

Analysis of Pollutant Loads in the Wastewater of a Hydrocarbon Industry and Evaluation of the Effectiveness of Their Treatment

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Abstract

This study evaluates the effectiveness of the wastewater treatment system at a hydrocarbon refinery in Chad. Pollutant loads, including Chemical Oxygen Demand (COD), 5-day Biochemical Oxygen Demand (BOD5), total hydrocarbons, heavy metals (As, Cr, Pb), phenols, and sulfides, were measured before and after treatment. Samples were analyzed using standard methods at the industry laboratory and the national water laboratory. Before treatment, the wastewater exhibited extreme pollution: COD up to 3000 mg/L, BOD5 up to 1925 mg/L, and hydrocarbons up to 1000 mg/L. The combined physicochemical and biological treatment demonstrated high effectiveness, with removal rates exceeding 95% for both COD and BOD5, and a reduction of hydrocarbons to less than 10 mg/L. The pH of the treated effluent was stable (6.5 - 8.5). However, residual concentrations of arsenic and chromium occasionally exceeding local standards were detected, indicating the need for targeted tertiary treatment. The study concludes that the system is generally effective but recommends enhanced monitoring and optimization of heavy metal removal.

Keywords

Industrial Wastewater, Hydrocarbons, Heavy Metals, Physicochemical Treatment, Biological Treatment, Treatment Efficiency

1. Introduction

The industrial sector, particularly the oil industry, is a major source of aquatic

discharges laden with complex pollutants [1]. These effluents contain a mixture of organic compounds (hydrocarbons, phenols) and inorganic compounds (heavy metals, sulfides, nitrogen compounds) which, if discharged without adequate treatment, pose serious ecotoxicological and health risks to ecosystems and surrounding populations [2] [3]. In N'Djamena, within the context of industrial development, wastewater management from hydrocarbon production units constitutes a critical environmental challenge [4]. Industrial wastewater generally has a more specific composition directly linked to the type of industry used. Regardless of the organic or mineral pollution load and its biodegradability, it contains toxic substances. In daily refining operations, the products resulting from the transformation of raw materials cannot be discharged directly into the environment. Industrial wastewater is a major environmental concern due to its potential impact on ecosystems and human health. The oil industry is one of the main sources of water pollution. Oil production is generally accompanied by the use and production of significant volumes of water. This produced water, often returning from the oil field as an emulsion in the crude oil, cannot be discharged or reused without prior treatment, as it must meet national discharge standards. Based on the possible and effective treatments that can be applied to this industrial wastewater, we opt for treatment aimed at almost completely eliminating the pollutant (hydrocarbon) and reducing all the pollution parameters that characterize it. We supplement this with physicochemical analyses to remove heavy metals and organic pollutants.

This study will be based on a combined approach of collecting and analyzing environmental data, as well as examining current management and regulatory practices in the oil industry. The expected results will contribute to strengthening the legislative and technical framework aimed at protecting the environment and improving the quality of water resources.

The problem of inorganic wastewater pollution in N'Djamena is particularly acute, especially in the context of the hydrocarbon production industry. These industrial activities generate discharges that can contain a variety of inorganic pollutants, including heavy metals and other harmful chemicals [4]. This pollution can have devastating impacts on the environment, affecting both water resources and surrounding soils [5]-[8].

In our research context, water is and remains central to many industrial processes, establishing a close relationship between industry and water [9]. Indeed, industries discharge substances that differ in nature (hydrocarbons, sulfur compounds).

The wastewater treatment plants of these industries typically employ a combination of physicochemical processes (sedimentation, flotation, coagulation) and biological processes (aerobic and anaerobic treatment) to meet discharge standards [10]. Regular evaluation of the performance of these systems is essential to ensure their effectiveness and regulatory compliance. This study aims to: (1) characterize the pollutant load of raw wastewater from a hydrocarbon industry; (2)

evaluate the effectiveness of the existing treatment system by calculating the removal rates of the main parameters; (3) verify the conformity of the final effluent with Chadian national standards and international references; and (4) identify the limitations of the current treatment and propose avenues for improvement, particularly concerning the elimination of residual heavy metals.

