The Treatment of Wastewater Produced from Al-Doura Refinery to Increase Production and Minimize Pollutant Materials

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Abstract
The undertaken study includes investigating the performance and effluent characteristics of the treatment plant of Al-Doura refinery. Influent concentrations for some important contaminants, which are TDS, oil and grease, TSS, COD, BOD, and turbidity were 2595 mg/L, 13934 mg/L, 466.45 mg/L, 2538.9 mg/L, 1739.2 mg/L, and 89.18 NTU, respectively, while the effluent concentrations were 1337.8 mg/L, 0.53 mg/L, 21.7 mg/L, 25.45 mg/L, 17.81 mg/L, and 7.08 NTU, respectively, giving removal efficiencies of 44.47%, 99.99%, 94.4%, 98.96%, 98.96% and 92.05%, respectively. All these results indicate that Al-Doura wastewater treatment plant was efficient in removing contaminants according to Iraqi and EPA specifications. Hence, the second part of this study concentrated on finding a simple and efficient treatment method to treat the effluent so that it can be reused in the boiler system. A pilot plant was designed and dedicated for this purpose, including three units of granular activated carbon filter, ultra filtration filter, and reverse osmosis filter. Average removal efficiencies of oil and grease, turbidity, COD, and BOD were 85.25%, 100%, 34.92%, and 31.11%, respectively at the granular activated carbon filter, with very low efficiencies for the removal of TDs and conductivity. Ultra filtration showed average removal efficiencies for COD and BOD of 30.81% and 32.31%, respectively. While the average removal efficiencies for TDs and conductivity was very low. The reverse osmosis filter removed TDs and conductivity very efficiently, giving average removal efficiencies of 97.63% and 95.43%, respectively. In addition, it provided good removal percentages for COD and BOD, with values of 61.73% and 64.1%, respectively. A recycling procedure was created and the results were eventually comparable to those conferred by some of the traditional approaches.

Keyword: Al-Duora refinery, EPAspifications, Pilot plant, boiler system.

معالجة المياه العادمة الناتجة من مصفاة الدورة لزيادة الإنتاج وتقليل المواد الملوثة

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الخلاصة
تضمن الدراسة التي تم إجراؤها دراسة آداء محطة المعالجة وخصائص الفلايت السائلة. كانت التركيزات المؤثرة لبعض الملوثات الهامة مثل المواد الصلبة الدائمة والزيوت والضحوام والمياه الصلبة النافقة و COD.

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Introduction

Oil refineries are significant water consumers and consequently are large wastewater producers [1]. This wastewater contain a large number of organic and inorganic compounds, emulsified and free oil, phenols, suspended solids, a variety of color taste and odor-producing compounds, sulfides, chlorides, and acids. Many of these compounds are known for their toxicity, persistence, and bio-accumulation in the environment [1].

Plant operators, particularly those of refineries and petrochemical plants, are concerned about the treatment of wastewater generated by industrial operations [2]. The petroleum refining industry produces a large amount of wastewater due to the amount of water used in refining the processes, particularly for cooling systems [2].

In areas of limited water resources, reuse has often to be practiced and therefore, good quality of effluent water is required. Also, in areas of rich waters, the wastewater has to be efficiently treated for the removal of hazardous contaminants. During the last few decades, the presence of harmful organic chemicals in the received water and the discarded effluent water has shifted the focus of wastewater treatment [3]. Oil refining produces untreated wastewater drainage that generates significant environmental problems, as well as a reduction in oil output. Oil pollution is caused by a variety of factors, including sediment extraction and various maritime transportation systems [4]. Untreated wastewater from oil refining, on the other hand, produces toxins such as phenol and hydrocarbons, the latter of which has serious health consequences due to its toxicity [5].

