Tikrit Journal of Pure Science Vol. 29 (5) 2024

https://doi.org/10.25130/tjps.v29i5.1672

TJPS

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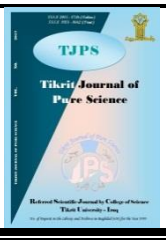
المجلات الاكاديمية العراقية

Tikrit Journal of Pure Science

ISSN: 1813 – 1662 (Print) --- E-ISSN: 2415 – 1726 (Online)

Journal Homepage: http://tjps.tu.edu.iq/index.php/j



Evaluating the efficiency of oil waste treatment plant in AL- Qayyarah Refinery - Iraq

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ARTICLE INFO.

Article history:

-Received: 6 / 7 / 2024

-Received in revised form: 27 / 7 / 2024

-Accepted: 1 / 8 / 2024

-Final Proofreading: 13 / 8 / 2024

-Available online: 25 / 10 / 2024

Keywords: AL- Qayyarah Refinery, Oil Waste Treatment Plant, Pollutants.

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ABSTRACT

The study included an evaluation of the efficiency of AL-Qayyarah refinery oil waste treatment plant. For this purpose, monthly samples were collected for a period of six months from October 2023 until March 2024, the first station (before treatment) represents the water coming out of the crude oil filter units. As for the second station (after treatment) it is located in the refinery waste treatment unit, the site represents the treated water. many physical and chemical tests were conducted on water, they ranged of temperature values before the treatment ranged between (17-33) compared to its value after the treatment (15-31), and the electrical conductivity values before the treatment ranged between (295-405)µS/cm, while after the treatment it was (349-471)µS/cm. As for total dissolved solids, their average before the treatment was(182.5)mg/L, while their average after the treatment was(194.6)mg/L as for salinity, its values ranged between(0.7-0.75) mg/L before the treatment and between (0.6 -0.8) mg/L after the treatment ,pH value before the treatment was between(6.12 -7.91) compared to its value after the treatment as it ranged between (6.81-7.95), while the values of the chemical requirement for oxygen before the treatment were (85108)mg/L, Their concentrations values after the treatment amounted to(73_125) mg/L, and polycyclic aromatic hydrocarbons (PAHs) (73.46-155.17)mg/L before the treatment, and after the treatment it reached (35.53-52.53) mg/L, while oils and greases reached values that ranged between (26.16-165.68) mg/L before the treatment compared to their results after the treatment which ranged between (94.15-23.18) mg/L. Finally, the total organic carbon had an average value before treatment (134.1) mg/L, while after treatment their average values reached (120.8) mg/L.

Tikrit Journal of Pure Science Vol. 29 (5) 2024
TJPS
https://doi.org/10.25130/tjps.v29i5.1672

تقييم كفاءة محطة معالجة المخلفات النفطية في مصفى القيارة – العراق

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الملخص

تضمنت الدراسة تقييم كفاءة محطة معالجة المخلفات النفطية في مصفى القيارة ، ولأجل ذلك تم جمع عينات شهرية ولمدة ستة اشهر من شهر تشرين الأول 2023 ولغاية شهر اذار 2024 تمثل المحطة الاولى (قبل المعالجة) المياه الخارجة من وحدات تصفية النفط الخام, اما المحطة الثانية (بعد المعالجة) فتقع في وحدة معالجة مخلفات المصفى وتمثل الموقع المياه المعالجة (Treated water) .أجريت العديد من الفحوصات الفيزيائية والكيميائية على المياه ، إذ تراوحت قيم درجة الحرارة قبل عملية المعالجة مابين (17– 33) مقارنة مع قيمتها بعد المعالجة (15–31), وقيم التوصيل الكهربائي تراوحت قبل عملية المعالجة ما بين (295–405) مايكروسيمنز / سم وبعدها كانت (349 – 471) مايكروسيمنز / سم , أما بالنسبة المواد الصلبة الذائبة الكلية فبلغ معدلها قبل عملية المعالجة (182.5) ملغم / لتر أما معدلها بعدها (194.6) ملغم لتر، أما الملوحة فتراوحت قيمها مابين (0.7–0.75) ملغم / لتر قبل المعالجة وبين (0.6–0.8) ملغم / لتر بعد المعالجة, الدالة الحامضية قبل المعالجة ما بين (6.12–7.91) مقارنة مع قيمتها بعد المعالجة اذ تراوحت ما بين (6.81–7.95) ، في حين كانت قيم المتطلب الكيميائي للأوكسجين قبل المعالجة (85–108) ملغم / لتر إما قيم تراكيزها بعد المعالجة فبلغت (73_125) ملغم / لتر , والهيدروكربونات العطرية متعددة الحلقات كانت بين (73.46–155.17)ملغم / لتر قبل المعالجة إما بعد المعالجة فبلغت بين (35.53–52.53) ملغم / لتر، في حين وصل الزيوت إلى قيم تراوحت ما بين (26.16–165.68) ملغم / لتر قبل المعالجة بالمقارنة مع نتائجها بعد المعالجة والتي تراوحت ما بين (23.18-94.15) ملغم / لتر ,وأخيرا فالمركبات العضوية الكلية فقد كان معدل قيمها قبل المعالجة (134.1) ملغم/لتر أما بعد المعالجة فقد بلغ معدل قيمها (120.8) ملغم/لتر.

