Impact Of Khartoum Refinery Waste Water Pollutants On The Environment

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1. Introduction

There is increasing concern among scientists and decision-makers about the negative impact created by the use of various types of energy on the environment. Problems of desertification, global heating, climatic changes and drought surmount the deleterious impacts of these activities. Since energy is inevitable in everyday life and in agricultural and industrial activities; and that the need for it is continual, great attention is nowadays being directed towards research into the deleterious impacts of energy use on the environment. The seeking of ways and means for reducing such impacts is becoming of paramount importance. This study concentrated on determining waste water at Khartoum Refinery and its impact to the surrounding environment.

Samples were tested at the Central Petroleum Equipment official laboratory. Obtained results were compared with Chinese and Sudanese Standards set up for the Refinery by members about the negative impact created by the use of various types of energy on the environment. Problems of desertification, global heating, climatic changes and drought surmount the deleterious impacts of these activities. Since energy is inevitable in everyday life and in agricultural and industrial activities; and that the need for it is continual, great attention is nowadays being directed towards research into the deleterious impacts of energy use on the environment. The seeking of ways and means for reducing such impacts is becoming of paramount importance. This study concentrated on determining waste water at Khartoum Refinery and its impact to the surrounding environment.

1.1 The Literature Review

(Hassan, 1981) Wrote an M.Sc. thesis on the traffic and noise pollution in central Khartoum city area. The thesis focused on air pollutants such as carbon monoxide and sulphur dioxide and their effects on human beings. (Van, 1982) investigated the air pollution control methods and equipment in the oil refining industry. (Bakhiet, 1999) studied the effects of the liquid petroleum gas as an engine fuel in Khartoum State. (Mining, 2014) The Ministry of Energy and Mining wrote a general report on the impact of petroleum industry on the environment. The report surveyed the general aspects of the impact without details or emphasis on the gaseous products of the refining process.

1.2 Khartoum Refinery Company (KRC)

Khartoum Refinery Company limited (KRC) is a joint venture between the Chinese National Petroleum Corporation (CNPC) and the Ministry of Energy and Mining (MEM) of Sudan, each holding fifty percent of the shares. The joint venture agreement of the Refinery was signed in March, 1997 and the construction was officially started in May 1998. The plant was formally put into production in 2000. With annual output is 2.2587 metric tons /year In this study, Khartoum Refinery at Al Gaili town, about 4 Km, possible 4 hours from Khartoum the Capital of Sudan, There are two valleys on both sides of the refinery flow direct to the river. It is taken as an example of possible pollution brought about during the processes of oil refining.

1.3 The Environmental Impact

The disposal of untreated waste water produced by crude oil refining has deleterious impact on the environment such as:-

1. Toxicity of water affects human beings and other living organisms.
2. Fires and explosions are likely to occur due to the presence of hydrocarbons.
3. High temperatures affect aquatic life and reduce dissolved oxygen.
4. Colour, turbidity and taste affect the quality of natural waters, if contaminated by such waste waters. There are three evaporation ponds constructed by the consultant group of Khartoum University (Studies, 2014) in order to receive the waste water (Table 1).

2. Objectives/Purpose of the study

1. To study of nature and concentration of pollutants in waste water resulting from the petroleum refining process.

ABSTRACT

Sudan has become one of the oil producing countries since 2000. Petroleum as an energy source represents 16 % of the energy balance of the country. The processes of prospecting, transportation, refining and utilization of petroleum may have serious negative impacts on the environment. This study focuses on the determination of pollutants in waste water at Khartoum Refinery. Likewise, the study reviewed means and ways adopted by the Refinery to reduce negative impact of such pollutants on the environment. Waste water pollutants analysed included: pH, oil and grease, sulphides, phenols, nitrogen and ammonia, total suspended solids (TSS), biological oxygen demand (BOD), and chemical oxygen demand (COD). It is found that analytical results of pollutants at the outlet of treated effluent are compatible with Chinese and Sudanese Standards as regards oil and grease; phenols; nitrogen and ammonia; total suspended solids; biological oxygen demand and sulphides. This demonstrates the effectiveness of treatment methods adopted by the Refinery in dealing with the above mentioned gaseous by products and water pollutants. However, methods adopted in controlling pH and chemical oxygen demand need revising. Some recommendations are proposed in order to curb the impact of this industry on the environment.

Keywords: Khartoum Refinery, Refinery waste water, Refinery waste water management, Refinery waste water Environmental Impact.
2. To review methods of treatment and management procedure followed by Khartoum Refinery in decreasing pollutants to the minimum possible level.
3. To determine pollutants in waste waters resulting from crude oil refining during refining process, using facilities available at the Central Petroleum Laboratories in Khartoum.
4. To propose recommendations to curb any possible environmental hazards.

3. Methodology

3.1. Khartoum Refinery waste water

Location and accessibility of the study area

The Khartoum Refinery is located on a semi rocky-desert land 15 km north-east of Al-Gaili village, and about 12 km. east of the River Nile (Fig. 1). Small villages are scattered around the Refinery area whose inhabitants are mainly farmers and shepherders, either illiterate or having incomplete primary education. However, some young men work as casual labourers in the Refinery (Mining, 2014).