The present industrial wastewater management trend emphasizes pollution avoidance through source reduction (clean technologies) and closed water systems, which include wastewater recycling [6]. Even if comprehensive recycling is not required in every scenario, it is a viable option for enterprises with significant water consumption when discharge limits are enforced or freshwater resources are restricted. One of the possibilities for fulfilling or supplementing plant water requirements that can be cost-effective is recycling refinery effluent for cooling water systems [7]. More efforts are needed to decrease the demand on water. Large quantities of water are consumed in Al-Doura Oil Refinery, which is one of the biggest refineries in Iraq. Thus, the present study was conducted to reduce the required water quantity by studying the possibility to reuse the effluent of wastewater treatment plant as a makeup for the boiler...
Ten runs were conducted for the period of two months (June and July). The samples were taken from each unit during the run and the average was calculated.

**Materials and methods**

**The study site**

Al-Daura refinery is one of the biggest oil refineries in Iraq, located to the southeast of Baghdad. It consists of three main departments, which are the light oil department, lube oil department, and power and utilities department. Other additional departments include those of maintenance, mechanical, safety, firefighting, studies, engineering, research, quality control, training, development, environment, accounting, stores, purchasing, personal, and administration.

-Al-Daura refinery receives an average amount of 100000 m3/day of crude oil from different oil fields in Basra, NaftKhana, Kirkuk, and East Baghdad.

Al Daura refinery consumes 750-1000 m3/hr of water. Physical and chemical treatments for intake water are made to remove the suspended solids. About 33% of this water is used to generate steam which is used in many industrial processes, including atmospheric and vacuum distillation in order to reduce the boiling point of the crude oil. These two processes produce wastewater that is mainly polluted with hydrocarbons. The feed water to boilers that generate steam is treated by many ion-exchange stations to remove the dissolved solids. The cooling tower consumes about 18% of the feed water as a makeup for losses that occur due to evaporation. In addition, there is a leakage of around 750 m3/day. The wastewater of this industrial activity is nearly unpolluted, unless being contaminated due to mixing with the hydrocarbon leaks. The remaining feed water (about 49%) is used in other activities, such as services, domestic uses, cleaning, and fire extinguishing.

The accumulated wastewater which is produced from the different units in the refinery is around 850 m3/day, which is a higher amount than the makeup water required for a boiler system. This wastewater can be reused in the boiler system after passing certain treatment steps to remove the contaminants which can cause damages and fouling in the boiler system.

**General description of the waste-water treatment plant**

The Dora refinery was first operated in 1955. It is located in the southern region of Baghdad city on the right bank of the Tigris River. The average wastewater amount from the refinery is approximately 750 cubic meter per hour at normal conditions, reaching 850 cubic meters per hour in rainy seasons. The wastewater is discharged to the Tigris River after treatment. The refinery wastewater contains several pollutants, including variable concentrations of oil, phenols, suspended solids, sulfides, oxygen demand, bearing material, and other harmful contaminants. A treatment plant was constructed and operated in 1980. In spite of this, it was noticed that the quality of the refinery discharged effluents had exceeded in several occasions the Iraqi discharged water quality limitations, leading to harmful environmental impacts on the Tigris River. The location of Dora refinery along the Tigris River in Baghdad is at the immediate upstream of the industrial complex. The present Dora refinery wastewater treatment plant started the operation in 1980 and the two old API separators, constructed earlier in 1955, were connected with the new treatment facilities. Figure 1 shows the treatment plant units.
Field and Experimental Work
The field works were conducted to determine the performance of the WWTP of Al-Daura refinery units by checking the influent and effluent concentrations for some of the contaminant parameters. These units are series stages consisting of mechanical treatment stages, which include the API (American Petroleum Institute) tank and the Scraping tank, the chemical stage which includes the neutralization tank, the physical stage which includes the flotation tank, the biological stage which include the biological treatment tank, and the final settling tank. The work continued for the period of four months. Influent and effluent samples, from the entrance of the API tank and from the influent pipe of the final sedimentation tank, were taken and tasted. The most important parameters tested include TDS, oil and grease, TSS, COD, BOD, pH, and turbidity.