Introduction

Iraq is one of the countries that suffer from the risks of pollution, especially the risks of pollution from oil waste in all its forms, which are rich in hydrocarbon compounds, as Iraq is one of the oil-producing countries in addition to having many crude oil refineries and transportation lines to oil depots, electrical stations, and gas stations. Crude oil and its derivatives are the most widespread and widely used and a primary source of pollution. Oil pollutants are also considered the most complex mixture of hydrocarbon compounds that cause a serious pollution problem that leads to the deterioration of water properties [1]. Industrial pollution is one of the most important issues that has taken up a large area at the local and

https://doi.org/10.25130/tjps.v29i5.1672

international levels because of the great risks it poses to the ecosystem and to the health of society alike as a result of the increase in the volume of pollutants released into the water. Water pollution is one of the major problems facing humans, and there is an urgent need to There is a concerted effort to treat and reduce it, and what complicates the problem is that humans have a clear role in increasing its danger due to its various activities that have become a threat to human life, in addition to its impact on other living organisms, which causes a change in the natural balance of the environment and its various living and non-living components [2]. Hydrocarbons are among the most important environmental pollutants found in crude oil, as they cause many problems to the environment in which they are present, as they are toxic to most living organisms and some of them are carcinogenic. In addition, crude oil contains some heavy elements such as copper, cadmium, lead, and nickel, which accumulate within the tissues of organisms [3]. The goal of establishing various waste treatment units is to protect human health and the environment by reducing the percentage of pollutants excreted in the water and eliminating pathogenic factors. Physical, chemical, and biological processes are applied to eliminate or reduce pollutants, and the specifications of the resulting water depend on the efficiency of the work of the purification and treatment units in those plants [4].

Aim of the study:

1. Evaluating the quality of effluents resulting from the AL-Qayyarah Refinery production units.

2. Estimating the efficiency of the treatment plant for oil waste resulting from the refinery by measuring some physical and chemical parameters of water samples before entering and after exiting from the refinery.

Study area

The current study was conducted in two sites, The first site represents the water coming out of the crude oil filtration units inside the Qayyarah refinery, where this water is used in (steam production, cooling of pumps, as well as washing some parts of the units) inside the refinery's production units. The second site is located in the refinery waste treatment unit, and the site represents treated water in the waste water treatment plant resulting from the refinery, Inside the Qayyarah refinery, the site coordinates were (35°47'17.74" N 43°17'01.72" E), located on the right coast of the Tigris River in the south of the Qayyarah district, located about 60 km south of the city center of Mosul in Nineveh Governorate (Figure 1).

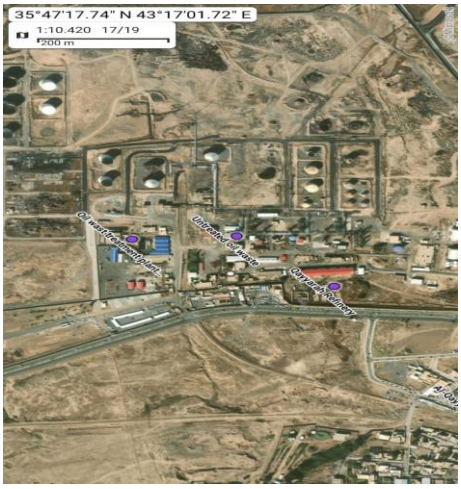

Fig. 1: AL- Qayyarah Refinery

Materials and methods

Water samples were collected monthly from October 2023 to March 2024 during the six-

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month study period except for a section of tests that were measured once every two months (i.e. an average of three months). This is due to the difficulty of measuring these parameters, as our basic laboratory does not measure These components, and laboratory analysis was conducted according to the measurement methods mentioned in [5]. Table (1) represents the working methods for the analysis conducted in this study.