Waste water is one of the main liquid wastes produced during oil refining process at Khartoum Refinery Company (KRC).

The refinery units

The Refinery consists of the following production units (Mining, 2014):

- Crude Distillation Unit (CDU), capacity: 2.5 mt/y, consisting of an electric desalter and crude distillation products purification plant.
- Residual Fuel Oil Catalytic Cracking Unit (RFCC), capacity: 1.8 m t/y, consisting of reaction and regeneration, distillation, absorption and stabilization, energy recovery, Sulphur and mercaptan removal sections.
- Reforming Unit, capacity: 150000 t/y and consisting of pre-treatment and reforming sections.
- Diesel Hydro Treating Unit (DHT), capacity: 500000 t/y, consisting of hydrogen recovery and diesel hydrogenation sections.
- Sour Water Stripping Unit, capacity: 400000 t/y. Utilities include: a power plant, a waste water plant, an air separation and compression unit and a river water purification plant (1500 m³/h) (Abdelmoneim, 2005).

Describe of the process

- Oily water comes from the process oily water of each production unit, drain oily water of each unit, dewatering process of the oil tank farm, oily rain, over flow water from column bottom pool, and back wash water from the filter pool of the circulation water plant. Caustic wastewater stores in the surge drum first and then enters into the neutralization pool slowly according to pH value, add acid to neutralize and then to the oily water waste system. The total purified compression air capacity is 197.7Nm³/min unpurified compression air capacity is 107.1m³/min. Cooling Compressed air, removing water and carbon dioxide (CO2) in air, air cooling to liquefied temperature, air liquefying fractions, removing hazard pollutant in air for treatment sour water from all processing units enters sour water system and sent into sour water stripping unit.
- Oily water and alkaline water gather in oily water system and alkaline water system and then enter into wastewater treatment unit. Wastewater from living area and control rooms treated in cesspool then sent by domestic wastewater system into wastewater treatment plant. Production
- Waste water system collects wastewater from cooling towers; domestic wastewater not polluted by oil, sulfur and phenols, this kind of wastewater is drained into wastewater treatment plant and then pumped into lagoon out of the refinery without treatment. Sour water from all processing
- Units treated in sour water stripping unit with a capacity 400,000 tone/year then 49.6t/h could be reused and the other would be sent into wastewater treatment plant. After pre-treatment wastewater containing pollutant would drain into wastewater treatment for final treating. Then drain into lagoon to meet the national emission control regulation. Wastewater treatment plant is the main environment protection facility to degrade pollutants in water. The capacity is 300t/h. The oily water from processing unit into wastewater treatment plant. (Alhassan, 2014)

3.2. The waste water discharge includes waters from the following sources

a. Hydro-carbon polluted waters
   i.e. processing water from oil processing units, bottom drainage from oil tanks, laboratory discharge, and discontinuous discharges of various utilities from polluted areas.

b. domestic sanitary water
   Which also joins the Refinery discharge as, water used in cooling or other treatment operations contains a number of organic and inorganic pollutants. Waters from the desalted and the condensed acidic water from Crude Distillation Unit (CDU) and Residual Fuel Oil Catalytic Cracking Unit (RFCC) contain sulphides, phenols, ammonia, H2S, and different amounts of oil. Other water pollutants include:-

c. Suspended and dissolved solids
   Biodegradable materials measured by Biological oxygen demand (BOD). Organic matter that oxidizes with other chemicals coming from oil waste water measured with Chemical oxygen demand (COD). The chemical oxygen demand was rapidly measured calorimetrically. In this study, the reduction of these substances practiced by the Refinery operators to permissible levels by physical, chemical and biological means is tested. This is because polluted waste waters can affect ground water, the Nile waters quality or the soil.

b. Refinery waste water characteristics

   Chemicals characteristic

   The toxicity in waste water coming from the Refinery operation in oil Crude Distillation Unit (CDU) and Residual Fuel Oil Catalytic Cracking Unit (RFCC), its chemical oil, consist of sulphide, phenol, organic acids...
and inorganic salts and using of water in cooling down the machines. The water discharge contains about 5% of these chemicals oil. (Alhassan, 2014)

**Physical characteristic**

Change in the taste, odour, colour or increase in its turbidity or temperature which reduces the content of dissolved oxygen

**Environmental hazards**

Possibility of break out of fires or explosions due to the presence of hydrocarbons. Chemical irritation, inflammation or chemical pneumonia. (KRC, 2002).

3.3 Waste water treatment plant

Waste water treatment plant capacity=300m³/h and it consist of:-

1. **Oil separator pond No.1**

   It is a physical method, efficient for removing suspended hydrocarbons. The first step in the removal of hydrocarbons from water is usually by gravity separation. Through properly selected separator tanks with skimmers, most free oil and unstable oil emulsions can be separated from the water. It is the most economical way to remove large quantities of free oil from water after passing the water through large tanks to allow the phases to separate. The effectiveness of these tanks depends on droplet size and how long the water detention time with in the tank. Oil separator reduces oil concentration to a value of 25 mg/L, with an average of 15 mg/L.