The following equation was used to calculate the removal efficiency:

\[
\text{Removal efficiency} = \frac{\text{Concentration in} - \text{Concentration Out}}{\text{Concentration in}} \times 100 \quad (1)
\]

Pilot Plant Experiments
A pilot plant was designed, built, and operated. It consisted of a collection tank No.1, water pump No.1, flow meter, activated carbon filter, collection tank No.2, water pump No.2, ultrafiltration filter, collection tank No. 3, water pump no.3, reverse osmoses filter, and a collection, as shown in Figure 2.
Procedure of the Work
The treated water collection tank No.1 was filled with the refinery treated wastewater which was collected from the effluent treated wastewater pipe before the disposal to the river. From the collection tank, the treated water was pumped by pump No.1 through the activated carbon filter (ACF). The filtrated wastewater was collected in another collection tank No.2. The samples were taken before and after this filter, which represents unit (1). From the collection tank No.2, after the ACF, the filtrated water was pumped by pump No.2 through the ultrafiltration filter (UF). The filtrated water was collected in another collection tank No.3. The samples were taken before and after this filter, which represents unit (2). From the collection tank No.3, after the UF, the filtrated water was pumped by pump No.3 through the reverse osmosis filter. The permeate and concentrate were collected. The samples were taken before and after this filter, which represents unit (3).

3. Results and Discussion
3.1 Performance of the Current Refinery Wastewater Treatment Plant
The performance of the currently used wastewater treatment plant was evaluated by measuring some important parameters at four points in the treatment plant. Twenty runs were conducted for this purpose.

3.1.1 Removal Efficiency of Turbidity and TSS
The percent removal values of turbidity and TSS achieved by Al-Daura refinery wastewater treatment plant were recorded during different reading dates. From the results obtained from all units, we found that the best percent removal value for turbidity was achieved when the influent turbidity was 105 NTU, as shown in Figure 3.

TSS is one of the contaminants which is present in the refinery wastewater; therefore, it is important to find a proper way to remove it before its discharge into the environment. As shown in table, influent and effluent TSS concentrations for the wastewater treatment plant were recorded. This table also shows the performance of this plant through the values of removal efficiencies which ranged from 85.9% to 98.21%. The influent concentrations ranged from 234 to 727 mg/L with an average of 466.45 mg/L, while the effluent concentrations ranged from 10 to 33 mg/L) with an average of 21.7 mg/L, which is lower than the allowable
limit of Iraqi Standard and EPA Specification (25 mg/L). Figure 4 shows the removal efficiency with different influent TSS concentrations.

**Figure 3**- Turbidity overall removal efficiency of different influent concentrations for Al-Daura WWTP

**Figure 4**- TSS overall percent removal efficiency of different influent concentrations for Al-Daura WWTP

3.1.2 TDS removal efficiency

Figure 5 shows the concentration and total removal efficiency of TDS for Al-Daura refinery wastewater treatment plant during different reading dates. The maximum removal efficiency (70%) occurred when the influent concentration was 4700 mg/L, whereas the minimum removal efficiency (20.3%) occurred when the influent concentration was 2005. From the total percent removal values for all units, we found the highest removal efficiency for the TDS when the influent TDS concentration was high. These removal values are due to the TDS removed with the settled sludge, which is produced from different units and then transferred to the thickener in the plant. The removal values can also be due to other chemical or physical
reactions. Also, catching of solids can occur by the floating oil which is removed from the surface of the water. The effluent concentrations ranged 1064 -1657 mg/L with an average value of 1337.05 mg/L, which is higher than that of the Iraqi Standard Specifications of 1000 mg/L and EPA Specifications of 500 mg/L (EPA, 2007).

