) was an analytical grade. The magnetic stirrer had a speed range of 60 -1600 rpm, while the weighing balance had a precision of 0.01g.

2.3 Methods

2.3.1 Treatment of Produced Water using a Chemical Coagulant

The treatment process of the produced water followed a standardized jar test-style protocol using a magnetic stirrer to determine the impact of varying coagulant dosages on water quality. Four distinct treatments were prepared to assess the aluminum sulfate dose-response on the produced water. Each sample consisted of 200ml of raw produced water and various doses of aluminiumsulphate. To ensure effective chemical reaction and floc formation, the addition of varying dosages of the coagulant into the produced water was followed by a rapid mixing at 500 rpm for 2 minutes and slow mixing at 200 rpm for 10 minutes. The supernatant was filtered using a Whatman filter paper of 5 microns. The permeate was then analyzed for irrigation suitability. The samples were labeled as shown in Table 1.

Table 1: Sample Treatments for Produced Water (PW).

Sample ID	Coagulant Dosage
T_0 (Raw Produced water)	200ml PW + 0.0g of AluminiumSulphate
T_1	200ml PW + 0.1g of AluminiumSulphate
T_2	200ml PW + 0.2g of AluminiumSulphate
T_3	200ml PW + 0.3g of AluminiumSulphate

2.3.2 Characterization of the Chemical and Physicochemical Properties of Raw and Treated Produced Water.

The water samples (T_0, T_1, T_2, T_3) were subjected to chemical analysis to determine the concentration of various cations to enable the determination of the salinity indices and irrigation water quality index for a chemically treated produced water, which is the scope of this study. The samples were analyzed for pH, electrical conductivity (EC), and cations. All analyses and measurements were conducted in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA, 2017)

The pH and EC were measured using a calibrated digital multimeter. The electrode was immersed in the permeate, and both readings were taken as displayed on the screen. Cations including Ca^{2+}, Mg^{2+}, Na^+ were analyzed following standard methods as recorded in the APHA 3111B. The sodium (Na^+) concentration was determined using the Flame Photometric Method (as part of APHA 3111B). The sample was sprayed into a gas flame, and the intensity of the emitted yellow light at a specific wavelength (589 nm) is proportional to the concentration of sodium ions in the water. The Atomic Absorption Spectroscopy (AAS), known as the "gold standard," was used for determining calcium (Ca^{2+}) and magnesium (Mg^{2+}).

2.4 Determination of Irrigation Water Quality Indices

To quantify the potential suitability of the treated produced water, several globally accepted ratios and indices were employed, including the sodium adsorption ratio (SAR), Kell's ratio (KR), and Magnesium adsorption ratio (MAR).

2.4.1 Sodium Adsorption Ratio (SAR)

SAR predicts the potential for sodium to accumulate in the soil, which can degrade soil structure. It is calculated using Equation 1 (Ayers & Westcott, 1985):

$$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}} \text{----- (2)}$$

2.4.2 Kelly's Ratio (KR)

KR is used to classify water based on sodium content relative to calcium and magnesium. A ratio greater than 1 indicates an excess of sodium. It is calculated using Equation 3 (Kelly, 1963):

$$KR = \frac{[Na^+]}{[Ca^{2+}] + [Mg^{2+}]} \text{-----} (3)$$

2.4.3 Magnesium Adsorption Ratio (MAR)

MAR assesses the magnesium hazard. High magnesium levels can lead to soil alkalinity and decreased infiltration. It is calculated using Equation 4 (Raghunath, 1987)

$$MAR = \frac{[Mg^{2+}]}{[Ca^{2+}] + [Mg^{2+}]} \times 100 \text{-----} (4)$$

It is standard practice to express the concentration of all ions (cations Ca^{2+} , Mg^{2+} , Na^+) in milliequivalents per litre ($\frac{meq}{L}$) when calculating these indices.

