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Treatment of Contaminated Collected Wastwater at Petroleum Fuel Filling Stations for Using as Make Up Water for Cooling Tower in Petroleum Refineries

Thabit A. Ahmed*, Saba S. Ayob, Mohammed A. shahatha, Shaymaa R. Khorshead, and Mohammed J. Mohammed

Petroleum Research and Development Center, Ministry of Oil, Baghdad, Iraq.

*Corresponding Author E-mail: thabitabaas@yahoo.com

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Abstract

The collection of washing wastewater (oily water) in petroleum service stations represents an environmental problem particularly after the introducing of cars washing stations to the petroleum station site. The generated water from washing and maintenance of the petroleum stations, rain water is collected in the storage tank. This water contains hydrocarbons and suspended solids with high organic load. Discarding this type of water to the water bodies like rivers without treatment causes increasing of pollution. This study aims to manage generated wastewater in petroleum service stations successfully by using methods keeping the source of water and protect the environment from the pollution. Alsmood and Alnaher petroleum stations which are located at the east of Baghdad were taken as case study. A mixed sample of wastewater from both two stations was prepared. The sample was fully tested to study the expected specifications of water.The mixed samle was underwent to many treatement stages(oil skimming,coagulation-flocculation, sand filteration).The oil concentration of the raw smixed sample was decreased from (5% , 50000mg/L) to 1mg/L . The turbidity value was reduced after filteration from 175 to 1.4 NTU and also the total suspended solids(TSS) was decreased from 272 mg/L to 4 mg/L. The chemical oxygen demand (COD) underwent reduction during wastewater treatment from 730 to 44 mg O2 /L . Badse on the research fndings,the proposed scenario to manage the watstewater is installing a wastewater (oily water) treatment plant with 100m3/day capacity next to Aldura refinery in Baghdad to treat the water for reusing application as a make-up water for the cooling towers.

Keywords: Fuel filling stations; API; DAF; Coagulation; Flocculation; Cooling towers

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1. Introduction:

Fuel filling stations are essential community facility in modern societies, also they are a potential pollutant to the stormwater drain system. The pollutants in fuel filling stations come out in daily basis from different activities, such as mechanical workshop, car washing, refueling and the use of petroleum products, oils, grease, solvents and detergents. These pollutants are transported and discharged into stormwater drains by using clean water. These pollutants result from. [1]

- Leakage of fuel from storage tanks, especially from single-walled underground tanks.
- spillage of fuel, lubricants, engine coolant and hydraulic.
- Disposal of vehicle wash facilities wastewater.
- Inadequate disposal of wastes car parts, batteries, tires and fluids derived from mechanical servicing.

Currently, the available conventional treatment technologies for fuel filling station wastewater comprise a physical, chemical and biological methods, despite that, some soluble organic compounds remain untreated, that cause an increased level of pollutants in the treated water effluent. However, there is no single technology to meet all the requirements due to the variable nature of the wastewater. [2] Various technologies are used for oil and Total Suspended Solids removing from oil contaminated water. For oil removing, corrugted plate interceptor (CPI) separator is oil-water gravity separator, developed by the oil company shell for oily wastewater treatment. CPI oil separator enables gravity separation with high efficiency by using corrugated plates that provide excellent treatment for high flow rates. the simple structure of the CPI reduces the construction cost and simplifies the maintenance process. The mechanism of CPI in removing oil from wastewater depends on gravity, and it does not need energy to operate [3]. Tilted Plate Interceptor (TPI) Separator is a general term used for such type of separators. The separator when used in liquid-liquid separation (mostly free oil removing from water) is called a TPI or CPI separator [4]. A high -effect centrifuge is another process for oil-water separation. The centrifuge is often used for low pressure water streams due to the device is motor driven, and this type of equipment has high energy demand and high maintenance [5]. An American Petroleum Institute (API) Separator is a separation device depends on gravity, designed by finding velocity of oil droplets rising that depends on the density and size of oil droplets. The design of API is based on density difference between oil and wastewater, and because that difference is much smaller than density difference between suspended solids and water, most suspended solids settle in the