2. Materials and Methods

Sampling campaigns were conducted at the industrial site. Raw wastewater samples were taken at the inlet of the wastewater treatment plant (points: Oily Wastewater and Highly Concentrated Wastewater). Treated wastewater samples were collected at the outlet of the final discharge basin. Three replicates were performed at each point over a period of 61 days. Samples were collected in polyethylene bottles previously washed with acid, stored at 4 °C, and analyzed within 24 hours. The wastewater treatment process combines:

Physical pretreatment, which includes screening, grit removal, and gravity separation of light hydrocarbons.

Physicochemical treatment, which includes coagulation-flocculation (using aluminum salts) and dissolved air flotation to remove suspended solids and some metals.

A biological treatment process using activated sludge in the aerobic basin removes BOD/BOD₅, followed by an anaerobic denitrification stage.

Finally, the final clarification stage allows for secondary settling and sand filtration.

2.1. Materials Used

A thermometer

A pH meter

A 100 ml beaker

A conductivity meter with electrodes

A container for the water to be analyzed

A turbidimeter

A volume of distilled water

A test tube

A DR-2800 spectrophotometer

A BOD sensor bottle

A test tube

A temperature-controlled cabinet

A round tube

A thermoreactor (DRB 2800)

A pipette

Reagents:

Potassium hydroxide 1310-58-3 (100%)

Respirometric BOD nutrient buffer billows

(COD reagent 1): oxidant

(COD reagent 2): catalyst

Distilled water

2.2. Method

The analyses were conducted jointly by the industry laboratory and the national water laboratory, following recognized standard protocols.

Samples were taken at different stages of treatment:

Section PK-102: representing the makeup water/external source (control).

Section C-101: representing the main tributary of oily water (before treatment).

Sections C-103 and C-107: representing the effluent during treatment (after biological/physicochemical stages).

Discharge basin: Final effluent after complete treatment.

These points allow for monitoring the evolution of water quality at each stage.

Field parameters: pH, temperature, and electrical conductivity were measured in situ using a calibrated multiparameter meter (model, brand).

Laboratory parameters: COD and BOD₅: Measured respectively by the reflux fermentation method (APHA 5220 B) and the manometric method using respirometers (APHA 5210 B).

Total hydrocarbons were extracted using solvent extraction and determined by IR spectrophotometry (standard method).

Heavy metals (As, Cr, Pb) were analyzed by atomic absorption spectrometry (AAS) after acid digestion (APHA 3111 B).

Suspended solids (SS), turbidity, sulfides, phenols, ammonia nitrogen: Determined by spectrophotometry according to the respective APHA standards (2540 D, 2130 B, 4500-S²⁻ D, 5530 B, 4500-NH₃ B).

Microbiological parameters (*E. coli*, total coliforms): Membrane filtration method (APHA 9222 B).

Quality assurance: Analytical blanks and reference standards were used for each series of analyses. The limits of detection (Ld) for metals were 0.001 mg/L for lead (Pb), 0.005 mg/L for arsenic (As), and chromium (Cr).

2.3. Data Processing and Efficiency Indicators

The initial biodegradability coefficient ($K = \text{COD}/\text{BOD}_5$) was calculated to characterize the raw effluent. The removal rate (%) for each parameter was calculated as follows: $[(\text{Inlet concentration} - \text{Outlet concentration})/\text{Inlet concentration}]100$. The results were compared to the discharge standards of the Chadian hydrocarbon industry and to the WHO guidelines for drinking water (as a reference for protection).