2.4.4 Ecological Hazard Quotient (EHQ)

Produced water contains TPH and salts. With SAR, MAR, and Kelly's ratio quantifying the potential suitability of the treated produced water regarding the presence of salts, it is also pertinent that the effect of TPH is assessed. To determine the level of TPH pollution, the ecological hazard quotient (EHQ) was employed in this study, like previous work (Ukoha-Onuoha et al., 2022). EHQ is a simple water pollution index used in the analysis of the degree of pollution with a single numeric value. It is the ratio of the measured concentration (C_i) of the contaminant to the standard permissible concentration (S_p) of the contaminant, as shown in Equation 5. EHQ describes pollution in two broad categories: no contamination ($EHQ < 1$) and contamination ($EHQ > 1$).

$$EHQ = \frac{C_i}{S_p} \text{ } 5$$

The standard permissible concentration for TPH used in this work was 10 mg/l according to the Nigerian Upstream Petroleum Regulatory Commission (NUPRC). NUPRC was previously known as the Department of Petroleum Resources (DPR). It is the regulatory body that regulates total petroleum hydrocarbons (TPH) in effluents via the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN). Although the EGASPIN guideline stipulated 10 mg/L for THC, in this work, TPH was used. TPH is usually reported as a surrogate measure for petroleum hydrocarbon contamination and used for environmental studies in the Niger Delta. Comparison with EGASPIN thresholds when THC is not being determined is customary in the Niger Delta (Adewuyi et al. 2012; Olawuyi and Tubodenyefa 2018) and indeed for the interpretation of petroleum hydrocarbon levels for environmental screening purposes within the petroleum industry of Nigeria. Nevertheless, THC and TPH are analytically different compounds; hence, the comparison only served as a conservative semi-quantitative compliance status check.

III. RESULT AND DISCUSSION

3.1 Evaluation of the Effectiveness of Coagulation on Produced Water

Table 2 shows that the raw produced water (T_0) exhibits high levels of mineralization and organic contamination with an electrical conductivity (EC) of 2.740 dS/m and a TPH level of 312.082 mg/L. The EC value indicates dissolved salts that could hamper soil structure, while TPH indicates the presence of emulsified hydrocarbons, which can impede soil aeration and be toxic to plant roots. The chemical treatment process utilizing alum as a coagulant neutralized the negative charges of suspended particles and oil droplets, allowing them to clump into "flocs" and settle (coagulation-flocculation). The analysis shown in Table 2 details the physicochemical transformation of produced water through a graduated chemical coagulation process. The data tracks the transition from the raw state (T_0) through three increasing dosages of aluminiumsulphate (T_1, T_2 , and T_3). The key observations in sample T_1 and T_2 with 0.1 g and 0.2 g of alum, respectively, show a reasonable reduction of TPH and EC. Sample T_3 with 0.3 g of alum shows a critical breakpoint in efficiency. It achieves near-total removal of hydrocarbons ($<0.01\mu\text{g}$), resulting in a drop in TPH of 99.99% compared to the raw water. This reflects the optimum coagulant dose for TPH removal as 0.3 g, but with a tradeoff in alum residue in the supernatant that resulted in a 60% increase in EC from T_2 . Aluminium-based coagulants, particularly aluminiumsulphate and sodium aluminate, are associated with aluminium residues in supernatant that increase with coagulant dose (Krupinska, 2020).

Table 2: Effect of Coagulant Dose on Organic and Inorganic Contaminant Removal

Parameters	T_0	T_1	T_2	T_3
Na^+ (mg/L)	58.421	11.231	5.806	4.265
Ca^{2+} (mg/L)	120.01	17.484	10.776	10.256
Mg^{2+} (mg/L)	48.802	4.601	3.018	2.857
TPH (mg/l)	312.082	29.171	26.465	<0.01
EC (dS/m)	2.740	0.01	0.008	0.02

3.2 Evaluation of the Potential Salinity and Sodicity Hazard of Raw and Treated Produced Water

Salinity hazard is measured by EC, and according to the FAO guidelines (Ayers & Westcot, 1985), the EC threshold value for irrigation water is 0.75 dS/m, which presents the raw produced water as unfit for irrigation purposes. Mapping Table 2 with Table 3, the raw produced water (T_0) with an EC of 2.74dS/m is classified as C4, indicating that the raw produced water has a high potential of causing soil salinity. However, upon treatment with aluminum sulphate of 0.1 g, 0.2 g, and 0.3 g all the treated samples are classified as C1 samples with EC ranging 0.008 – 0.02 dS/m. The chemically treated samples, therefore, pose little to no risk of osmotic stress to plants.