2. **Floatation pond- No. 2 and No.3**

   It is a mechanical and chemical method by using air stripping from compressors to evaporate organic compounds (VOC ?s) and by adding chemicals (PAC) in order to remove dissolved hydrocarbons. (Mining, 2014)

3. **Bio-chemical pond, No. 4**

   Biological treatment is used to remove low levels of dissolved hydrocarbons from wastewater streams. Biological treatment consists of mixing oxygen and nutrients with water in a tank. The bacteria then degrades organic compounds as well as altering chemical form of heavy metals, sulphur, phenols, nitrogen and ammonia. This method is too slow for oil industry applications, because the high salinity of produced water inhibits biological growth, and hence biological treatment will not be effective in most cases.

4. **Filtration**

   One way to remove oil droplets from water is to pass the water through wet filters. This method is used also to remove suspended solids. Sand or gravel filters are common media used in this process. In some special cases when the pH of waste water is too low or very high the KRC waste water treatment plant uses a system control bypass in order to discharge the waste water to the oxidation pond without treatment (Center, 2005)

4. **Analysis of effluent water**

   In order to detect the type and concentration of pollutants present in the Refinery waste water, ten water samples were taken simultaneously, five from the inlet and five from the outlet waste water pond after treatment. On 02/August/2014, the researcher uses the Petroleum Central Laboratories samples Glass Bottles, and should be analysed immediately to avoid any change in concentration. The parameters analysed include: Oil and grease, Sulphides, Phenols, Nitrogen and Ammonia, Total suspended solids (TSS), Biological oxygen demand (BOD) and Chemical oxygen demand (COD).

   The experiments were done in accord with standard methods for examination Refinery waste water like:

1. The pH was done in Central petroleum Laboratory using a fixed pH. Meter type APHA 4500 PH method.
2. The instrument used for measuring the phenols is measured by HACH -8047 method.
4. The Sulphide was measured using the Methylene Blue Method under HACH 8131 method.
5. Chemical Oxygen Demand (COD), measured by Calorimetric Measurement Method.
6. Biological oxygen Demand (BOD) is measured APHA-5210B method; the test took 5 days at 20 C°.
7. Nitrogen and Ammonia was measured by HACH programme.
8. APHA 5520 D method for the determination of oil and grease. See appendix-3.

4.1 Analytical equipment

See appendix-1 for the equipment and appendix-3 for the method

Following is a list of equipment used for waste water analyses at the Central Petroleum Laboratories (see Appendix-1 for the details).

1. UV Spectro photometer for the analyses of the sulphides, Nitrogen and ammonia and the phenols (Plate 1).
2. TSS Water Bath for the analysis of total suspended solids (Plate 2).
3. PH Meter for the determination of pH (Plate 3).
4. COD Reactor measuring the chemical oxygen demand (Plate 4).
5. Rota Vaporate (plate 5).
7. The Oven (plate 7) for the determination of oil and grease.
8. BOD Incubator for aiding measurement of biological oxygen demand (Plate 8).

6. Result/Findings

The samples was taken on 02/August/2014 from Khartoum refinery from inlet and outlet waste water pond at 9.00 am, and analysed at Petroleum Central Laboratories at 1.00 pm at Khartoum City the capital of Sudan. The samples were taken in samples bottles from Petroleum central laboratories.
Tables (2) and (3) show results of analyses for pH, sulphide, nitrogen and ammonia, chemical oxygen demand (COD), oil and grease, total suspended solids (TSS), phenols and biological oxygen demand (BOD) from the inlet and outlet waste water, respectively. The levels of the analysed parameters dropped as in Table (6) showing the results in the inlet and outlet treated water and the Sudanese and Chinese Standards as follows:

1. pH. dropped from 7.15 to 4.57; the result was compared by Sudanese and Chinese standards (Table 6), the outlet water concentration is 4.57 this mean that the outlet water is acidic. And not compatible to the Sudanese and Chinese standards (6-9) and not suitable for drinking purposes.

2. Sulphide dropped from 654.00 mg/L to 25.00 mg/L; the sulphide is dropped to the lower level and it compatible to the standards (1 mg/L).

3. Nitrogen and ammonia from 47.6 mg/L to 9.96 mg/L; the nitrogen is dropped to the lower level, it is (15 mg/L) in Chinese standards and (10 mg/L), while it is (10mg/L).

4. Chemical oxygen demand from 450.00 mg/L to 327.00 mg/L; is dropped in the outlet treated water to 327.00 mg/L but it still high and exceed than the lower level. COD is not compatible with those standards. Sudanese standards for treated waste water quality that should not exceed 100 (mg/L), while, Chinese Standards should not exceed 150 (mg/L).

5. Total suspended solids from 183.00 mg/L to 32.00mg/L; the TSS is dropped to the lower level. To meet the Sudanese standards (30mg/L) and Chinese standards (70 mg/L) was treated in the first and second ponds.

6. Phenols from 0.2 mg/L to 0.03; the phenols dropped to lower level and meet to the Sudanese and Chinese standards for treated waste water (0.5 mg/L).

7. The biological oxygen demand from 40 mg/L to 12 mg/L, it dropped to lower level and meet the Sudanese and Chinese standards for treated waste water (30mg/L).

