

# Water Management in the Petroleum Refining Industry

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## 1. Introduction

Petroleum refining industry uses large volumes of water. The water demand is up to 3 m<sup>3</sup> of water for every ton of petroleum processed (US EPA, 1980, 1982; WB, 1998). Almost 56% of this quantity is used in cooling systems, 16% in boiling systems, 19% in production processes and the rest in auxiliary operations. The water usage in the Mexican refineries is almost 155 millions m<sup>3</sup> per year; it is 2.46 m<sup>3</sup> of water per ton of processed petroleum (PEMEX, 2007). The water supply and distribution for the different uses depend on the oil transformation processes in the refineries, which are based on the type of crude petroleum that each refinery processes and on the generated products. The cooling waters are generally recycled, but the losses by evaporation are high, up to 50% of the amount of the used water. The reduction of the losses and the increase of the cycles of recirculation represent an area of opportunities to diminish the water demand. The requirements with respect to the quality of the water used in the cooling systems are not very strict (Nalco, 1995; US EPA, 1980), which makes possible to use treated wastewater as alternative water source (Sastry & Sundaramoorthy, 1996; Levin & Asano, 2002). The water for the production processes and for services must be of high quality, equivalent to the one of the drinking water. For the boilers and some production processes, the water must be in addition demineralized (Powel, 1988; Nalco, 1995). The Mexican refineries have demineralizing plants which generally use filtration and ion exchange or reverse osmosis systems.

The quantity of the wastewater generated in the refineries is almost 50% of the used fresh water (US EPA, 1982; WB, 1998; EC, 2000). Different collection systems are used in the refineries, depending on the effluent composition and the point of generation. The waters that are been in contact with petroleum and its derivatives contain oil, hydrocarbons, phenols, sulfides, ammonia and large quantities of inorganic salts (US EPA, 1995; Mukherjee et al., 2011). Following the implemented production processes, organic acids, dissolving substances and aromatic compounds may be also present in the wastewater. These effluents are conducted by means of an oily drainage towards the pre-treatment systems for the oil and oily solids separation. The optimization of the production processes, the appropriate control of the operation procedures and the implementation of appropriate water management practices have yield significant reductions of the wastewater flows and of the level of the contaminant loads. Consequently the quality of wastewater discharges can be improved reducing this way their environmental impact and the treatment costs (IPIECA,

2010). One of the first recommendations were with regard to the management of sour water and spent caustics (US EPA, 1982, 1995; WB, 1998; EC, 2000). The sour waters that contain ammoniac, phenol, hydrogen sulphide and cyanides require previous treatment before being mixed with other effluents. Spent caustics that contain sulfides, mercaptans and hydrocarbons must be also collected and treated individually.

The waters that do not have been in contact with petroleum are collected by means of separated drainages (EC, 2000). This is the case of the cooling towers blowdowns that basically contain dissolved or suspended mineral salts, as well as the effluents from filter backwashings and resin regenerations or the inverse osmosis rejections. The concentrates discharges from the resin regeneration and the inverse osmosis rejections require a special management, whereas the cooling towers blowdowns and the effluents from filter backwashings need only a slight treatment and after this they can be successfully reused (US EPA, 1982). The sanitary wastewaters are also treated individually. Surface water runoff is generated in the refineries during the raining periods. Special sewage system is constructed for the recollection and conduction of this water. Theoretically this sewage system does not receive contaminated waters, nevertheless some accidental spills and discharges can be received. That is why retention tanks are constructed for these waters to remove the main pollutions, oil and solids.

