

Control And Prevention Of Wastewater Pollution

From Amerya Petroleum Refining Company

A.A.Bakry

Amerya Petroleum Refining Company

ABSTRACT

An oil refinery normally uses large quantities of water, for cooling and other process purpose. This water is treated from contaminants and finally returned to a lake or sea, outside the refinery.

Amerya Petroleum Refining Company (**APRC**) uses conventional and special treatment methods for wastewater to remove all pollutants and to reduce the oil content in refinery final effluent water to a limit of 10 ppm , as the maximum permissible limit for environmental protection as designated by the Egyptian Act No. 4 for the year 1994 . About 80% of oil in wastewater is separated by API (American Petroleum Institute) separator method and returned to refinery. Small oil droplets, emulsion and suspended matter escaped from API separator but were removed successfully in the dissolved air flotation (**DAF**) with chemical additives as the secondary treatment stage for wastewater. The flotation method with chemical additives and filtration were used to reduce the suspended solids and oil content to permissible levels (10 ppm)

Furthermore, biological treatment unit was constructed to remove the dissolved oxygen consuming contaminates, e.g. phenolic compounds and traces of hydrocarbon derivatives. It was found that the BOD and COD of the effluent were reduced, and 100% removal of the trace amount of phenol was achieved in effluent.

INTRODUCTION

Water pollution is one of the serious problems facing petroleum industries. Large quantities of water are used in refinery operation, as much as 30 to 80 tons of water per ton of crude oil processed for operations, such as cooling where enormous amounts of heat are removed. This wastewater is finally collected in some sewer system and treated before discharging to lake or sea. Wastewater contain diverse range of pollutants including oil, phenols, sulfides, spent acids, spent caustic soda, pollutants , and suspended solids. It leads to pollution of water and increasing the biological activity combined with decreasing the solubility of oxygen in water, thereby adversely effecting aquatic life. Because nonvolatile components remain at the surface of water forming a thin oil layer and preventing water from absorbing oxygen from air, they promote unhealthy anaerobic conditions. Sulfides, mercaptans and other sulfur compounds in water produce obnoxious smells and can impart a black colour to receiving waters or corrode the process equipment including the transmission lines and wastewater treatment plant. Phenols, spent acids, spent caustic soda and sulfids impart taste and odor to water, making it unsuitable for drinking and dangerous to health.

APRC used different treatment systems for wastewater to control and reduce pollutants in discharged effluent water to comply with the Law 48/1982 and Law 4/1994 regarding the protection of water streams and environment from pollution. Great efforts were spent to minimize the amount of pollutants in wastewater by abating pollution sources before treatment system such as:

- 1- Modification of process or equipment to produce less-polluting streams.
- 2- Use of surface condenser in place of barometric condenser.

3- Controlling the condensed water from phenol extraction unit by its reuse in a closed system in order to improve its quality for recycling and reducing corrosion and phenol losses.

4- Removal of the dissolved hydrogen sulfide (H_2S) and ammonia from sour

Water which is collected from different process units in the refinery before discharge as oily water.

The existing treatment systems in APRC can be classified into:

a) Conventional methods, which include the gravity oil separator (API Separators)

b) Special methods, which consist of:

i) Air flotation with chemical additives (Coagulants & Flocculants)

ii) Filtration (Sand Filters).

iii) Biological treatment (Activated Sludge).

The present study is therefore focused on the environmental protection in refinery by controlling and prevention of water pollution. This study shall give some light on wastewater treatment in APRC, as a typical case study for petroleum refineries.