3. Result

We present the results of physicochemical and microbiological analyses of several water samples, identified and collected directly at the hydrocarbon industry

treatment plant. The parameters measured include pH, electrical conductivity (EC), turbidity, heavy metal concentration (lead, arsenic, chromium), and the presence of bacteria indicative of fecal contamination (*Escherichia coli* and total coliforms).

Before treating wastewater from the hydrocarbon industry, certain values must be met to comply with environmental requirements before discharging this water into the receiving environment. These values are assigned to parameters that characterize the degree of water pollution.

Table 1 shows the discharge limits:

Table 1. Standards for the Chadian hydrocarbon industry.

Measured parameters:	pH	DCO (mgO ₂ /l)	DBO5 (mgO ₂ /l)	NH ₄ ⁺ (mg/l)	Phosphate (mg/l)	Sulfate (mg/l)	Phénol (mg/l)	Huile (mg/l)	SS (mg/l)	Cyanure (mg/l)
Acceptable value	6 - 9	120	30	50	1.0	1	0.5	10	150	0.5

Table 1 provides information on the standard parameters for wastewater inlet at the wastewater upgrade pond (CI 101) and high-concentration wastewater (PK203).

3.1. Characterization of Raw Wastewater

The raw wastewater exhibited a very high pollutant load (**Table 2**). The COD reached 3000 mg/L for the high concentration effluent, with a COD/BOD5 ratio (K) of 1.5, indicating a relatively biodegradable organic fraction. The oily effluent had a K of 2.6, suggesting lower biodegradability. Significant concentrations of hydrocarbons (900 mg/L), phenols (50 mg/L), sulfides (50 mg/L), and metals (detectable) were measured. **Table 2** provides information on the characteristics of the raw wastewater before treatment.

Table 2. Characteristics of raw wastewater before treatment.

Measured parameters	Oily wastewater	Highly concentrated wastewater
pH	7.5	9.5
COD (mgO ₂ /l)	800	3000
BOD5 (mgO ₂ /l)	300	1925
Ammonia nitrogen (mg/l)	30	60
Sulfide (mg/l)	10	50
Phenol (mg/l)	20	50
Hydrocarbon content	900	900
Suspended solids (mg/l)	300	600
K coefficient (COD/BOD5)	2,6	1,5

Table 2 provides an overview explaining that before undergoing the treatment process, wastewater is subjected to various analyses that yield approximate values for harmful substance concentrations, ultimately determining the treatment's

effectiveness. **Table 3** presents the results of the analyses on oily wastewater and highly concentrated wastewater before treatment:

3.2. Treatment Performance

The treatment resulted in a drastic reduction in the pollutant load (**Table 2**). Removal rates were excellent for COD (95% - 98.6%), BOD5 (98% - 99.7%), and hydrocarbons (>99.9%). The pH of the final effluent remained stable at 6.9. The final BOD5/COD ratio ($K_f = 0.145$) indicates very high residual degradability. **Table 3** presents the results on the characteristics and disposal efficiency after treatment.

Table 3. Characteristics and removal efficiency after treatment.

Parameter (Unit)	Value after treatment	Local standard (Max)	Elimination rate (%)	Compliant
pH	6.9	6 - 9	-	Oui
COD (mg O ₂ /L)	40	120	95 - 98.6	Oui
BOD5 (mg O ₂ /L)	5.8	30	98 - 99.7	Oui
Hydrocarbons (mg/L)	0.15	10	>99.9	Oui
Phenols (mg/L)	0.5	0.5	97.5 - 99.0	Oui (limite)
TSS/Turbidity (NTU)	3	150 (MES)	99.0 - 99.5	Oui

3.3. Specific Results on Heavy Metals and Microbiological Parameters

Heavy Metals: Lead (Pb) concentrations were below the detection limit (<0.003 mg/L) in all final samples. However, traces of arsenic (up to 0.036 mg/L in sample C-107) and chromium (up to 0.06 mg/L) were detected, sometimes exceeding the WHO reference value of 0.01 mg/L for arsenic.