Table 1: represents the methods for the analysis conducted in this study

NO	Examination	Unit	Name of the device or tools	Source
1	Temperature	Celsius	Mercury thermometer	-
2	Electrical Conductivity	µS/cm	Electrical conductivity meter WTW C and 720inolab	APHA,2017
3	Total Dissolved Solids	mg/L	Electrical conductivity meter WTW C and 720inolab	APHA,2017
4	Salinity	mg/L	Electrical conductivity meter WTW C and 720inolab	APHA,2017
5	pH	-	(pH Meter) Romanian origin	APHA,2017
6	Dissolved oxygen	mg/L	Determination with standardsodium thiosulphate (0.025N)	APHA,2017
7	Chemical Oxygen Demand (COD)	mg/L	Device Spectrophotometer Type Wagtech (American made) at a wavelength of 490 nm	APHA,2017
8	Polycyclic aromatic hydrocarbons	mg/L	Gas Chromatograph (GC) device, Shimadzu type, Japanese manufacture, model 2010	APHA,2017
9	Oil and Greases	mg/L	Gas Chromatograph (GC) device, Shimadzu type, Japanese manufacture, model 2010	APHA,2017
10	Total Organic Carbon	mg/L	Japanese-made Horiba Oil Content device	APHA,2017

Results and Discussion

Water temperature (WT)

The results in the current study, as shown in Tables 2 and 3, showed that water temperature concentrations before the treatment process reached (33, 32, 24, 17, 22, 23) C^O, respectively, while their temperature after the treatment process reached (31, 30, 22, 15, 20, 21) C^O, respectively, during the months of the current study. The variation in temperature results from the difference in season and time of measurement, and the increase in the water temperature in the pre-treatment station is also due to the use of water for cooling work within the production units in the refinery, as this leads to an increase in the water temperature by (8-11)C^O. It is clear that water temperature begins to gradually decrease in treatment plant after the treatment. Likewise, the rise in water temperatures inside the AL-Qayyarah refinery is may be due to a many of technical reasons, the use of steam boilers and air heat exchangers in cooling operations can contribute to increasing the temperature if the system is not managed with high efficiency, in addition to the rise in temperatures in Iraq in general as a result of the changes occurring due to global climate change [6].

Electrical Conductivity (EC)

It is clear from Table (2) that the highest value of electrical conductivity is (405) µS/cm during the month of November compared to the lowest

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value, which is (295) µS/cm during the month of October before the treatment process, while Table (3) shows that the highest electrical conductivity value was (471) µS/cm during the month of October, and the lowest value was (349) µS/cm during March, it is clear that the electrical conductivity value is not affected by the increase in the percentage of chemical pollution in the stations inside the refinery, meaning that there is no strong correlation between the increase in the percentage of chemical pollutants in the water and the increase or decrease in electrical conductivity values, the reason may be due to the fact that most of the oil waste discharged from production units are organic compounds, and as we know that organic materials do not conduct electricity, therefore the value of electrical conductivity did not increase with an increase in the percentage of pollution in the stations [7].

Total Dissolved Solids (TDS)

The results shown in Tables (2 and 3) showed that the concentrations of dissolved solids before the treatment process reached (148, 203, 196, 184, 187, 177) mg/L, respectively, while their concentrations after the treatment process reached (237, 203, 189, 178). (186, 175) mg/L, respectively, during the months of the current study. It was observed that there was no significant difference in the percentage of total dissolved salts for the stations inside the refinery, this may be due to the quality of the oil waste, as most of it is sedimented or suspended materials, the reason may also be due to the fact that the treatment plant consists of physical separation units only, and no chemicals are used in the treatment plant, such as alum, which helps increase the percentage of total dissolved solids [8], and the somewhat low concentrations in the stations inside the refinery may be due to the precipitation of these oily wastes and the possibility of oxidation of the organic matter in them [9].