Refinery Liquid Waste – Treatment Methods

A very important task for refineries is to decrease the quantity of wastewater which has to be treated; therefore the prevention of contamination is a permanent purpose for refineries engineers by the reduction of water use. Prevention and remedial measures should be incorporated for the treatment of refinery liquid effluent streams and this includes⁽¹⁻⁴⁾

I – In – Plant Pretreatment

They include facilities upstream which carry out the primary treatment. These include the reduction of oil leakage by proper maintenance of pumps, pipe fitting and joints^(5,6). The modification of a process or

equipment can minimize the amount of resulting wastewater or concentration of polluting material in it such as, the recycling of waste streams from desalting the crude oil and the use of air coolers instead of water cooler Sour water condensates containing significant amount of ammonia, hydrogen sulfide, and mercaptans are collected from different process units and discharged to sour water treatment unit. The object of the unit is to remove these pollutants by steam stripping to a lower concentration depending on its design. Fig (1) is a simplified flow diagram of the existing sour water treatment unit in APRC, and Table (1) shows the properties of influent & effluent from the unit.

II- Conventional Methods In APRC

1- Gravity - oil separators ^(7,8)

Oil in wastewater may be present as free oil, emulsions, or dissolved (soluble oil). Free oil consists of discrete oil globules of sufficient size to rise to the surface of water under quiescent condition and it is easily separated by gravity. Emulsified oil described as intimate two phase mixtures of oil and water with one phase dispersed as minute globules in the other phase. Emulsions are generally oil in water, water in oil or dual phase. Dissolved oil forming a true molecular solution with water and it is only removed by special methods of treatment (i .e . biological treatment) . The function of an oil – water separators is to separate free oil from refinery wastewater. The most universally used gravity oil separators is that of American Petroleum Institute type (API) in which separated oil is skimmed off at the surface and the settled solids with some absorbed oil is removed from the bottom . Oil droplets of diameter less than 150 microns can't be removed.

There are two API – type (clean and oily rectangular basin separators) in APRC designed to eliminate any suspended oily matters and to reduce oil content in the effluent water. The first clean separator of

15000 m³ / hr and 80 % efficiency, separate oil from the clean water, i . e., the effluent water from the refinery cooling systems, of oil content 10 ppm . The second oily separator of 6000 m³ / hr and efficiency more than 80% , separates oil from the oily water , I . e . , water drainage from the equipment , storage tanks, crude oil desalters and boilers blow downs, of oil content more than 1000 ppm, which is shown in fig (2).

A rectangular separator is based on gravity setting of oil droplets under reduced velocity of phases. The depth – to – width ratio of separator is between 0 . 3 to 0 . 5 in order to obtain at low velocity. The depth varies from 0 . 9 to 2 . 4 m , and the width from 1 . 8 to 6 m. The gravity separator is designed for removing of free oil droplets having certain terminal velocity (V_t) . The droplets having terminal velocity below the design velocity, such as fine dispersions and emulsified oil can not be removed. The terminal velocity is defined by:

$$V_t = D^2 \cdot \Delta \rho \cdot g / 18\mu \quad [1]$$

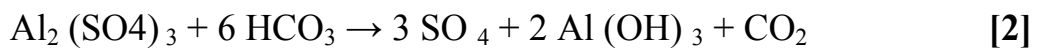
The terminal velocity increases by increasing the droplet diameter (D) and decreasing the viscosity of water (by elevated the temperature). Also, when difference between water and oil densities ($\Delta \rho$) increased, the terminal velocity increased.

Although, the major part of oil can be removed in API conventional separators, the effluent will always contain residual amounts of finely dispersed, emulsified oil and dissolved compound e. g., phenols. In case, therefore, where the quality requirements of effluent are particularly stringent, this type of treatment is followed by chemical flocculation, dissolved air flotation (DAF) and biological methods. Fig (3) shows the different methods for wastewater purification in APRC.

2 – Flotation method (9–12)

It is use of air bubbles to float suspended matter and lift it to the surface. The flotation method includes several techniques such as dissolved air, induced air and electro-flotation (9 – 10) . In dissolved air flotation (DAF), air is dissolved in wastewater at a pressure of 2 – 4 atm . till saturation level. Upon releasing the pressure, fine air bubbles will form and cause flotation of suspended solids. The floated material collects at the surface forming a layer of scum which thickens with the time because of the entrapped air release. The releasing air forms tiny bubbles which adhere to the suspended matter causing it to float to the surface where the formed sludge or foam is skimmed off. This process not only clarifies the effluent but also, decrease the oxygen demand of the waste (BOD). Also dissolved air can reacts with dissolved oxygen demand of the waste. DAF bubble size is a bout 50 to 100 microns, so, it is more effective for smaller suspended solids .