The oily wastewater is the most contaminated effluent of the above described. After the pretreatment, the wastewaters must be submitted to biological and advanced treatments for accomplishment of the requirements for discharge in the receiving body (WB, 1998; Eckenfelder, 2000; EC, 2000). The effluent obtained after the advanced treatment is apt for reuse in the cooling system, compensating therefore the losses by evaporation. It may be also used in other processes and services of the refinery. This way, besides reducing the water consumption, the danger of contamination of the receiving bodies can be eliminated. The first pretreatment process of the oily wastewater is the oil-water separation. The conventional rectangular-channel separators, developed by the American Petroleum Institute (API) are widely used for this purpose, and their design criteria are summarized in the publication API, 1990. Many other separators had been developed based on the oil-water separation theory and some of them, as the parallel plate and corrugated plate separators, had been implemented in the petroleum refineries (WEF, 1994). The oil separators remove only the fraction of free oil; the emulsified and the dissolved oil remain in the separator effluent. Therefore, destabilization of oil-water emulsions followed by separation by dissolved air flotation (DAF) is required for the further pretreatment of the oily wastewaters (Eckenfelder, 2000; Galil & Wolf, 2001; Al-Shamrani et al., 2002). Different biological treatment processes have been used for refinery wastewater treatment, such as aerated ponds, activated sludge, biological contactors, sequential bath reactors and moving bed reactors (Galil & Rebhun, 1992; Baron et al., 2000; Lee et al., 2004; Schneider et al., 2011). The first researches that had been done for recycling of the biologically treated refinery effluent involved: activated carbon adsorption alone or in combination with ozonation or sand filtration (Miskovic et al., 1986; Guarino et al., 1988; Farooq & Misbahuddin, 1991). The membrane technology development allowed additional options, such as ultrafiltration and reverse osmosis (Zubarev et al., 1990; Elmaleh & Ghaffor, 1996; Teodosiu et al., 1999; Daxin Wang et al., 2011). The implementation of the advanced treatment technology allowed reusing of the biologically treated wastewater and freshwater savings in the refineries. Baron et al. (2000) reported a case study of water management project for the use of

reclaimed wastewater in one Mexican refinery. Lime softening and filtration were implemented for the advanced treatment of the secondary effluent. The use of seawater as alternative fresh water source was considered in this project. Reverse osmosis (RO) system was installed for the seawater demineralization and the performed evaluation indicated that the RO facility assures the Refinery a reliable water supply resulting in reduction of the freshwater consume.

The objective of the presented here study was to develop appropriate water resource management options for reaching complete wastewater reuse and water use minimization in two Mexican refineries. The technological feasibility of the wastewater reuse was based on evaluation of the current wastewater treatment performance and experimental tests on alternative treatment processes with a view to improve the quality of the reclaimed water and enable its recycling.

## 2. Methodology

The study of the refinery wastewater treatment for reuse began with the characterization of the main effluents. Evaluation of the current wastewater treatment systems were performed based on three samplings performed in different periods of the year. The following parameters were considered: Oil and Grease (O&G), Chemical Oxygen Demand (COD), Soluble Chemical Oxygen Demand (COD<sub>soluble</sub>), Biochemical Oxygen Demand (BOD<sub>5</sub>), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Phenols, Ammonium Nitrogen (NH<sub>4</sub>-N), Total Kjeldahl Nitrogen (TKN), Total Phosphorus (P<sub>total</sub>), S<sup>2-</sup>, Hardness, Alkalinity, pH, Conductivity, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>, Cl<sup>-</sup>. Based on the obtained characterizations, appropriate water handling options were analyzed. Treatability tests were performed for all of the proposed treatment processes to obtain the values of the design parameters. The performance of gravity oil-water separators varies with changes in the characteristics of the oil and wastewater, including flow rate, specific gravity, salinity, temperature, viscosity, and oil-globule seize (API, 1990). That is why tests for natural flotation were performed in situ using acrylic columns with 0.25 m diameter and 2.5 m high. Sampling taps were located at 0.5 m depth intervals. The columns were felt with the tested wastewater and samples were drawn off at selected time intervals up to 120 min. The samples were analyzed for O&G and TSS. Additional samples for COD were obtained for the study in refinery R2. The results were expressed in terms of percent removal at each tap and time interval. These removals were plotted against their respective depth and times and the flotation and settling curves were obtained. Then the data were used to develop the removal-surface loading rate relationships.

The destabilization of oil-water emulsions was studied by means of jar tests in an equipment Philips y Bird PB 700. Different mineral coagulants, polymers and their combinations were evaluated in the effluents from the oil separators. The commercialized products were: Aluminium sulphate (SAS), polyaluminium chloride (PAX-XL19, PAX-260XLS, PAX-16S, PAX-XL60S), ferric chloride (PIX-111), ferric sulphate (PIX-145 and Ferrix-3). The coagulants were tested individually and combined with polymers. The following anionic polymers were used: OPTOFLOC A-1638 and AE-1488 (high molecular weight and high charge density); SUPERFLOC A-100 HMW (high molecular weight and moderate charge density) and PHENOLPOL A-305 (high molecular weight and low charge density). Cationic polymers were: SUPEFLOC C-1288, C-1392, C-1781 and LACKFLOC-C-5100 (high molecular weight and