Microbiology: Significant fecal contamination (*E. coli* and total coliforms) was found in some raw water samples (e.g., C-107: 13,400 total coliforms). This contamination was eliminated in the treated final effluent (PK-102: absent).

Post-treatment values are derived from the same final effluent, but reductions are expressed relative to each specific influence.

3.4. Data Visualization

3.4.1. pH Analysis Results

pH control is crucial for the efficiency of biological processes. A low pH can inhibit nitrification as noted by Guerguezi and Achour 2005 [11]. The stabilization of the outlet pH suggests good buffering in the treatment basin, likely due to the alkalinity produced during denitrification.

All samples exhibit a slightly acidic to neutral pH (6.49 - 6.83).

No sample exceeds the usual drinking water limits (generally 6.5 - 8.5).

The pH is consistent with natural water, but slight acidity can promote metal solubilization.

This result is related to the stability of the treatment process, as our observations indicate that the inlet pH is often acidic (5.44 - 6.95), while the outlets are neutral to slightly alkaline (6.5 - 8.6).

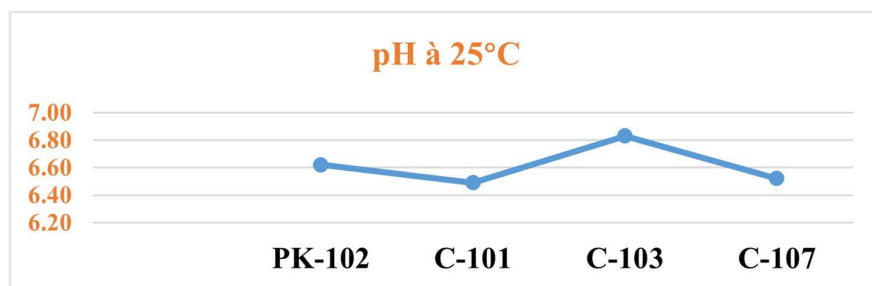


Figure 1. pH Evolution (Inlet vs. Outlet).

In this figure (**Figure 1**), the curve shows the pH evolution (inlet vs. outlet). A bar chart shows the average pH (with error bars) for the inlet (acids to alkalis) and outlet samples (all clustered around 6.9, neutral).

3.4.2. Turbidity

A bar chart of turbidity values (NTU) for points C-107 (very high), C-101 (moderate), and PK-102/C-103 (low).

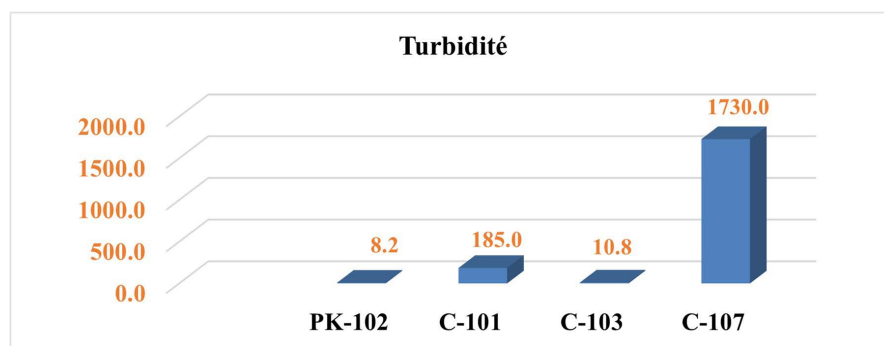


Figure 2. Turbidity of the different sampling points.

Turbidity values are highly variable, as highlighted in **Figure 2**.

High turbidity (C-107, C-101) can be due to suspended solids (clays, organic matter), often associated with runoff or microbiological contamination.

3.4.3. Microbiological Parameters: *E. coli* and Total Coliforms

Wastewater contains all microorganisms excreted with fecal matter. This normal enteric flora is accompanied by pathogenic organisms. **Figure 3** shows the results of the analysis of the microbiological parameters of *E. coli* and total coliforms.