Chemicals are commonly used to aid the flotation process. These chemicals, for the must part, function to create a surface or a structure that can easily absorbed by entrap air bubbles, and modify the surface characteristics of finely dispersed particles to be removed. Inorganic chemicals, such as the aluminum and ferric salts can be used. Aluminum sulfate reacts with alkalinity of wastewater giving a precipite of aluminum hydroxide according to the following reaction:



The action of flocculants may be enhanced by addition of a colloidal material, which will improve the coagulation by increasing the bulk and weight of floc, into wastewater. Polyelectrolytes are often used for this purpose. These compounds are known to be large molecular size and most have multiple electrical charges along the molecular chain of carbon

atoms. The addition of these chemicals (coagulant & flocculants) will greatly increase separation efficiency of floatation to about 95 %.

3- Filtration ^(3,9,11)

It is a physical treatment method to reduce the amount of suspended solids in wastewater stream, by passing the mixture through a porous media. Filtration may serve as the primary turbidity removal process. The most common practice is gravity filtration by sand filter which it be used as a polishing step after gravity oil separator to reduce the content of both suspended solids and oil from wastewater. Granular filtering materials don't retain very finely suspended matter, to obtain good filtered water. When the filter becomes clogged, it must be restored to its original condition by efficient and economic washing

4-Biological treatment ⁽¹³⁻¹⁶⁾

It is considered an advanced treatment for industrial waste streams. It is applied when it is necessary to remove the soluble organics and provide further removal of suspended solids Biological treatment is simply a slow rate oxidation process, in which microorganisms (bacteria) use the air oxygen to oxidize the organic matter in wastewater to the final products as CO₂, water and other inert products . The most important biological waste treatment system is the activated sludge system.

Activated sludge, by definition, is a suspension of microorganisms, active and dead. In order to ensure a healthy growth of bacteria and other organisms, nutrients addition is required. When the bacteria's food supply is unlimited, bacteria growth is restricted only by the ability of microorganisms to reproduce and the organic removal and cell growth is directly proportional to the number of microorganism. ⁽¹³⁻¹⁴⁾ Because the

number of microorganisms increases rapidly during this log – growth phase of metabolism, so the food supply becomes limited. ^(14–15)

Fig (5) shows the process flow diagram for APRC activated sludge. The essential features of the process are following:

Wastewater after sand filter enters the aeration tank, where the organic matter is brought into intimate contact with the sludge from clarifier. An aeration stage, followed by aeration (clarifier), and sludge recycled. Sludge from clarifier is heavily laden with microorganisms which are in active state of growth. Four mechanical aerators introduce air into the bioreactor. Microorganisms utilize the oxygen in the air and convert the organic matter into stabilized low energy compounds such as CO₂ and synthesize new bacteria cells. The effluent from the aeration tank containing the flocculent microbial mass, known as sludge is separated in a settling tank or clarifiers. The separated sludge existing without contact with the organic matter becomes activated in the clarifier. All the activated sludge is recycled until the bacterial mass increases to certain level after which it is necessary to dispose some of the microorganisms, and this waste sludge is sent to thickener. This sludge is concentrated in the thickener and withdrawn to the drying beds for sludge dewatering under the effect of sun. The dry sludge is then removed and the filtered water is recycling back to aeration basin. Table (2) shows the average values properties of effluent water from activated sludge plant in APRC, compared with that of influent wastewater (Sand filler effluent stream). This table indicates that all the values below the limit's that required by low and 100 % of trace phenol removal.