**Figure 5-** Overall percent removal efficiency of different influent concentrations of TDS for Al-Daura WWTP

### 3.1.3 COD5 and BOD reduction efficiency

The COD and BOD5 are extremely essential metrics that must be monitored and reduced to the acceptable limits in the environment. These parameters can be found in high values in the industrial wastewater of a refinery, causing environmental problems if discharged to the environment before treatment. Figure 6 shows the COD and BOD5 values and their percent removal for WWTP of Al Daura Refinery during different reading dates. The influent values of COD ranged from 1654 to 4645 mg/L with an average of 2538.9 mg/L. The removal efficiency ranged from 98.43 to 99.48%. The influent values of BOD5 ranged from 3271 to 1117.6 mg/L with an average of 1739.2, while the removal efficiency ranged from 98.43 to 99.48%. The average COD and BOD5 values in the effluent were 25.45 and 17.36 mg/L, receptively. These values fell within the Iraqi and EPA Standards for COD (100mg/L) and BOD5 (20mg/L). Figures 6 and 7 show the removal efficiencies for COD and BOD5 with the influent concentrations.
Oil and grease are some of the most important contaminants in the refinery wastewater which must be minimized to the allowable limit to prevent any future environmental problem. Therefore, a proper method must be found to reach the acceptable limit of the effluent. The design of the wastewater treatment plant is very efficient to remove this contaminant, as indicated in Figure 8 which shows the removal efficiency of Al-Daura WWTP. The removal efficiency value ranged from 99.98% to 100%. The results infer that the plant is efficient in removing this contaminant. The average oil and grease effluent concentration was 0.49 mg/L, reaching to values that are compatible with the Iraqi and EPA Standards, which impose values of 10 and 15 mg/L, respectively.
3.2 Analysis of the proposed Pilot Plant

Based on the results of the abovementioned tests that investigated the performance of the Al Doura Refinery wastewater treatment plant, it was clear that there is a need for an ideal method to control the processes of petroleum refining and petrochemical wastewater discharges. Such method should eliminate contaminants at the source. Process modifications and in-plant control practices are often rendered impractical from a technological and economic point of view. Therefore, physical, chemical, and biological treatment processes must be optimized and properly utilized to effectively remove the critical pollutants contained within these effluents [8].

A petroleum refinery is typically made up of a number of interconnected processes that separate, change, and rebuild the crude molecular structure to produce the required products. The products include kerosene, gasoline, distillate fuel, residual fuel oil, and other miscellaneous products. However, the petroleum refinery is a complex combination of interdependent processes that generate wastewater effluents containing different pollutants [9]. In this study, it was clear that the treatment plant had an acceptable level of performance, but the effluent could not be used directly in the boiler system. This is due to the fact that the water used in this system must have higher characteristics and specifications than those conferred by the existing treatment plant. Thus, the work was directed to find a simple treatment method with low cost to treat the effluent and bring it to the quality that renders it more usable in the boiler system. This aim could be reached by using the pilot plant study.

According to the results obtained from studying the effluent concentrations of different parameters, it was decided to use a pilot plant that consisted of three units; an activated carbon unit, ultrafiltration unit, and reverse osmoses unit. The effluents from Al Doura WWTP are used as influents to the pilot plant. The activated carbon filter is used for the removal of oil, grease, and trace amounts of hydrocarbons present in the effluent, which could potentially foul or damage the ultrafiltration membrane which represents the next filter. An ultrafiltration filter was used to remove particles down to approximately 0.01 μm. This membrane works as a pretreatment for the next unit. After the ultra-filtration filter, reverse osmosis (RO) is used to remove dissolved salts and metals from the refinery effluent, potentially yielding product water that can be reused at the refinery. At 99 percent rejection rates or greater, RO membranes will selectively allow the flow of pure water while excluding salts. Ten runs were achieved for the period of two months (June and July). The samples were taken from each unit...
during the run and the average was taken. The results are discussed in the following paragraphs.

3.2.1 TDS removal efficiency using the pilot plant

The average final effluent concentration was 33.7 mg/L, which is lower than the allowable level for water reuse in the cooling system (400mg/L-950 mg/L). From the total percent removal values for all units, we found that the best percent removal (94.99) for TDS was achieved at influent TDS concentration of 1950mg/L, as shown in Figure 9.