- PK-102: absence → microbiologically safe water.
- C-101, C-103, C-107: significant presence, especially C-107 (13,400 total coliforms).

The presence of *E. coli* indicates recent fecal contamination. This water is not

potable without treatment.

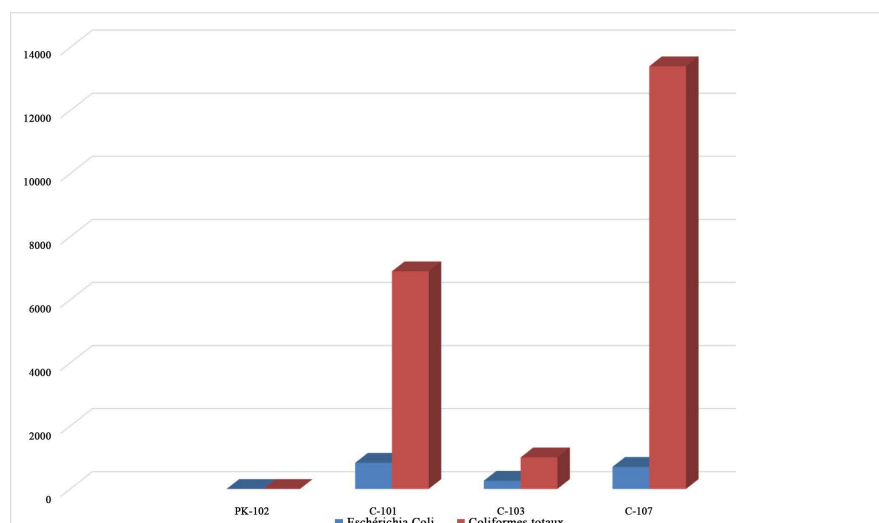


Figure 3. Diagram of microbiological parameters *E. coli* and total coliforms.

In light of these results, we recommend the following:

Mandatory treatment for C-101, C-103, and C-107 before consumption.

An investigation into the sources of contamination for arsenic and fecal bacteria.

Enhanced monitoring of points C-107 and C-101.

Given these results on the significant reduction of hydrocarbons after treatment, we believe this is consistent with the biological and physicochemical processes used in oily water treatment. According to Jakubauskaitė, V and al. (2024) [12], flotation and biodegradation systems can reduce petroleum hydrocarbons by more than 95% under optimized conditions. The variability in inlet concentrations can be attributed to fluctuations in industrial activities, as highlighted by Zhang *et al.* (2020) [13].

The presence of *E. coli*. The presence of coliforms, while unexpected in the petroleum industry, can be explained by:

Sanitary or facility cleaning water mixed with industrial effluents.

External inputs through runoff or contaminated rainwater.

The possible resuspension of bacteria adsorbed onto suspended solids.

3.4.4. Electrical Conductivity (EC)

Conductivity varies considerably: from 85.4 $\mu\text{S}/\text{cm}$ (C-103) to 490 $\mu\text{S}/\text{cm}$ (PK-102).

We observe that high conductivity (PK-102, C-107) can indicate significant mineralization or contamination by dissolved salts. A low C-103 value suggests water with low mineral content, possibly of surface origin or with a low ion concentration. **Figure 4** shows the evolution of electrical conductivity at 25°C. This result demonstrates, as highlighted above, the salt contamination.