Table 3: EC and SAR values for different classes of salinity and sodium hazard (Minhas and Qadir, 2024)

Salinity hazard	Class	EC (dS/cm)	Sodium hazard	class	SAR
Low	C1	0.1-0.25	Low	S1	<10
Medium	C2	0.25 – 0.75	Medium	S2	10-18
High	C3	0.75 – 2.25	High	S3	18-26
Very high	C4	2.25 – 5.0	Very high	S4	26-31

Sodicity (Sodium) Hazard is evaluated using the Sodium Adsorption Ratio (SAR), which measures the relative concentration of Na^+ to Ca^{2+} and Mg^{2+} . Figure 1 shows that the SAR values of the raw and chemically treated produced water samples were all less than 10, an indication that, regarding sodicity, all the water samples are in the S1 class (Abdel-Fattah et al., 2020). A combination of the salinity and sodicity hazard classification puts the raw produced water in the C4-S1 class, while all the treated samples are in the C1 – S1 category. The C1-S1 classification implies that chemical treatment with aluminiumsulphate across all dosages (T_1 to T_3) maintained or improved the suitability of the water for irrigation purposes regarding these specific indices.

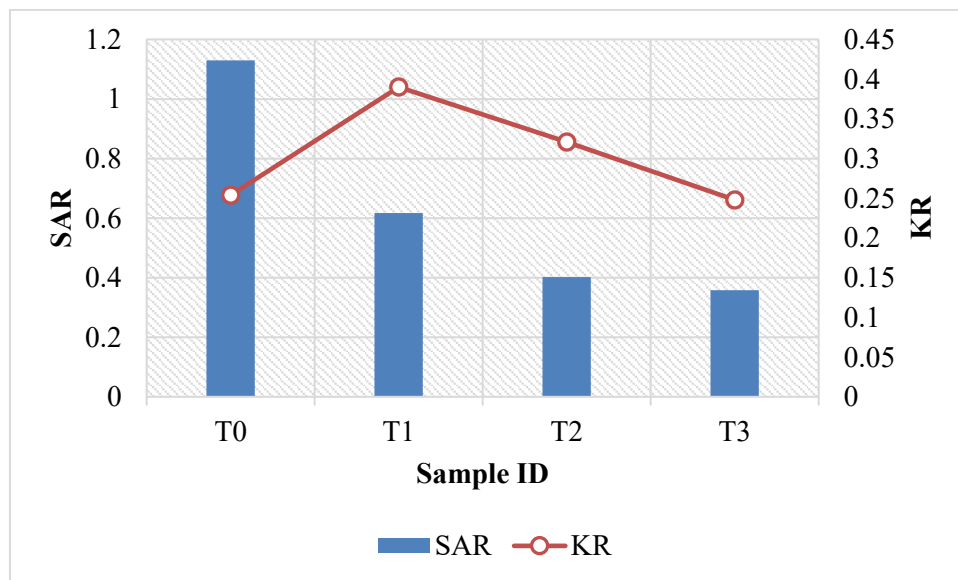


Figure 2: Effect of coagulant dose on sodicity

As for Kelly's Ratio (KR), a ratio of less than 1.0 is considered Suitable for irrigation, and all recorded values are well below 1.0 (Figure 1). This explains that the water is unlikely to cause a sodium-related soil imbalance like SAR (Amadi, 2016). Another important ratio is the Magnesium Adsorption Ratio (MAR), also known as Magnesium Hazard (MH). High magnesium levels can adversely affect soil structure and crop yield by inducing soil alkalinity (Zeid et al., 2022), hence the need for the MAR. Figure 2 shows that all water sample values were below the 50% critical value for MAR. This describes all water samples as suitable for irrigation with respect to magnesium hazard.