CONCLUSION

Amerya Petroleum Refining Company uses different treatment methods for wastewater to reduce all pollutants to permissible limits, and 100% removal of the trace amount of phenol. The total annual operating cost of existing treatment units in APRC ranged from 5 to 6 millions Egyptian pounds , which included the total cost of utilities , chemicals consumption , equipment depreciation , labor....etc. Generally, the projects for the environmental protection from pollution has no return or profit , but existing systems in APRC has a return of approx . 20% to 25% of total annual operating cost expressed as recovered oil to crude distillation units, as shown in fig (4). Recovered oil is blended with crude oil for reprocessing in the refinery.

NOTATIONS

| | |
|----------------|---|
| API | American petroleum Institute |
| BOD | Biological oxygen demand (PPM) |
| COD | Chemical oxygen demand (PPM) |
| DAF | Dissolved air flotation |
| D | Diameter of an oil globule (m) |
| G | Gravitational acceleration 9.80 (m/s ²) |
| PPM | Part per millions or mg. / liter |
| V _t | Terminal velocity (m/s) |
| μ | Viscosity of liquid(poise) |
| ρ | Density (kg/m ³) |

References

- 1- Beychock , M . R., "Aqueous wastes from petroleum and petrochemical plants", Willey , London (1973)
- 2- Azad , H . S, "Industrial wastewater management Hand book" McGraw – Hill, New York (1976)
- 3- El Hizawy, A. M., Trans. Egypt. Soc. Chem. Eng., Vol. 6, No. 1 (1980)
- 4- Hepple , P. , water pollution by oil , Appl. Sci . Pub. Ltd, U. K. (1973)
- 5- Asher, N. G, Chem. Eng. 17, Vol. 4 (1982)
- 6- Eckenfelder, W. W., Water Sci. Tech. 14, Vol. 112 (1982)
- 7- Kandil, S. S, Technological specifications of oil separators in Amerya Refinery, El – Nasr petrol. Co. Tech. report No. 9 (1969)
- 8- Brunsmann, S., Water pollution control Federation J. 34, 516 (1974)
- 9- Matcalf and Eddy Inc., Wastewater Engineering, Treatment Disposal and Reuse, Tata, McGraw Hill, New Delhi (1979)
- 10- Amer , A. , El – Kayar , A. , Hussein , M. and zatout A.A., Petroleum Conf. No. 14, Vol. 2 (1998)
- 11- Hosny , A , Bull. Electrochem. Vol 1 (1997)
- 12- Burkardt , C . w., Hydrocarbon Proc. 62 (1983)
- 13- Rao, C.S., Environmental pollution control Engineering, John Wiley and sons, New York (1991)
- 14- Besse, E.B., The treatment of industrial waste, McGraw – Hill, New York (1969)
- 15- Nour El – Din, H. M., 14th Petroleum Conf., Vol.2, Cairo (1998)
- 16- Schroeder, E. D., Water and Wastewater treatment, McGraw – Hill New York (1977)

Table (1)

Design basis of sour water treatment unit in APRC

| Properties | | Inlet (feed) | Effluent | % Removal |
|-----------------------------|-----|-----------------|----------|-----------|
| Sulfide content | PPM | 65000 | 130 | 98 |
| Ammonia (NH ₃) | PPM | 3000 | 300 | 90 |

Table (2)

**Properties of influent and Activated Sludge Plant effluent water
in APRC**

| Properties | | Inlet (feed) | Effluent | Limits of law |
|-----------------------------------|-----|-----------------|----------|------------------|
| Oil content | PPM | 10 | 4 | 10 MAX. |
| Chemical Oxygen Demand (COD) | PPM | 200 | 90 | 100 MAX. |
| Biological Oxygen Demand (BOD) | PPM | 125 | 50 | 60 MAX. |
| Suspended Solids | PPM | 40 | 20 | 60 MAX. |
| Phenol | PPM | 4 | NIL | 1 MAX. |