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separator basin bottom as sediment layer, and the oil rise to the separator top, the wastewater then will be in the middle layer between the oil and the suspended solids.The oil layer is usually skimmed off and re-processed or disposed of subsequently, and a chain and flight scraper (or equivalent device) and a sludge pump extract the bottom sediment layer. The water layer shall be sent for further treatment consisting, as a general rule, of a Dissolved Air Flotation (DAF) unit for further removal of any residual oil and, subsequently, of a certain type of biological treatment unit for removal of undesirable dissolved chemical compounds. The API technology is highly efficient and low-cost; therefore, it has been chosen for oil removing from contaminated water in this research [6]. Coagulation and Flocculation is the process by which colloidal particles and very fine solid suspensions initially present in a wastewater are combined into larger agglomerates [7]. Dissolved Air Flotation (DAF) is a process in which fine gas bubbles are used to separate small, suspended particles that are difficult to separate by settling or sedimentation. Gas is injected into the water to be treated, and particulates and oil droplets suspended in the water are attached to the air bubbles, and they both rise to the surface. As a result, foam develops on the surface, which is commonly removed by skimming. The dissolved gas can be air, nitrogen, or another type of inert gas. The efficiency of the flotation process depends on the density differences of liquid and contaminants to be removed. It also depends on the oil droplet size and temperature. Minimizing gas bubble size and achieving an even gas bubble distribution are critical to removal efficiency [8].A hydrocyclone separator improved treatment methods have resulted from the continuous demand for higher treatment capacity in very limited space. The benefits of this type of equipment are high reliability (no moving parts), low maintenance, very little space needed, and a better separation effect and high capacity [9].

1.1 The problem statement and suggest proposal treatment of case study.

Most of fuel stations in Iraq have an underground water tank with 1.5 to 2 m3 capacity. This tank is called slope tank. The washing water, gasoline spills, gas oil spills, spent lubricants, and dust are drained to the slope tank. The only management of this type of contaminated water is discarding it outside the station and it may cause some environmental problems for air, soil and ground water.

The philosophy of this scenario depends on installing of a central small-scale plant for treatment of transferred oily water from different fuel stations in Baghdad. The design capacity of the plant is assumed 100 m^3/day.

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The major parts of the plant include:

- Equalization tank (2 x 50 m^3)• API separator
- DAF (Dissolved Air Flotation and clarifier with combined Coagulation Flocculation process).
- Sand filter
- Two storage tanks of treated water (10 m^3)
- One storage tank of sludge (1m^3)

These parts are explained in Figure (1).

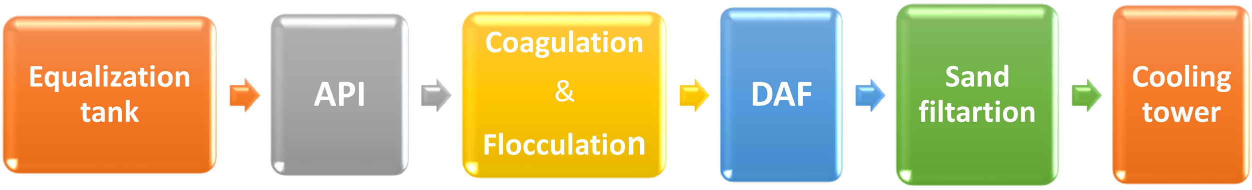

Fig. (1): Process flow diagram (PFD) for Oily Water Treatment

The target parameters of water to be treated are oil and total suspended solids (TSS). Generally, the obtained specifications of treated water led to use it safely in cooling tower.

2. Experimental work

2.1 Treatment of Case study

2.1.1 Characterization of oily wastewater

Two samples of contaminated water at the waste water tanks of fuel stations were sampled, and analyzed after mixing the two samples with 1:1 ratio. The fuel stations that selected for water sampling were Alsmood Station and Alnaher Station located in the east of Baghdad. The laboratory analyzing of the mixed sample showed the specifications explained in Table (1) below:

Table (1): Characterization of oily wastewater

No.	Test	Unit	Result	Standard Method
1	pH	………	7.17	ASTM D-1293
2	TSS	mg/L	272	ASTM D- 5903
3	Turbidity	NTU	175	ASTM D-1889
4	(EC)	µs/cm	1354	ASTM D-1125
5	Color (True)	Pt-Co	69	APHA 9225-C
6	Color (Apparent)	Pt-Co	1036	APHA 9225-C
7	COD	mg/L	730	ASTM D1252
8	M. Alkalinity	mg/L	244	ASTM D 1067