8. The oil and grease dropped from 128.40 mg/L in the inlet waste water to 10.00 mg/L in the outlet waste water. Comparing this result with the Chinese and Sudanese Standards (Table 4 and 5), the maximum permissible limit of Oil and grease is (10 mg/L). So the Oil and grease value in the outlet treated water is compatible with Chinese and Sudanese Standards for water quality.

9. The outlet treated waste water is not suitable for drinking, but it can be used in the evaporation pond for raising fish, plantations and cooling of engines.

10. It is clear from the analyses carried out in this study that the methods adopted by the Refinery are ineffective in bringing the levels of the pH and the chemical oxygen demand to the permissible, harmless concentrations. Likewise, it is clear that oil and grease; phenols; nitrogen and ammonia; the total suspended solids (TSS); the sulphide and the biological oxygen demand (BOD) values in the outlet treated water are all compatible with those standards. It is clear that the control of these parameters is not effective and needs revising.

11. Also, the discharge of these polluted waters on the ground depending on its rocky nature around the Refinery does not exclude the presence of fractures in these rocks that would render them permeable. Hence, the possibility of contamination of any water underground cannot be ruled out completely.

12. Furthermore, the manner by which the chemicals used in oil refining are stored in the storage place at Refinery laboratory should be under specific lighting, ventilation, temperature and humidity control, the specifications, standards and methods also needs revising. The package of recommendations suggested in this study is likely to alleviate most of the present deleterious environmental impact.

7. Discussion

The results of waste water analyses

The major water pollutants tested in this research work included: oils and grease, sulphides, phenols, ammonia, total suspended solids (TSS), biological oxygen demand (BOD) and chemical oxygen demand (COD). These parameters were analysed on 02/August/2014 from 1.00 pm to 5.00 pm at Petroleum central laboratories, Khartoum, Sudan. (Table 2) shows the results of the analyses of the inlet waste water and (Table 3) shows the results of the analyses of the outlet treated water. The results of the analyses will be discussed in the light of the Chinese and the Sudanese Standards limits of Liquid Wastes Resulting from Petroleum Refining.

7.1 The pH

The pH values dropped from 7.15 in the inlet waste water (Table 2) to 4.57 in the outlet waste water (Table 3). Comparing these results with the Chinese Standards shown in (Table 4) the permissible limit of pH ranges between 6-9; while it ranges between (6-9) in the Sudanese Standards (Table 5). So the pH value in the outlet waste water indicates that the water is acidic.

7.2 The Sulphides

The sulphide values dropped from 654.00 µg/L in the inlet waste water (Table 2) to 25 µg/L in the outlet waste water (Table 3). Comparing this result with Chinese and Sudanese standards (Table 4 and 5), it is evident that the results of the sulphides are well above those standards (1.00 mg/L), since 25µg/L =0.025mg/L. So the Sulphide value in the outlet treated water is compatible with those standards.

7.3 The Nitrogen and Ammonia

The Nitrogen and Ammonia values dropped from 47.60 mg/L (Table 2) in the inlet waste water to 9.96 mg/L (Table 4) in the outlet waste water. Comparing this result with the Chinese Standards (Table 3), the maximum permissible limit of Nitrogen and Ammonia is 15 mg/L; while it is 10 mg/L in the Sudanese Standards (Table 5). So the Nitrogen and Ammonia values in the outlet treated water are compatible with those standards.

7.4 The Chemical oxygen demand (COD)

The COD values dropped from 450.00mg/L (Table 2) in the inlet waste water to 327.00 mg/L (Table 3) in the outlet waste water. Comparing this result with the Chinese Standards (Table 4), the maximum permissible limit of COD is 100 mg/L; while it is 150 mg/L in the Sudanese Standards (Table 5). So the COD value in the outlet treated water is not compatible with those standards.

7.5 Oil and grease

Oil and grease values dropped from 128.40 mg/L (Table 2) in the inlet waste water to 10.00 mg/L (Table 3) in the outlet waste water. Comparing this result with the Chinese and Sudanese Standards (Table 4 and 5), the maximum permissible limit of Oil and grease is 10 mg/L. So the Oil and grease value in the outlet treated water is compatible with both Chinese Standards and Sudanese Standards for water quality.

7.6 The total suspended solid (TSS)

The TSS values dropped from 183.00 mg/L (Table 2) in the inlet wastewater to 32.00 mg/L (Table 3) in the outlet waste water. Comparing this result with the Chinese and Sudanese Standards (Table 4), the maximum permissible limit of TSS 70.00 mg/L; and with the Sudanese Standards (Table 5), the maximum permissible limit is 30 mg/L. It clear that the result of TSS is compatible with those standards.

7.7 The Biological oxygen demand (BOD)

The BOD values dropped from 40 mg/L (Table 2) in the inlet waste water to 12 mg/L (Table 3) in the outlet waste water. Comparing this result with the Chinese and Sudanese Standards in (Table 4 and 5) the maximum permissible limit of BOD is 30 mg/L. So the BOD value in the outlet treated water is compatible with those standards.