Salinity

The results shown in Table (2, 3) showed that the concentrations of Salinity before the treatment process reached (0.7, 0.75, 0.7, 0.7, 0.7, 0.7) mg/L, while after the treatment process they reached (0.8, 0.65, 0.6, 0.7, 0.7, 0.7) mg/L. This relative increase in salts inside the AL-Qayyarah refinery stations is due to the crude oil used in the production units inside the refinery containing various heavy metals accompanying it from the extraction well. At the beginning of the refining (filtering) process in the production units, this oil is exposed to washing with water, and the crude oil it gets rid of part of the minerals accompanying it, which is the part that is in the form of dissolved salts in it, and these salts will be present in the oil waste present in the water coming out of the production units [10].

pH

The values of the acid function, as shown in Table (2), before the treatment process ranged between (6.12 - 7.91), where its lowest value was during the month of March and the highest value was during the month of October, compared to its values after the treatment process, which ranged between (6.81 - 7.95). Shown in Table (3), where its lowest value was during the month of January and its highest

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value during the month of October, the relatively low values in the stations located inside the AL-Qayyarah refinery can be explained by the biological oxidation of the organic materials present in the oil waste polluting the water coming out of the production units inside the refinery and their analysis, and the resulting organic acids, carbon compounds, and hydrogen sulfide that result from this decomposition, which forms sulfuric acid when oxidized aerobically [11].

Dissolved Oxygen (DO)

As expected, the stations located in the AL-Qayyarah refinery recorded a small percentage of dissolved oxygen, as the oxygen percentage reached between (1.4-6.0) mg/L. The highest value in the station after treatment in March was (6) mg/L, while the lowest value was in January at the same station, where it reached (1.4) mg/L, as shown in Tables (2, 3). The reason for this may be attributed to the large quantities of organic materials contained in the chemical wastes excreted from the production units, which leads to the consumption of dissolved oxygen as a result. The increase in the biological oxygen requirement (BOD5) by bacteria and other microorganisms that use it to decompose biodegradable organic materials into their primary materials, and this in turn leads to a very significant depletion of dissolved oxygen [12].

Chemical Oxygen Demand

It is clear from Tables (2 and 3) that the average values of the chemical requirement for oxygen were (98.06) mg/L before the treatment process, while the average values after the treatment process were (89.63) mg/L. This is due to the nature of these wastes in the AL-Qayyarah refinery, Which are organic and inorganic materials, as these materials have a demand for oxygen from the organic load and inorganic compounds reduced and discharged with the filter wastes from the various production units and laboratories. Also, there is a high load of organic materials contained in the chemical waste coming out of the production units, which is difficult to remove. They are completely biodegraded by aerobic bacteria, which are often toxic to microorganisms and can be chemically oxidized to carbon dioxide, water, and ammonia, which raises the chemical oxygen requirement values for these wastes [13].

Polycyclic Aromatic Hydrocarbons (PAHs)

The hydrocarbon values, as shown in Table (2), before the treatment process ranged between (73.46 - 155.17), where their lowest value was during the month of October and the highest value during the month of February, compared to their values after the treatment process, which ranged between (35.539 - 52.53). It is shown in Table (3), where its lowest value was during the month of December and its highest value during the month of February. It is clear that the values of hydrocarbons after treatment are much lower than their values after treatment, and this indicates the high efficiency of the treatment unit inside the refinery in getting rid of multiple aromatic hydrocarbons. Despite most of the other components measured in our study, there was no change in their values after they left the treatment unit. If there is a change, it is small and may not be significant, according to a recent study (Environmental Protection Administration,

2024) on the effect of physical processes in removing petroleum pollutants. From industrial wastewater, it is clear that the sedimentation process contributes to removing part of the suspended solids that are often associated with hydrocarbons. When these particles are removed during sedimentation, the concentration of hydrocarbons in the water decreases. In addition, the process of skimming greases and oils helps in removing oils and greases floating on the surface. Water, and since many petroleum hydrocarbons are in the form of oils or greases, skimming oils leads to reducing the concentration of PAHs in the treated water [14]. Also, as the water passes through the treatment unit, some light hydrocarbons can evaporate or disperse in the air, which contributes to a decrease in their concentration. In addition, some hydrocarbons may collect and settle at the bottom of tanks or basins during sedimentation processes, thus reducing their presence in the outgoing water. There may also be changes in the physical properties of the water between the two stations, such as temperature or flow rate, which affects the efficiency of the physical processes in removing hydrocarbons [15].