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9	Total Hardness as $CaCO_3$	mg/L	511.5	ASTM D 1126
10	Ca^{+2}	mg/L	139.5	ASTM D 511
11	Mg^{+}	mg/L	39.06	ASTM D 511
12	Cl^{-}	mg/L	153.89	ASTM D 512
13	$SO4^{=}$	mg/L	267.81	ASTM D 516
14	Oil & Grease	mg/L	(After removing supernatant oil (5% v/v)	ASTM D-3921
15	Ni	mg/L	Nil	APHA 3500
16	Pb	mg/L	0.039	APHA 3500-B
17	Mn	mg/L	0.088	APHA 3500-B
18	Fe	mg/L	0.181	APHA 3500-B
19	Zn	mg/L	0.004	APHA 3500-B

2.2 Stages of Treatment

2.2.1 Collecting oily sample wastewater

Two equalization tanks (5 x 4 x 2.5m + 0.5m freeboard) with 50 m^3 volume of each one will receive water from vehicles.

2.2.2 Oil Removing

The removing of oil from the mixed sample was conducted in the lab by using rotary belt as explained in Figure (2).

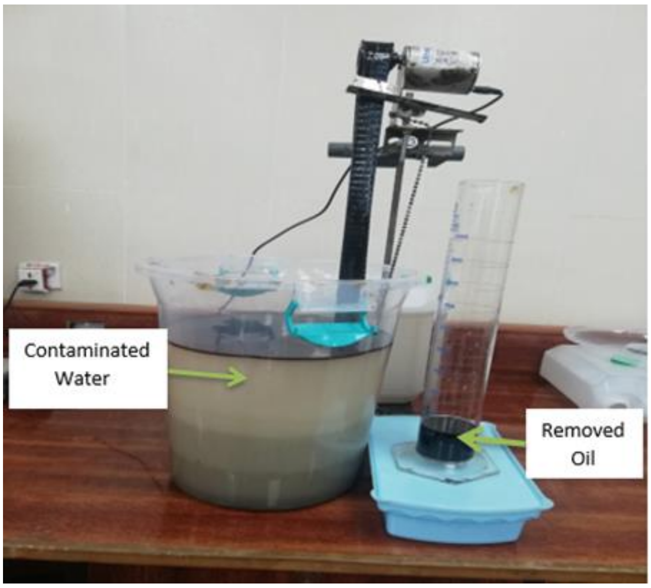

Fig. (2): Lab Simulation of oil removing method

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API technology will be adopted in this study for oil recovery in the proposed oily water treatment plant for using as make up water in Al-Dura refinery cooling tower, and because of the high efficiency and low cost of this technology, it has been chosen for oil removing from the contaminated water.

2.2.3 Total suspended solids Removing by Coagulation and Flocculation process

In this step, the fine particle size of the suspended particles is removed by Coagulation – Flocculation process. A Jar test method was conducted in the lab. It is considered a simulation method of clarification of water used in any full-scale treatment plant. A jar test conditions were, 150 rpm, 1 min for high-speed mixing (coagulation) and 150 rpm,5 min for low speed (flocculation).

Poly aluminum chloride (PAC) was used as a coagulant [10] to destabilize the water colloidal system and a cationic modified polyacryl amide (EBAGROS®A-158C) was used as a flocculant to gather the flocs. The other solutions used for pH adjustment are hydrochloric acid and sodium hydroxide.

Some specifications of the chemicals used in Jar Test as in Table (2) and the results obtained by using Jar Test method for the mixed contaminated water are illustrated in Tables (3, 4, 5 and 6) with different concentrations of PAC:

Table (2): Some specifications of chemicals using in Jar test

Chemical		Specifications
Coagulant	PAC (Chinese commercial production type)	- Al2O3% 30 ± - Water insoluble 1.0 - PH (1% solution) 4-5 - Nitrogen % ≤ 0.05 - As % ≤ 0.0005 - Pb % ≤ 0.0003 - Cd % ≤ 0.0006 - Hg % ≤ 0.00002 - Cr+6 % ≤ 0.0002 - SO4-2% 9.0
Flocculant	EBAGROS®A-158C (Japanese production type)	- modified polyacrylamide - High molecular weight
pH adjustment	Sodium hydroxide (NaOH)	25% concentration
	Hydrochloric acid (HCl)	6N concentration

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Table (3): Coagulant: PAC deferent concentration, Flocculent: modified polyacrylamide, 2mg/L (based on prior studies).