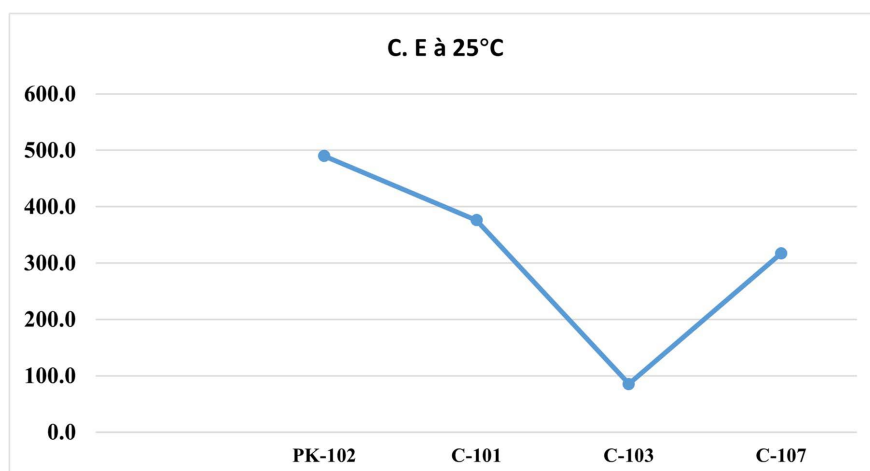


Figure 4. Evolution of electrical conductivity at 25°C.

3.4.5. Heavy Metals

Figure 5 shows the result of our analyses in a grouped bar chart showing the concentrations (mg/L) of Arsenic and Chromium for samples C-101, C-107 and PK-102, with a horizontal line indicating the WHO limit for As (0.01 mg/L).

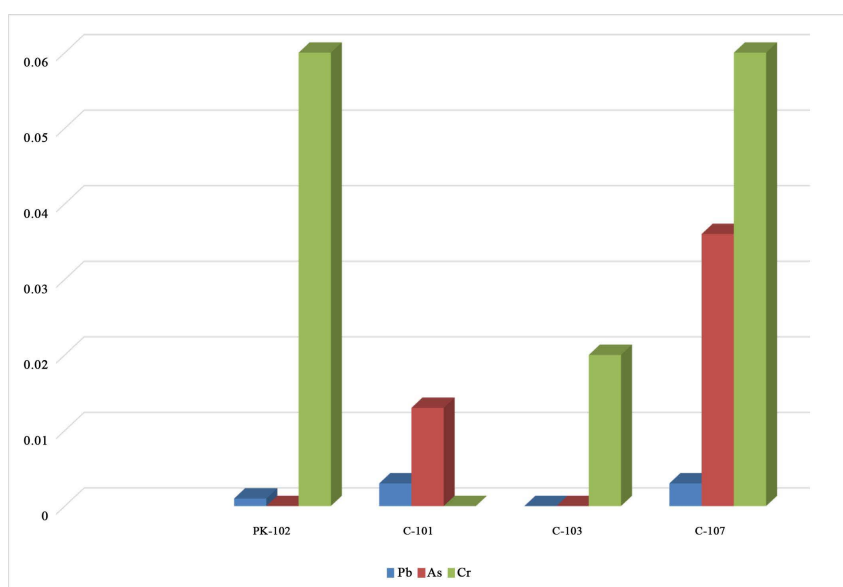


Figure 5. Residual concentrations of heavy metals.

Lead (Pb): All values are below 0.003 mg/L, therefore compliant with drinking water standards (limit generally 0.01 mg/L).

Arsenic (As): Present in C-101 (0.013 mg/L) and C-107 (0.036 mg/L).

Comment: The C-107 value exceeds the WHO standard (0.01 mg/L). Possible source: natural dissolution or industrial pollution.

Chromium (Cr): Present in PK-102 and C-107 (0.06 mg/L).

Based on this result, we recommend monitoring for chromium if it is hexavalent chromium, which is toxic.

Heavy metals represent a significant group of hazardous contaminants often found primarily in industrial wastewater [14]. Heavy metals, stable and highly persistent compounds, are environmental contaminants that can accumulate and be transferred to higher organisms in food webs, leading to serious ecological and public health problems [15] [16].

3.5. Degradability Parameters: COD, Sulfides, Phenols

Observations:

- COD frequently exceeds 800 mg/L at the inlet but is reduced to less than 120 mg/L at the outlet.
- Volatile sulfides and phenols are also effectively removed.