7.8 The Phenols

The Phenols values dropped from 0.20 mg/L (Table 2) in the inlet waste water to 0.03 mg/L (Table 3) in the outlet treated water. Comparing this result with the Chinese and the Sudanese Standards in (Table 4 and 5), the maximum permissible limit of Phenols is 0.50 mg/L. So the Phenols values in the outlet treated water are compatible with the Chinese standards and Sudanese Standards for water quality.

For comparison with the Chinese and Sudanese Standards, Table (6) shows the outlet values determined for pH, sulphide, nitrogen and ammonia, chemical oxygen demand (COD), Oil and grease, total suspended solid (TSS), biological oxygen demand (BOD) and phenols.

6.9 Management of environmental hazards produced by waste water pollutants

A waste water plant was added at Khartoum Refinery in order to treat the waste water for reuse in industrial or other activities. Also, the treatment protects surface and underground water from pollution.

Pollutants such as mineral oil, pH, total suspended solids (TSS), nitrogen and ammonia, sulphides and chemical oxygen demand (COD) are monitored daily but the data are not available by Khartoum Refinery Company. The researcher took samples from the inlet and outlet waste water plant and tested in Central Petroleum laboratory to be sure about that the waste water is under the Sudanese and Chinese standards for waste water. The biological oxygen demand (BOD) is monitored bi-weekly by the Refinery waste water analysis plant and by the Health Safety Environment (HSE) laboratories. Mechanical, chemical and biological means are used in the waste water treatment plant to decrease the pollutants to the minimum possible level.

Acknowledgement

This humble effort would not have been possible without the help of others. I would like to thank my supervisor Dr. Abdel-Halim Hassan El-Nadi for his continuous and exceptional help and guidance. I would also like to extend my thanks to the KRC engineers for acquainting me with the different activities in the various Units of the KRS and helping me with the analysis of SO2, NOx and CO. I should also thank the staff of the Ministry of Energy and Mining and the Sudan Petroleum corporation for access to their reports. My thanks should be extended to the Central Petroleum Laboratories (CPL), My Thanks should be extend to Dar Al Ulom University.

References

Appendix

Appendix 1: Equipment used in testing waste water from the Refinery

Figure 1: Analytical equipment -Petroleum Central Laboratories-Sudan-Khartoum

Table 1: Evaporation pond dimensions and activity volumes

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Area of pond</td>
<td>650x420</td>
<td>m²</td>
</tr>
<tr>
<td>Depth</td>
<td>2.2</td>
<td>m</td>
</tr>
<tr>
<td>Pre-treatment effluent</td>
<td>460</td>
<td>m³/h</td>
</tr>
<tr>
<td>Daily discharge</td>
<td>11000</td>
<td>m³</td>
</tr>
<tr>
<td>Estimated evaporation area</td>
<td>800000</td>
<td>m²</td>
</tr>
<tr>
<td>Estimated evaporation loss</td>
<td>6800</td>
<td>m³/day</td>
</tr>
<tr>
<td>Daily excess water</td>
<td>4200</td>
<td>m³</td>
</tr>
</tbody>
</table>

(Mining, 2014)
Appendix 2: Tables showing the results

Table 2: The Results from inlet waste water analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test Method</th>
<th>Unit</th>
<th>Result</th>
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</thead>
<tbody>
<tr>
<td>pH value at 25°C</td>
<td>APHA 4500 PH</td>
<td>µg/L</td>
<td>7.15</td>
</tr>
<tr>
<td>Sulphide</td>
<td>HACH 8131</td>
<td>µg/L</td>
<td>654</td>
</tr>
<tr>
<td>Nitrogen and Ammonia</td>
<td>HACH 8038</td>
<td>mg/L</td>
<td>47.6</td>
</tr>
<tr>
<td>COD</td>
<td>HACH 8000</td>
<td>mg/L</td>
<td>450</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>APHA 5520 D</td>
<td>mg/L</td>
<td>128.4</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>APHA 2540D</td>
<td>mg/L</td>
<td>183</td>
</tr>
<tr>
<td>BOD</td>
<td>APHA- 5210B</td>
<td>mg/L</td>
<td>40</td>
</tr>
<tr>
<td>Phenols</td>
<td>HACH -8047</td>
<td>mg/L</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 3: The outlet waste water values determined for pH, Sulphide, Nitrogen and Ammonia, COD, Oil and Grease, TSS, BOD and Phenols (Khartoum Refinery Company, 2014) for comparison with the Chinese and the Sudanese Standards.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Results outlet Waste water</th>
<th>Maximum limit in Chinese standards</th>
<th>Maximum limit in Sudanese Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value at 25°C</td>
<td>4.57</td>
<td>6-9</td>
<td>6-9</td>
</tr>
<tr>
<td>Sulphide</td>
<td>0.025 mg/L</td>
<td>1 (mg/L)</td>
<td>1 (mg/L)</td>
</tr>
<tr>
<td>Nitrogen and Ammonia</td>
<td>9.96 mg/L</td>
<td>15 (mg/L)</td>
<td>10 (mg/L)</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>327.00 mg/L</td>
<td>100 (mg/L)</td>
<td>150 (mg/L)</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>10.00 mg/L</td>
<td>10 (mg/L)</td>
<td>10 (mg/L)</td>
</tr>
<tr>
<td>Total suspended solids (TSS)</td>
<td>32.00 mg/L</td>
<td>70 (mg/L)</td>
<td>30 (mg/L)</td>
</tr>
<tr>
<td>Biological oxygen demand (BOD)</td>
<td>12.00 mg/L</td>
<td>30 (mg/L)</td>
<td>30 (mg/L)</td>
</tr>
<tr>
<td>Phenols</td>
<td>0.03 mg/L</td>
<td>0.50 (mg/L)</td>
<td>0.50 (mg/L)</td>
</tr>
</tbody>
</table>