No	PAC concentration mg/l (coagulant)	Flocculent mg/l	Parameter	Result
1	50 mg/l	2 mg/l	PH	7.27
			TSS mg/L	9
			EC µs/cm	1086
			Color (True) Pt-Co	50
			Color (Apparent) Pt-Co	115
			Turbidity NTU	3.02
			COD mg/L	136
2	60 mg/l		PH	7.19
			TSS mg/L	9
			EC µs/cm	1344
			Color (True) Pt-Co	38
			Color (Apparent) Pt-Co	109
			Turbidity NTU	3.76
			COD mg/L	144
			Silica mg/L	9.6 as SiO2
3	70 mg/l		PH	7.28
			TSS mg/L	8
			EC µs/cm	1291
			Color (True) Pt-Co	46
			Color (Apparent) Pt-Co	120
			Turbidity NTU	4.73
			COD mg/L	145
4	80 mg/l		PH	7.21
			TSS mg/L	8
			EC µs/cm	1380
			Color (True) Pt-Co	45
			Color (Apparent) Pt-Co	106
			Turbidity NTU	3.39
			COD mg/L	135

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with the increase of PAC dose from 50-80 mg/L, it was a limited effect on reduction of both COD, and TSS. The results were ranging (80%-81%), (96.7%-97%) respectively for COD, and TSS.

2.2.4 Dissolved Air Flotation (DAF)

DAF can remove particles as small as 25µm. If coagulation is added as pretreatment, DAF can remove contaminants 3–5 µm in size. In one reported study, flotation achieved an oil removal of 93%. Flotation cannot remove soluble oil constituents from water. Because flotation involves dissolving a gas into the water stream, flotation works best at low temperatures. If high temperatures are present, a higher pressure is required to dissolve the gas in the water. Energy is required to pressurize the system to dissolve gas in the feed stream. Coagulant chemical may be added to enhance removal of target contaminants. Chemical coagulant and pumping costs are the major components of operation and maintenance costs for flotation. Solids disposal will be required for the sludge generated from flotation.

When the density differential is not sufficient to separate oil and oil- wetted solids, air flotation may be used to enhance oil removal. In this method, air bubbles are attached to the contamination particles, and thus the apparent density difference between the particles is increased.

DAF is a method of introducing air to a side stream or recycle stream at elevated pressures in order to create a supersaturated stream. When this stream is introduced into the waste stream, the pressure is reduced to the atmospheric, and the air is released as small bubbles. These bubbles attach to contaminants in the waste, decreasing heir effective density and aiding in their separation. The most important operational parameters for contaminant removal by dissolved air flotation are: [11]

- Air pressure.
- Recycle or slip stream flow rate.
- Influent Total Suspended Solids (TSS) including oil and grease.
- Bubbles side.
- Dispersion.

Air pressure, recycle and influent TSS are normally related in an air-to-solids (A/S) ratio expressed as:

A/S = KSa (fp-1) R/SSQ

Where:

K= a constant, approximately 1.3

Sa= the solubility of air at standard conditions, ml/L

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f= Air dissolved /Sa, usually 0.5-0.8

P= operating pressure, atm

R= recycle rate, gpm

SS= influent suspended solids, mg/L

Q= Wastewater flow, gpm

The A/S ratio is most important in determining effluent TSS. Recycle flow and pressure can be varied to maintain an optimal A/S ratio. Typical values are 0.02-0.06.