Oils

The results shown in Table (2, 3) showed that oil concentrations exceeded the standards specified by the Iraqi environment in some months before the treatment process, as they ranged between (26.16-165.68) mg/L, while oil concentrations decreased after the treatment process, as they ranged Between (23.18- 94.15) mg/L, but it remained higher than the standards set by the Iraqi environment, which it set at less than 1 mg/L in drinking water, as this increase in concentrations before the treatment process is attributed to the quality and nature of these wastes, which are Of course, it contains many quantities of oils and greases, a small part of which is dissolved in water, and another part settles to the bottom after the loss of the volatile parts, where its density becomes higher than the density of water, due to the presence of the large organic chain that is not subject to evaporation, while the largest part of it remains floating above the surface of the water[16]. also noted that there is a noticeable and high decrease in the concentration of oils after the treatment process, and this indicates the efficiency of the treatment process, especially in the physical stage of treatment. This is due to the characteristic that characterizes these fatty materials, which is that their density is less than the density of water, so they float on the surface of the water and are therefore easy to remove by mechanical methods. [11].

Total Organic Carbon (TOC)

It is clear from Table (2) that the highest value of total organic compounds is (163.2) mg/L during the month of October compared to the lowest value, which is (117.9) mg/L during the month of February before the treatment process, while Table (3) showed that the highest the value of total organic compounds was (189.4) mg/L during the month of October, and the lowest value was (79.5) mg/L during the month of February. We notice a relative difference after the treatment process (except in the month of October), despite the weak effectiveness of the treatment plant in reducing the concentrations of

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most of the factors mentioned previously, however, it is clear to note their ability to reduce the concentration of total organic carbon (TOC), and this is due to the use of the process of oils skimming and sedimentation to remove large particles of organic materials and oils that float on the surface of the water. These particles may contain TOC, and therefore TOC concentrations are effectively reduced when these molecules are removed. By removing large organic materials from the water, the chance of them decomposing and transforming into smaller, more compatible organic materials that can bind to TOC is reduced [17]. also, removing large organic matter by fat skimming and sedimentation can improve the efficiency of subsequent treatment such as filtration or advanced oxidation, which contributes to further reducing TOC concentration. Therefore, it can be said that the process of oils skimming and sedimentation plays an important role in reducing TOC concentration in water by removing large organic materials and improving the effectiveness of post-treatment processes in removing organic materials. present in water [18].

Table 2: Results of physical and chemical analysis for oil waste before the treatment process

Month / Measurement	October	November	December	January	February	March	adjusted
Water Temperature	33	32	24	17	22	23	25.16
Electrical Conductivity	295	405	386	367	367	354	362
Total Dissolved Solids	148	203	196	184	187	177	182.5
Salinity	0.7	0.75	0.7	0.7	0.7	0.7	0.708
pH	7.91	6.85	7.01	6.43	7.06	6.12	6.89
Dissolved Oxygen	2.0	2.4	3.6	1.8	2.6	5.2	2.93
Chemical Oxygen Demand (COD)	85.0	-	108.0	-	101.2	-	98.06
Polycyclic Aromatic Hydrocarbons	73.46	-	91.96	-	155.17	-	106.80
Oils and Greases	103.61	-	165.68	-	26.16	-	98.48
Total Organic Carbon	163.2	-	121.3	-	117.9	-	134.1

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Table 3: Results of physical and chemical tests for oil waste after the treatment process

Month / Measurement	October	November	December	January	February	March	adjusted
Water Temperature	31	30	22	15	20	21	23.16
Electrical Conductivity	471	402	363	375	379	349	389.8
Total Dissolved Solids	237	203	189	178	186	175	194.6
Salinity	0.80	0.65	0.60	0.70	0.70	0.70	0.69
pH	7.95	7.01	7.04	6.81	7.16	7.01	7.16
Dissolved Oxygen	2.2	3.0	4.2	1.4	4.2	6.0	3.5
Chemical Oxygen Demand (COD)	125.0	-	73.0	-	70.9		89.6
Polycyclic Aromatic Hydrocarbons	41.29	-	35.53	-	52.53	-	43.10
Oils and Greases	45.75	-	94.15	-	23.18	-	54.30
Total Organic Carbon	189.4	-	93.6	-	79.5	-	120.8

Conclusion

The results showed the inefficiency of the oil waste treatment plant in removing pollutants, as no actual treatment operations are performed in the plant other than the process of skimming fats and oils. In most analysis, the plant was not efficient in reducing the concentrations of many parameters, for example Total Dissolved Solids, Salinity, and Total Organic Carbons. and It was a little effective in reducing the concentrations of Polycyclic Aromatic Hydrocarbons and Oils.

Conflict of interests

The authors declared no conflicting interests.

Sources of funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Author contribution

Authors contributed equally in the study.

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