Table 4: Chinese standards used for waste water treatment (Khartoum Refinery Company, 2014)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Maximum limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value at 25°C</td>
<td>6-9</td>
</tr>
<tr>
<td>Sulphide</td>
<td>1 (mg/L)</td>
</tr>
<tr>
<td>Nitrogen and Ammonia</td>
<td>15 (mg/L)</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>100 (mg/L)</td>
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<tr>
<td>Oil and grease</td>
<td>10 (mg/L)</td>
</tr>
<tr>
<td>Total suspended solids (TSS)</td>
<td>70 (mg/L)</td>
</tr>
<tr>
<td>Biological oxygen demand (BOD)</td>
<td>30 (mg/L)</td>
</tr>
<tr>
<td>Phenols</td>
<td>0.50 (mg/L)</td>
</tr>
</tbody>
</table>

(Mining, 2005)
Table 5: Sudanese Limit of Liquid Waste From Petroleum Refining (Ministry of Energy and Mining, Regulations for protection of the environment in the petroleum industry, 2014).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Maximum limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value at 25°C</td>
<td>6-9</td>
</tr>
<tr>
<td>Sulphide</td>
<td>1 (mg/L)</td>
</tr>
<tr>
<td>Nitrogen and Ammonia</td>
<td>10 (mg/L)</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>150 (mg/L)</td>
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<td>Oil and grease</td>
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<td>Phenols</td>
<td>0.50 (mg/L)</td>
</tr>
</tbody>
</table>

(Mining, 2005)

Table 6: The outlet waste water values determined for pH, Sulphide, Nitrogen and Ammonia, COD, Oil and Grease, TSS, BOD and Phenols for comparison with the Chinese and the Sudanese Standards.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Results inlet</th>
<th>Results outlet</th>
<th>Maximum limit in Chinese standards</th>
<th>Maximum limit in Sudanese Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value at 25°C</td>
<td>7.15</td>
<td>4.57</td>
<td>6-9</td>
<td>6-9</td>
</tr>
<tr>
<td>Sulphide</td>
<td>654</td>
<td>0.025 mg/L</td>
<td>1 (mg/L)</td>
<td>1 (mg/L)</td>
</tr>
<tr>
<td>Nitrogen and Ammonia</td>
<td>47.6</td>
<td>9.96 mg/L</td>
<td>15 (mg/L)</td>
<td>10 (mg/L)</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>450</td>
<td>327.00 mg/L</td>
<td>100 (mg/L)</td>
<td>150 (mg/L)</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>128.4</td>
<td>10.00 mg/L</td>
<td>10 (mg/L)</td>
<td>10 (mg/L)</td>
</tr>
<tr>
<td>Total suspended solids (TSS)</td>
<td>183</td>
<td>32.00 mg/L</td>
<td>70 (mg/L)</td>
<td>30 (mg/L)</td>
</tr>
<tr>
<td>Biological oxygen demand (BOD)</td>
<td>40</td>
<td>12.00 mg/L</td>
<td>30 (mg/L)</td>
<td>30 (mg/L)</td>
</tr>
<tr>
<td>Phenols</td>
<td>0.2</td>
<td>0.003 mg/L</td>
<td>0.50 (mg/L)</td>
<td>0.50(mg/L)</td>
</tr>
</tbody>
</table>

Appendix 3: The methods used in testing Refinery waste in Petroleum Central Laboratory, Khartoum

The Waste Water Analyses Test Methods

1. The Analysis of the Sulphide by Methylene Blue Method

The analysis is fully computerized. First the HASH PROGRAM is selected and the number 3500 for the sulphide analysis is entered and the ENTER key is pressed so that the display showed: HACH PROGRAM: 3500 Sulphide, with the wavelength(λ), 665nm, is automatically selected, 25 mL from the sample were measured into a sample cell and 25 mL of deionized water were transferred into a second sample cell (the blank). To each cell 1.0 ml of Sulphide 1 Reagent was added and whirled in order to mix. 1.0 ml of Sulphide 2 Reagent was added to each cell. Then, A5-minute reaction period was stored by pressing the soft key under START TIMER. When the timer beeped, the blank sample was placed into the cell holder and the light shield closed. Then the soft key under ZERO was pressed and the display showed 0µg/L S2- . Finally, the prepared sample was placed in the cell holder and the light shield closed. The result in µg/L Sulphide (or chosen units) was taken.