2.2.5 Proposed Design of DAF Unit in Oily Water Treatment Plant

Dissolved air flotation process is usually combined with coagulation – flocculation process. The basic calculations of proposed combined DAF and coagulation flocculation unit are:

DAF Tank Dimensions

Assuming:

surface loading rate = 2 m/h

recycle ratio = 10 %

Tank length(L) to width(W) ratio = 2:1

Tank depth = 1.2 m

Surface Area of the Tank= (flow rate+ (flowrate*recycle ratio))/ (surface loading rate)

= (100 +(100 *0.10) m^3/d)/ (2 m/h *24 h/d) =2.2916 ≅ 2.3 m^2

Surface area=L*W=2W*W

2.3=2 W^2

W= √ ((2.3)/2) ≅1.07 m

L=2*1.07=2.14 m

The simplified proposed design of DAF to be use in the oil water treatment plant and its facilities are shown in Figure (3):

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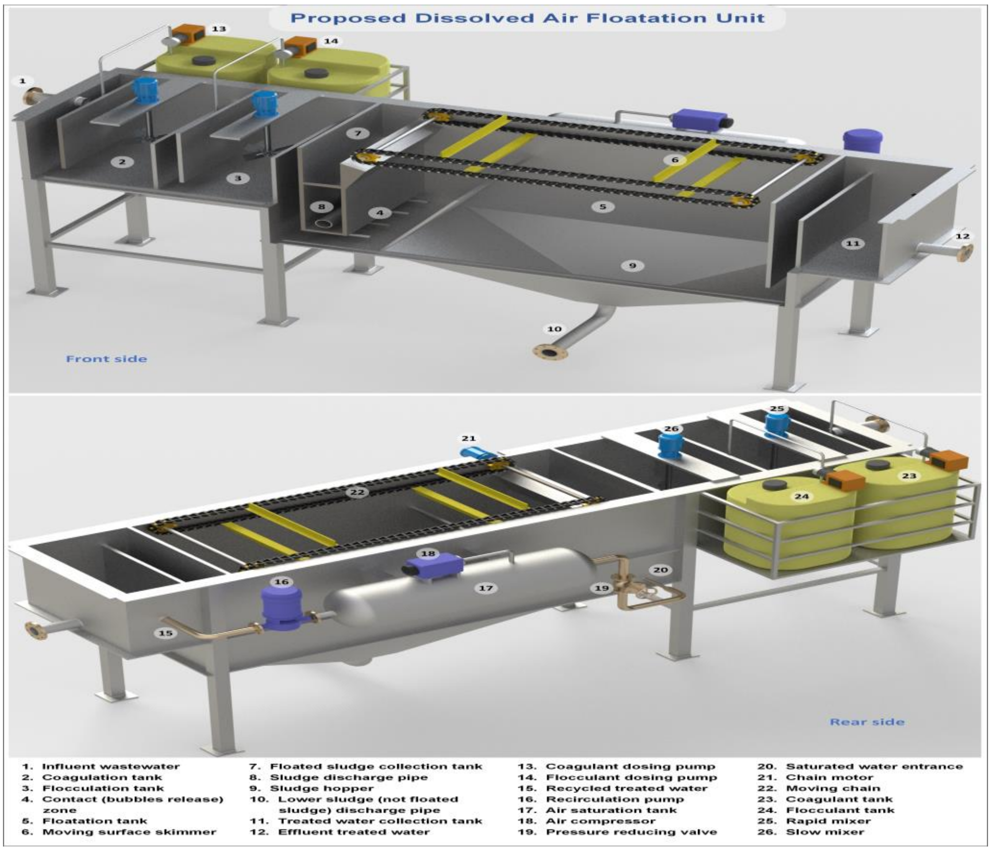

Fig. (3): Proposed DAF unit (designed and drawn by the research team)

2.2.6 Sand Filtration

A lab scale gravity flow vertical filter was designed, it consists of two separated layers (Anthracite, and Sand respectively), as shown in Figure (4). The particle size of the materials is shown in Table (7).

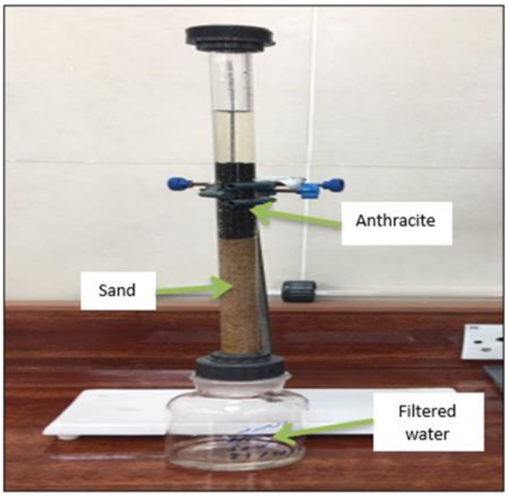

Fig. (4): A photograph of sand filtration in the lab

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Table (4): Particle size of anthracite and sand