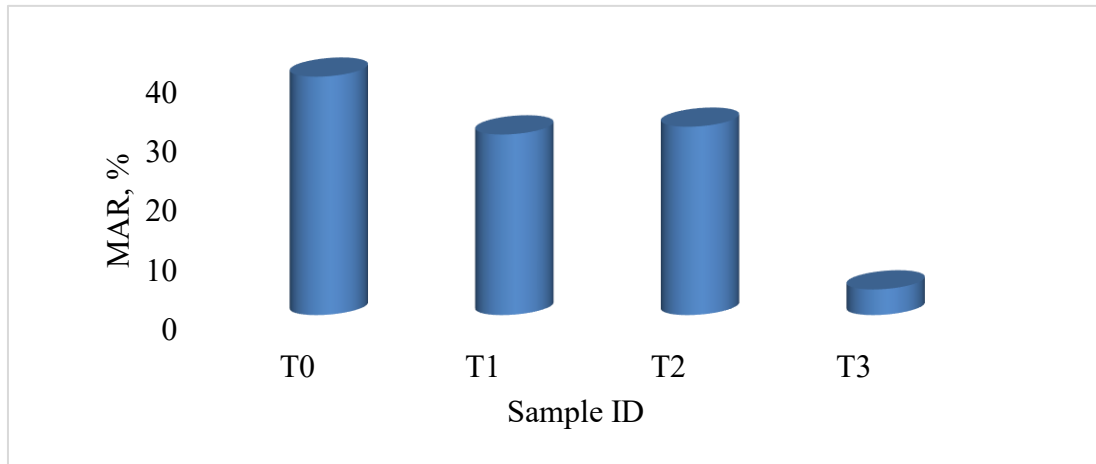


Figure 3: Effect of coagulant dose on magnesium hazard

3.3 Ecological Quotient Hazard

Figure 4 shows that the EQH of the untreated PW sample was far greater than unity, suggesting the need for treatment. However, only T3 with a removal efficiency of 99.99% was less than unity. T₁ and T₂, with removal efficiencies of 90.65% and 91.52% respectively, showed EQH greater than 1, implying that for water to be suitable for irrigation, in addition to being categorized as C1-S1, TPH should be < 0.01 mg/l.

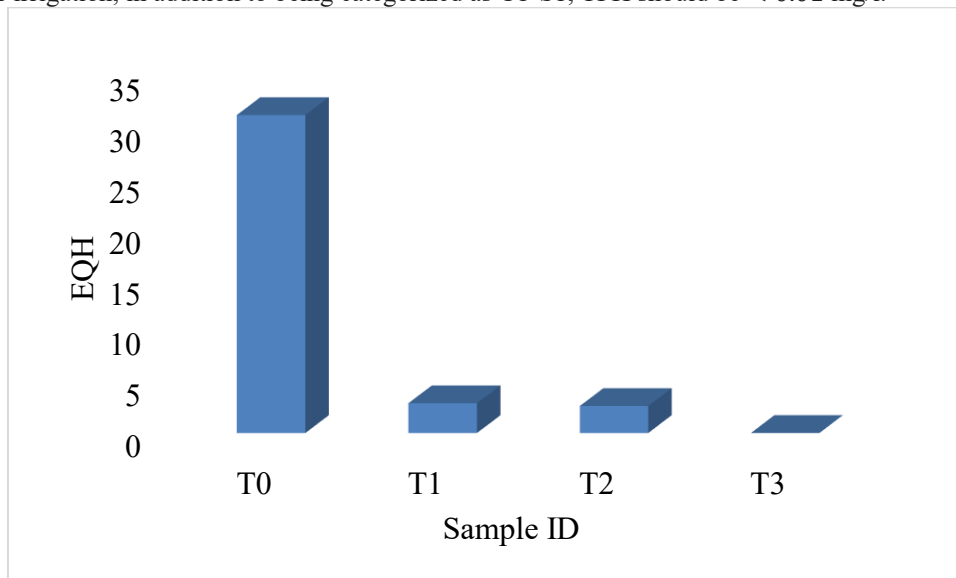


Figure 4: Irrigation Water Toxicity Potential

IV. Conclusion

This study conducted a comprehensive assessment of the suitability of chemically treated produced water from oil and gas operations in Port Harcourt for irrigation purposes. By analyzing key irrigation quality indices, the Sodium Adsorption Ratio (SAR), Kelly's Ratio (KR), Magnesium Adsorption Ratio (MAR), and ecological hazard quotient (EHQ), the following conclusions are drawn: the results demonstrate that both raw (T₀) and treated (T₁, T₂, T₃), Water samples pose a negligible sodicity hazard. All SAR values were consistently below 1.2, far below the critical threshold of 10, categorizing the water as "Excellent" for irrigation.

Furthermore, KR values remained below the unit limit (< 1.0), confirming that the sodium concentration relative to calcium and magnesium is optimal and unlikely to cause soil dispersion or structural degradation while the raw produced water (T_0) was within the suitable range for magnesium content (40%), though it is close to the 50% threshold where magnesium begins to adversely affect soil productivity. EHQ was less than unity for only T_3 . Notably, the T_3 (0.3g) treatment proved the most effective, reducing MAR to a safe level of 4.3%, effectively eliminating the potential for magnesium-induced soil alkalinity and TPH-induced toxicity.

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