high charge density); SUPERFLOC C-498 (moderate molecular weight and high charge density); ECOFLOC (high molecular weight and moderate charge density). The test conditions during the study in refinery R1 were: rapid mixing at 120 rpm during 3 min, slow mixing at 30 rpm during 20 min, separation time of 25 min. The tests with the effluents in refinery R2 were performed as follows: rapid mixing at 150 rpm during 3 min, slow mixing at 20 rpm during 15 min, separation during 30 min. The effect of wastewater acidification and alcalinization was first determined using  $H_2SO_4$  and NaOH. Then tests with dose variation were carried out and the best product and dose were selected for each case. The pH effect on the removal efficiency was determined for some of the tested products. The analyzed parameters were O&G, COD and TSS. Turbidity and color were also followed in the refinery R2 study.

Once selected the best chemical reagents, the separation process of the formed flocks and oil with dissolved air flotation (DAF) was evaluated. A bench scale DAF unit consisting of an compressor, a 3 L stainless steel unpacked saturator vessel and a 5 L flotation cell was used. The flotation cell has a variable speed-controlled impeller providing rotational speeds between 100-300 and 20-100 rpm for rapid and slow mixing respectively. The process of dissolved air flotation was studied with previous flocculation. The tested wastewater was introduced to the flotation cell which was first used for the flocculation. The flocculant was added and mixed with the wastewater for 3 min at 150 rpm, followed by slow mixing for 15 min at 20 rpm for flocculation. At the end of the flocculation process the saturator vessel was connected to the flotation cell in order to transfer a controlled amount of previously pressurized treated water. At that moment the flotation was allowed to proceed. When released to the open cell, the dissolved air was transformed into a mass of fine air bubbles, which could attach to the flocs and carry them to the upper liquid surface. After determined retention time, samples of the treated water were collected for analysis. Two experimental runs were carried out with oily wastewater from refinery R1 and one with water from refinery R2. Chemical reagents, recycling ratio (R) and saturation pressure (P) were the variables during the first experimental run. Initial O&G concentration, P and R were the variables during the second run. Factorial experimental designs  $2^3$  were used in the first experimental run, adding central points for P and R. ANOVA was applied for the analysis of the obtained results. Experimental design  $3^3$  with two central points for P and R was used in the second run. The tests performed for refinery R2 used  $3^3$  experimental design and the variables were: P, R and HRT. The output parameters were O&G, COD, TSS, turbidity and color. All analytical procedures were based on the *Standard Methods for Examination of Water and Wastewater*, (2005). The biological and the advanced processes were evaluated based on the reports provided by the real scale facilities. The obtained water qualities of the effluents from the evaluated treatment processes were compared with the required ones for different kinds of reuse. Finally, the feasibility of the proposed water reuse options was determined for each refinery.

### 3. Results and discussion

#### 3.1 Water consumption, wastewater characteristics and evaluation of the current pretreatment systems

Surface water, such as water from river, reservoir and lagoon, are the main water sources for both studied refineries (R1 and R2). The current water consumption and the fresh water distribution for the different uses are presented in Table 1. The wastewater quantities represent 48% of the consumption in both refineries. There are two main oily effluents in each refinery and both refineries have separate treatment of the sour waters

and for the spent caustics. The refinery R1 has three stage oil separators. The discharge with the highest oil content passes through First Stage Separator (S1); the effluent from this separator is mixed with the second oily discharge and the mixture passes through the second (S2) and third stage separators (S3). The characteristics of the main oily effluents (D1 and D2) are presented in Table 2. The high O&G concentration in the oily wastewater indicates the necessity of prevention measures, such as process optimization and control implementation.

Refinery	Fresh water consumption		Water distribution per uses, %			
	Water-flow, L/s	Consumption, m <sup>3</sup> /t processed petroleum	Cooling tower make-up	Boiler make-up and power generation	Production processes	Service water
R1	384	2.10	58.1	19.5	11.9	10.5
R2	467	2.28	59.7	18.8	14.3	7.1