![Figure 9](image)

**Figure 9**- Overall percent Removal of TDS concentration for All Units

3.2.2 Conductivity reduction efficiency using the pilot plant

The average conductivity value of effluent water leaving the pilot plant was 73.905 μS/cm which is less than the allowable limit of the makeup water requirements for the cooling system (<700 μS/cm), as stated by (Membranes for Industrial Wastewater Recovery and Re-use. Figure (10), Figure 11.

![Figure 10](image)

**Figure 10**- Overall percent Removal of conductivity concentration for All Units
3.2.3 COD reduction efficiency using the pilot plant
The results also demonstrated that the pilot plant was efficient in reducing COD to an average value of 4.4 mg/L, which is below the allowable limit for the wastewater to be used as a makeup for the boiler systems (20-50 mg/L) [2]. The total percent removal for the pilot plant ranged from 76.92% to 87.5% with an average of 82.79%, as shown in Figure 12.

3.2.4 BOD5 reduction efficiency using the pilot plant
From the results of the total percent removal for all units, we found that the best percent removal (87.88%) for the BOD5 value was achieved when the influent BOD5 was 16.5 mg/L. The removal percentage ranged from 77.53% to 86.99% with an average of 83.46%, which is a high value because the BOD5 was reduced to an average of 2.87 mg/L, which is within the accepted value required for wastewater as makeup (<5mg/L) [2], as shown in Figure 13.
Figure 13- Overall percent Removal of BOD5 concentration for All Units.

Figure 14- Overall percent Removal of Oil and Grease concentration for All Units

3.10 Oil and Grease removal efficiency using the pilot plant

The overall results of removal efficiency of oil and grease for all units are shown in Figure 14. In the treated wastewater, which is needed as a makeup in the boiler systems, the oil and grease concentration must be zero mg/L to prevent any biological growth and fouling due to the accumulation of oil and grease particles.

4. Conclusions

Based on the result of the present work, a number of conclusions and recommendations was obtained in relation to the performance of the existing treatment plant of the Al Doura refinery as compared to the performance of the pilot plant which was proposed to study the ability to reuse the effluent as a makeup for the boiler system. The influent of the treatment plant is of high diversity, in both quality and quantity. This is due to the fact of having a single collection system of wastewater, rain water runoff, and domestic sewage from different processing units of the refinery. Wide fluctuations in the performance of the Dora refinery wastewater treatment plant were detected, which can be related to operational problems. The performance of the aeration tank in regard to the removal of dissolved organics and chemical
compounds was good. This is due to the good aeration process. A slight change in the PH value was observed along all units, indicating that the treatment plant works with a good performance. The average TSS and turbidity values in influent water entering Al Daura wastewater treatment plant during the study period were 466.45 mg/L and 89.13 NTU, respectively. The average effluent concentrations were 21.7 mg/L and 7.02 NTU, respectively, giving removal efficiencies of 92.05% and 94.4%.

The average TDS value in the influent water entering Al Daura wastewater treatment plant during the study period was 2594.7 mg/L. The average effluent was 1337.05 mg/L, giving removal efficiency of 44.49%. The average oil and grease concentrations in the influent water entering Al Daura wastewater treatment plant during the study period was 13934 mg/L. The average effluent concentrations was 0.53 mg/L, giving removal efficiency of 99.99%. The average COD and BOD influent values during the study period were 2538.9 and 1739.2 mg/L, respectively. The average effluent values were 25.4 and 17.36 mg/L, respectively, giving removal efficiencies of 92.05% and 94.4%.

All tested parameters of the effluent from the pilot plant were within the allowable limits of water required for cooling. Thus, the effluent from the pilot plant can be used as makeup for the boiler system. From the results of the removal efficiencies and effluent characteristics of the pilot plant, it can be concluded that the concentrations of some important parameters were lower than the required standards of makeup water for boiler water systems. Therefore, for cost saving, part of the effluent from the wastewater treatment plant can be treated then diluted with the other part.

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