2. The analysis of the Nitrogen, Ammonia by the Nessler Method

The soft key under HACH PROGRAM was pressed and the stored program for low range ammonia nitrogen (NH3-N) was selected by pressing the number 2400 and the ENTER key was pressed so that the display showed: HACH PROGRAM:2400N, Ammonia Nessler, with the wavelength(λ), 425nm, is automatically selected. A 25-mL mixing graduated cylinder was filled (the prepared sample). Another 25 ml mixing graduated cylinder was filled with deionized water (The blank). Three drops of polyvinyl Alcohol Dispersing Agent were added to each cylinder by holding the dropping bottle vertically. The cylinder was inverted several times to ensure proper mixing. Then 1.0 ml of Nessler Reagent was pipetted into each cylinder Stopper and inverted several times to ensure proper mixing. Next, the soft key under START TIMER was pressed so that a one-minute reaction period began. Each solution was poured into a sample cell. When the timer beeped the blank sample was placed into the cell holder and the light shield closed. Then the soft key under ZERO was pressed and the display showed: 0.000mg/L NH3. Finally, the prepared sample was placed into the cell holder then the light shield closed. The results in mg/L ammonia expressed as nitrogen (NH3-N) (or chosen units) were taken.

3. The analysis of the Phenols

The analysis is also fully computerized. First the HACH PROGRAM was selected and the number 2900 for phenols analyses was entered and the ENTER key was pressed. The display showed HACH PROGRAM 2900 phenols, with the wavelength (λ)460 nm is automatically selected. Then 300 mL of deionized water were measured into 500 mL graduated cylinder and the measured deionized water was transferred into a 500 mL separatory funnel (the blank). 300 mL of sample were measured into a 500 mL graduated cylinder. Then the prepared sample was transferred into...
another 500 ml separatory funnel and 5ml of hardness 1 buffer to each separatory funnel were added and stopped and shake in order to mix. Then the contents of one phenol reagent powder pillow were added to each separatory funnel, stopped and shake in order to dissolve. Then the contents of one phenol 2 reagent powder pillows were added to each separatory funnel, stopped and shaken in order to dissolve. 30 ml of chloroform were added to each separatory funnel, stopped. Then each funnel was inverted and temporarily vent, and vigorously shake for 30 seconds. Then the stoppers was removed in order to allow both funnels to stand until the chloroform settles to the bottom of the funnel. A large pea-sized cotton plug was inserted into the delivery tube of each funnel. The chloroform layers were drained into separate sample cells (one for the blank and one for each sample). Then the blank sample was placed into the cell holder and the light shield closed. Then the soft key under ZERO was pressed and the display showed: 0.000 mg/L phenol. Finally, the prepared sample was placed into the cell holder and the light shield closed. The result in mg/L phenols was taken.

4. Determination of the Total Suspended Solids

A disk with its wrinkled side up was inserted into the filtration apparatus under vacuum and washed with three successive 20-mL portions of reagent-grade water. The suction was continued in order to remove all traces of water. Then the vacuum was turned off, and the washings discarded. The filter was from the filtration apparatus and transferred into an inert aluminum weighing dish. The crucible and filter were then dried in an oven at 103 to 105 ºC for 1 h. To measure the volatiles the crucible was ignited at 550 ºC for 15 min in a muffle furnace, then cooled in a desiccator and weighed. The crucible and filter were then dried in an oven at 103 to 105 ºC for 1 h. To measure the volatiles the crucible was ignited at 550 ºC for 15 min in a muffle furnace, then cooled in a desiccator and weighed. The cycle of drying, igniting, cooling, desiccating, and weighing was repeated until a constant weight is obtained or until the weight change is less than 4% of the previous weight or about 0.5 mg, whichever less, and the crucible was stored in a desiccator until needed.

A sample volume to yield between 2.5 and 200 mg was chosen and the residue dried residue. If the volume filtered fails to meet the minimum yield, the sample volume was increased to 1L. If complete filtration takes more than 10 min, then the filter diameter was increased or the sample volume decreased. Sample analysis: Assemble filtering apparatus and being suction. The filter was wetted with a small volume of reagent and the sample was stirred with a magnetic stirrer at such a speed to shear larger particles, (if present) to obtain a more uniform (preferably homogeneous) particle size. Centrifugal force may separate point of sample with drawal is varied. While stirring, pipet a meas-samples, piped from the approximate midpoint of container but not in vortex. A point both mid depth and midway between wall in vortex was chosen. The filter was washed with three successive 10 ml volumes of reagent-grade water and allowed to drain completely after each washings. Suction was continued for about 3 mins after filtration is complete. Samples with high dissolved solids may require additional washings. The filter was then carefully removed from the filtration apparatus and transferred to an aluminum weighing dish as a support. Alternatively, the crucible and filter were removed complete from the crucible adapter. If a Gooch crucible was used the sample was dried for at least 1 h at 103C° to 105 C° in an oven and cooled in a desiccator to weighing temperature. The cycle of drying, cooling, desiccating and weighing was repeated until a constant weight is obtained or until the weight change is less than 4% of the previous weight or within 0.5 mg, whichever is less. About 10% of all samples were analyzed twice. Duplicate determinations should agree within 5% of their average weight if the volatile solids are to be determined. The residue was analyzed according to the programme 2540E.