Scientific Commentary: The reduction of COD and aromatic compounds such as phenols is typical of aerobic and anaerobic biological treatment processes. Kynadi, A. S., & Suchithra, T. V. (2017) showed that specialized bacteria (e.g., *Pseudomonas*, *Thiobacillus*) can degrade phenols and reduce sulfides. The residual presence of sulfides may indicate sulfate-reducing microbiological activity, as discussed by Desai, Uday, & Kalpana. (2021) [17] [18].

3.5.1. Ammoniacal Nitrogen (NH₄N)

Observations:

- Ammoniacal nitrogen concentrations in the inlets range from 2.54 to 17.6 mg/L.
- In the outlets, they are generally less than 1 mg/L, except for a few peaks.

Scientific Commentary: The removal of ammoniacal nitrogen is probably due to nitrification-denitrification. According to An, Z. (2022) [19], this process is efficient in activated sludge systems when pH and temperature are controlled. Residual peaks may be related to organic overloads or insufficient hydraulic retention time.

3.5.2. Total Phosphates

Total phosphates at the outlet of CI-107 range from 0.7 to 7.2 mg/L.

Phosphorus removal in conventional treatment systems is often limited without chemical precipitation or enhanced biological processes (e.g., EBPR). Ramler *et al.* (2022) point out that residual phosphorus concentrations can persist in the absence of specific treatment [20].

3.5.3. Cyanide

Cyanide is consistently below the detection limit (0.5 mg/L).

The absence of detectable cyanide is positive, as it is a toxic and regulated contaminant. According to Jumbo Pacheco, P. X., & Nieto Monteros, D. A. (2016), cyanides can be degraded by chemical or biological oxidation under aerobic conditions [21].

4. Discussion

Wastewater generated by the petroleum refining industry is characterized by a

high environmental pollutant load, including aliphatic and aromatic hydrocarbons, oil, grease, heavy metals, naphthalenic acid, and other recalcitrant organic and inorganic pollutants [22] [23]. The physicochemical characteristics of pre-treatment wastewater (PRW), such as pH, TDS, TSS, EC, BOD, COD, oil and grease, and phenol, have been well documented [1] [24]. The characteristics of the generated wastewater can vary due to several factors, including refinery configuration, type of refined petroleum, treatment process, and operating parameters [25] [26]. Various treatment methods are available for refinery wastewater, such as electrochemical treatment, membrane filtration, the use of biological media, adsorption, flotation and chemical coagulation, treatment using ultrasonically dispersed nanoscale zero-valent iron particles, titanium dioxide, vacuum ultraviolet and natural minerals, and hybrid technologies [10] [27].

Phenols and their derivatives from PRWs resist conventional treatment processes and pose serious environmental pollution and toxicity, remaining in the environment for extended periods [28]. PRWs have a highly complex nature, and treating these pollutants is very difficult [29]. Various physicochemical and biological treatment methods/technologies have been developed for the degradation of these toxic pollutants, but due to their high cost and incompatibility with existing treatment systems, they have not been implemented on a large scale [30]-[33]. Therefore, there is an urgent need to develop a cost-effective and efficient treatment technology to remove contaminants from PRWs.

PRW has detrimental effects, even at low concentrations, on aquatic and terrestrial flora, fauna, and exposed humans [34]-[36]. In contaminated soil, these toxic chemicals and heavy metals accumulate and cause damage over a longer period. Pollutants released by PRW are known to be toxic, carcinogenic, mutagenic, cytogenotoxic, and endocrine disruptors [2] [37].