	Anthracite	Sand
Particle Size (DV micron)	DV 10:647	DV 10:1120
	DV 50: 983	DV 50: 1770
	DV 90:2670	DV 90: >2670

2.2.7 Determination flow rate of filtration

To determine the flow rate of filtration in the lab, the following data was used:

- Height of filter = 42 cm
- Diameter of filter = 5 cm
- Velocity of filtration = 5m3/hr.m2 (Assumption)
- Surface Area = $\left(\frac{d}{2}\right)^2 * \pi$

$$= \left(\frac{5}{2}\right)^2 * 3.14 = 19.6\ cm^2$$

$$= 0.00196\ m^2$$

- V = Q/As → Q=V*As

  $Q = 5\ m/hr * 0.00196\ m^2 \rightarrow Q = 0.0098\ m^3/hr$

  $\therefore Q = 9.8\ l/hr \cong 10\ l/hr$

2.2.8 Design of sand filter in the lab

Based on water treatment literatures for full scale plant, a sand filter design as follow:

Sand zone depth = 0.5 m

Anthracite zone depth = 0.25 m

Gravel depth = 0.5 m with drain system

Active head of filter = sand head + anthracite head + gravel head with drain

= 0.5 + 0.25 + 0.5 = 1.25 m

Free zone (for backwash) or expanded head = (0.25 – 0.4) of active head

For this study, 0.4 was selected:

Free zone = 0.4 * 1.25 = 0.5 m

Total head of filter = active head + free zone = 1.25 + 0.5 = 1.75 m

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So, to find the height of both sand and anthracite of the lab scale sand filter (as in Figure 5), we used a tube with active head (the real height of media of the sand filter in the lab) of 30 cm (0.3 m), with the value of active head of full-scale filter (1.25m), we can find the factor to convert full scale to lab scale:

Factor= (active head of full scale)/ (active head of lab scale) = 1.25/0.3=4.166667

For anthracite head: 0.25/X=4.166667

X = 0.06 m = 6 cm

For sand head: 0.5/X=4.166667

X = 0.12 m = 12 cm

Gravel head = sand head = 12 cm

free zone = sand head = 12 cm

Figure (5) represents the design calculation of sand filter of proposed full-scale oily water treatment plant, and also the design of sand filter that was used in the lab to treat the water after coagulation – flocculation stage.

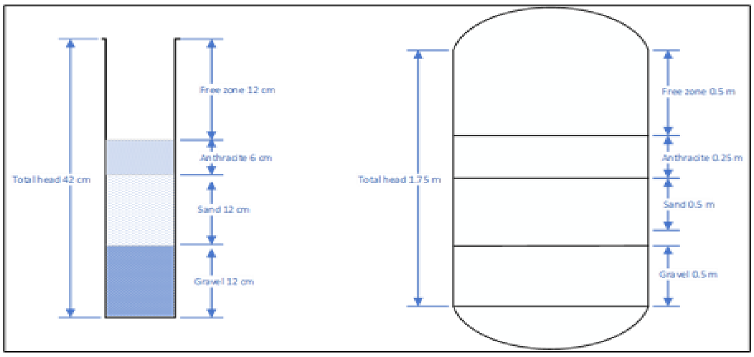

Fig. (5): Design of sand filter (-a- Laboratory and -b- Full Scale Plant)

2.2.9 Results of the sand filtration in the lab

After passing the treated water from clarification process across the designed and assembled sand filter, the laboratory results of tested treated water show good specifications to use the water as a makeup source for cooling tower Table (8). As the quantities of the water that treated by this scenario is relatively low, so the water recommended to be mixed with treated water produced by Reverse Osmoses process in the refinery. In this case the treated water will be diluted and the final specifications of water will meet the required specification of raw water used in cooling towers Table (1). In addition, it can be noticed that the turbidity of coagulation\flocuulation effluent has

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been reduced form 3.4 NTU to 1.4 NTU. However, this reduction is considered to be low, as the highest reduction 98 % has been acheived earlier.