Calculations

\[
\text{total suspended solids mg / L} = (A-B) \times 1000 / \text{sample volume (mL)}
\]

Where:

\[
A(mg) = \text{weight of filter + dried residue, and}
B(mg) = \text{weight of filter.}
\]

6. pH value

Instrument calibration: In each case follow manufacture’s instructions for pH meter and for storage and preparation of electrodes for use. Solutions for short-term storage of electrodes have conductivity greater than 4000 µmhos/cm was recommended. Tap water is a better subsume than distilled water but pH 4 buffers is the best for the single glass electrode and saturated KCL was preferred for a calomel and AG/AGCL reference electrode. Saturated KCL is the preferred solution for a combination electrode. Then electrodes wet by returning them were kept to storage solution whenever pH meter is not in use.

Before use, electrodes from storage solution were removed, rinsed and blotted dry with a soft tissue then placed in initial buffer solution and that is the potential point. Next a second buffer within 2 pH units of sample pH was selected and the sample and buffer were brought to the room temperature, such as 25ºC, or the temperature of a fresh sample. The electrodes were removed from first buffer, rinsed thoroughly with distilled water, blotted dry and immersed in second buffer. The temperature of measurement was recorded and adjusted temperature dial on meter so that meter indicates pH value of buffer at test temperature.

The pH value listed in the tables was used for the buffer used at the test temperature. Then electrodes from second buffer were removed, rinsed thoroughly with distilled water and dried electrodes as indicated above and immersed in a third buffer below pH 10, approximately 3 pH units different from the second; when only occasional pH measurements were made and the instrument was stable, standardized less frequently.

Sample analysis: equilibrium between electrodes was established and stirred sample to insure homogeneity; conditioned electrodes after cleaning by dipped them into sample for 1 min. Blotted dry, immersed in a fresh portion of the same sample, and read pH.

6. Chemical Oxygen Demand (COD) determination by APHA 5520 D, (for 0 to 40 mg/L range).

100 mL of sample were homogenized for 30 seconds in a blender. The COD Reactor was turned on preheated to 150 ºC.
The plastic shield was placed in front of the reactor. The cap of the COD Digestion Reagent vial was removed for the appropriate range and held at 45-degree angle in order to pipette 2.00mL (0.2 mL) for the 0 TO 15,000 mg/L range of sample into the vial. The cap of the vial was replaced tightly and the COD vial was rinsed with deionized water and wiped with a clean paper towel. Next the vial was held by the cap and over a sink, inverted gently several times to mix the contents and replaced in the preheated COD reactor. A blank sample was prepared by repeating steps 3 to 6, substituting 2.00 mL (0.2 mL for the 0 to 15,000 mg/L range) with deionized water and placed the blank in the COD reactor. The vials were then heated for 2 hours. After words, the reactor was turned off and the vials were left for 20 minutes to cool to 120 ºC or less, inverted several times while still warm and finally placed into a rack to cool to room temperature.

The sample was digestion described for the "Oxygen Demand determination. The key under HACH PROGRAM was pressed and the program number for ultra low range COD was selected by pressing 2700 with the numeric keys followed by ENTER. The display showed: HACH PROGRAM: 2700 COD, ULR with the wavelength(λ,350 nm) was automatically selected. Then the N Tube Adapter was inserted into the sample module by sliding it under the thumb screw into the alignment grooves and then fastened with the thumb screw. The outer surface of the blank was cleaned with a towel, and placed into the adapter with the Hach logo facing the front of the instrument and the light shield closed. The soft key under ZERO was pressed and the display showed: 0.00mg/L COD. The outer surface of the sample vial with a towel. Finally, the sample vial was placed into the adapter with the Hach logo facing the front of the instrument and the light shield closed. The results in mg/L COD (or chosen units) was then displayed.

7. Determination of Oil and Grease:APHA 5520 D method

Following APHA 5520 D Method. The sample bottle was marked at the water meniscus. Then 1:1 HCL or 1:1 H2SO4 was added to pH 2 or lower (5ml for 1L). Next the sample was transferred to a separatory funnel by liquid funnel and the sample bottle was rinsed with 30 mL extracting solvent and the solvent washings were added to the separatory funnel. The bottle was shaken vigorously for 2 min until the layers separated. The aqueous layer and a little amount of organic layer were drained into the original sample container. The centrifuged material was transferred into an appropriate separatory funnel and the solvent layer was drained twice through a funnel with a filter paper with an additional 10g of Na2SO4 solvent-rinsed. Then aqueous layers and any remaining emulsion or solids were added together into a separatory funnel. Then twice 30ml solvent was extracted each time. The solvent in the flask was distilled in a water bath at 85ºC for either solvent system. The solvent was collected in an ice-bath-cooled receiver. After the visible solvent condensation stops, the flask was removed from the water bath. Still at 85ºC, air was drawn through the flask for 15 min with an applied vacuum for the last 1 min. The sample was then cooled in a desiccator for at least 30 min and weighed. Finally, the sample volume was calculated by the difference from the initial volume.

8. Determination of the Biological Oxygen Demand (BOD)

The water sample was heated to within 20ºC of its incubation temperature (typically 200ºC, 680F). Then a clean graduated cylinder was used to pour the correct sample volume into a BOD Trak sample bottle. The sample dilutions for more information on BOD range selection.