Due to the wide range of toxic pollutants released by PRW, their accurate characterization and identification are very difficult. Plant bioassays have been developed as common tools for studying and assessing toxic chemicals from wastewater [35] [38]-[41]. Plant sensitivity to different compounds can be used in toxicity tests to identify toxins. Toxicity assessment using plant bioassays is well-documented for the screening and monitoring of environmental pollutants [42]. Phytotoxicity tests generally assess the impact of various compounds or pollutants on seed germination and subsequent growth, while plant cytogenotoxicity tests identify cellular and genetic damage, including genetic mutations and chromosomal aberrations [43].

4.1. Overall Treatment Efficiency

The hybrid treatment system (physico-chemical + biological) demonstrated remarkable efficiency in removing the organic load, with performance exceeding 95% for COD/BOD₅, consistent with studies reporting the effectiveness of such systems for oily waters [12] [13]. Stabilizing the pH around neutrality (6.9) is crucial for optimizing subsequent biological processes and ensuring compliance [11].

4.2. Issue of Residual Heavy Metals

The occasional persistence of arsenic and chromium in the final effluent, albeit at low concentrations, is the main point of concern. Heavy metals, which are non-biodegradable, are poorly removed by conventional biological treatments and can accumulate in the environment [44]. Their presence can originate from the raw matrix or from equipment dissolution. This result highlights the inherent limitation of the current process and justifies the recommendation of a polishing step (tertiary treatment) such as adsorption onto activated carbon or the use of membranes specifically designed for the retention of metal ions [27].

For residual arsenic and chromium, targeted tertiary treatment is recommended:

Adsorption onto activated alumina or iron oxide for arsenic.

Chemical precipitation using sulfides or hydroxides for chromium.

These technologies, already proven in the treatment of industrial effluents, could be integrated downstream of the biological treatment.

4.3. Biodegradability and Microbiological Quality

The significant reduction in the K coefficient (from 1.5 - 2.6 to 0.145) confirms the efficient transformation of complex organic matter into more readily degradable compounds. The complete elimination of indicators of fecal contamination in the treated effluent is essential to prevent health risks in the event of discharge into the environment.

4.4. Compliance and Operational Recommendations

The final effluent generally complies with strict Chadian standards for the majority of parameters. However, to ensure sustained performance and address occasional exceedances (metals), we recommend:

- 1) Enhanced monitoring: Implementation of continuous or more frequent monitoring for arsenic, chromium, pH, and hydrocarbons.
- 2) Optimization of primary/physicochemical treatment: Adjust the doses of coagulants/flocculants to improve the co-precipitation of metals upstream of the biological treatment.
- 3) Feasibility study of tertiary treatment: Evaluate the addition of an adsorption unit (activated carbon, local biochars) or targeted chemical precipitation for metals.
- 4) Sludge Management: Characterize and safely manage sludge from the treatment process, which may be contaminated with metals and hydrocarbons.

5. Conclusions

Industrial wastewater generally has a more specific composition directly related to the type of industry used. Regardless of the organic or mineral pollution load and whether it is biodegradable or not, it contains toxic substances. In daily refining operations, the byproducts of raw material processing cannot be discharged

directly into the environment.

This wastewater has a significant pollutant load, but the current treatment system provides satisfactory purification. This study demonstrates the high efficiency of the existing treatment system in a hydrocarbon industry in Chad for removing the organic load (COD, BOD5, hydrocarbons). Performance often meets and exceeds national regulatory requirements. However, the persistent detection of heavy metals (As, Cr) at levels requiring special attention highlights a significant limitation of the conventional process. These results support the optimization of current processes and the potential integration of metal-specific tertiary treatment to ensure comprehensive environmental protection and achieve even stricter quality standards. Regular and appropriate environmental monitoring remains essential [3] [13] [44].

Finally, this study has some limitations: (i) the sampling campaign, although repeated, covers a limited period and may not capture all seasonal or operational variability; (ii) chromium speciation analysis (Cr(III) vs. Cr(VI), which is much more toxic) was not performed; (iii) the costs and technical feasibility of the proposed tertiary treatments were not thoroughly investigated in this work [42].

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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