Table (5): Specifications of filtrated water

	Test	Unit	Result	Standard
1	pH	…………..	7.27	ASTM D-1293
2	TSS	mg/L	4	ASTM D- 5903
3	Turbidity	NTU	1.4	ASTM D-1889
4	(EC)	µs/cm	1660	ASTM D-1125
5	Color (True)	Pt-Co	10	APHA 9225-C
6	Color (Apparent)	Pt-Co	41	APHA 9225-C
7	COD	mg/L	44	ASTM D1252
8	M. alkalinity	mg/L	158.6	ASTM D 1067
9	Ca+2	mg/L	24	ASTM D 511
10	Mg+2	mg/L	39.06	ASTM D 511
11	Cl-	mg/L	123	ASTM D 512
12	SO4=	mg/L	580	ASTM D 516
13	Oil & Grease	mg/L	traces	ASTM D-3921
14	Silica	mg/L	< 9.6 as SiO2	Hetropolyblue
15	Ni	mg/L	Nil	APHA 3500
16	Pb	mg/L	0.019	APHA 3500-B
17	Fe	mg/L	Nil	APHA 3500-B
18	Zn	mg/L	Nil	APHA 3500-B
19	Mn	mg/L	Nil	APHA 3500-B

2.2.10 Treated Water Storage Tanks

Two tanks (2 x 10 m^3) for receiving treated water are including in the oily water treatment plant.

2.2.11 Sequences processes of oily water treatment

The simplified stages of treatment are explained in Figure (5), the general expected form of the oily water treatment plant is illustrated in Figure (6).

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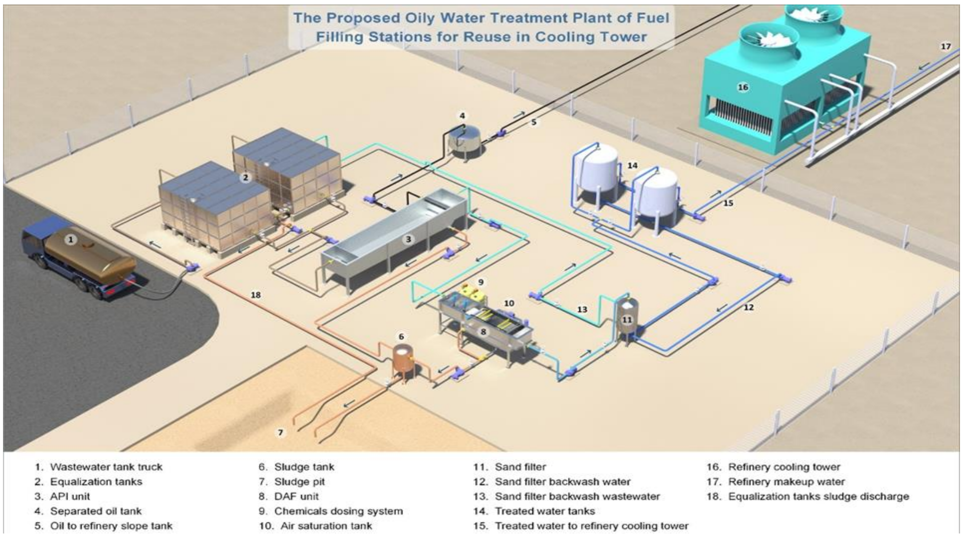

Fig. (6): Oily water treatment plant (designed and drawn by the research team)

3. Conclusions:

The contaminated wastewater from fuel filling stations poses a tremendous damage to the environment, since this water is discarded into the stream of sanitary waste or thrown to the outside of the station. From environmental perspective, this problem was addressed in this research to protect the ecosystem in sustainable way. The philosophy of contaminated water treatment in this research (oil removing, suspended solid reduction and filtration facility) proved good results and the treated water becomes suitable to use in cooling towers of the refinery after mixing it with treated water from the refinery Reverse Osmoses unit. The treatment followed prove a good reduction of oil, turbidity, and COD from 50000 to 1 mg/L ,175 to 1.4 NTU, 272 to 4mg/L and 730 mgO_2 /L respectively. Managing the polluted water depends on cost and environmental management regulations. We recommend adopting the scenario of installing a central water treatment plant beside Aldura petroleum refinery on the edge of Tigris River because this plant will treat the transferred contaminated water from different petroleum filling station spreading in Baghdad to provide another treated water to be used as makeup water for cooling towers in the refinery.

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