Table 1. Water consumption and uses in the studied refineries

Parameter	Oily discharge D1	Oily discharge D2	Efluent from S1	Efluent from S2	Efluent from S3
Flow, L/s	49±9	50±10	49±7	99±19	99±19
Temperature, °C	37±6	36±5	36±5	35±4	34±4
O&G, mg/L	11,455±5,230	7,880±4,870	2,291±1,350	69±7	27±5
COD, mg/L	8,316±2,980	6,806±1,990	2,245±1,105	1,390±228	448±81
TSS, mg/L	496±78	376±65	233±45	207±22	28±9
TDS, mg/L	964±248	1,390±295	894±196	1,160±220	1,138±206
Sulphates, mg/L	255±38	424±49	243±32	319±39	280±35
Chlorides, mg/L	249±47	119±22	229±34	230±37	228±33
Sulphides, mg/L	37±22	59±34	36±20	37±11	6±5
Fluorides, mg/L	3.5±2.2	4.3±3.2	3.5±2.4	5.3±2.2	2.6±2.1
Phenols, mg/L	0.40±0.44	1.63±0.85	0.37±0.25	0.51±0.32	0.22±0.21
NH <sub>4</sub> -N, mg/L	7.0±6.5	15.3±3.4	6.9±5.1	12.4±5.5	12.3±6.6
TKN, mg/L	12.4±7.9	28.0±9.2	11.2±6.1	20.4±8.5	20.3±7.4
Alkalinity, mg/L	133±38	200±55	132±26	149±44	132±29
Hardness, mg CaCO <sub>3</sub> /L	337±45	532±26	330±34	412±44	347±32
pH	7.20±0.12	7.22±0.11	7.15±0.13	7.33±0.11	7.38±0.10
Conductivity, µS/cm	2,570±387	1,989±266	2,375±306	2,250±278	2,153±255

Table 2. Characteristics of the oily effluents in refinery R1

The evaluation of the oil wastewater pretreatment indicated that the first stage separator provided average removals of 80%, 73% and 53% for O&G, COD and TSS respectively. The second stage separator present higher O&G removal, of 99%, the COD removal was of 69%, however the TSS removal was only 32%. The third stage separator has high hydraulic residence time, of 37 h and this contribute to an additional removal of O&G, COD and TSS of 61%, 68% and 86% respectively. Sulphides and phenols were partially removed in the separators. The rest of the components were not removed, precipitation phenomena were not observed. The oil specific gravity was determined of 0.92-0.95 (17-22°API) which allows the theoretic calculation of 0.07-0.11 cm/s rise rate of the oil globules with 0.15 mm diameter.

The three stage oil separators were well designed, considering all API recommendations (API, 1990); however the second and third stage separators are designed for flows 10 times higher than the real ones. The relatively low O&G removal obtained in the first stage separator is attributed to the deficient equipment for oil and sludge separation. The equipments of the second and third stage separators are also deficient and the obtained removals are attributed to the high retention capacity. Recommendation of better process control actions were made for the reduction of the oil concentrations in the wastewaters.

The refinery R1 has also two additional discharges. One of them (DS) is from a collector for mixture of sanitary discharges, cooling towers blowdowns and effluents from filter backwashings (average flowrate of 50 L/s). This wastewater has low COD and O&G, averages of 120 and 8 mg/L respectively; the TSS and TDS concentrations are 143 and 1,536 mg/L respectively. This effluent is currently discharged to the see without treatment; however TSS removal has to be implemented before its disposal.

The second additional discharge (D3) is from the area for crude petroleum storage and from oil demineralization (average flowrate of 13 L/s). This wastewater contains oil (980±490 mg/L) and high salinity, which is attributed basically to the chlorides (2,332±254 mg/L). The effluent is submitted to a pretreatment in corrugated plate separator and after this is discharged to the see. It has to be mentioned that a lot of organic matter is still present in the effluent after the oil separation, average COD of 783 mg/L and phenols of 0.13 mg/L were determined. Thus, this effluent needs additional treatment before its final disposal.

The refinery R2 has two API separators, one for each oily wastewater discharge. Corrugated plate separators (CPS) are used as a second separation stage. The characteristics of the oily wastewaters and of the effluents from the separators are presented in Table 3. The O&G concentrations were significantly lower compared with the determined in the oily wastewaters generated in the refinery R1. The oil specific gravities were determined of 0.897 (24°API) and 0.951 (16°API) for discharge 1 and 2 respectively. The theoretic rise rates were calculated of 0.17 and 0.07 cm/s respectively, considering 0.15 mm oil globules and the minimal temperatures for each discharge. The fraction of soluble COD was 25-40% of the total COD. The high salinity of the oily discharge 1 is due to effluents from oil desalination processes. The salinity is attributed basically to the chlorides. The values of the BOD<sub>5</sub> were 24-15% of the COD. Ammonia nitrogen represented 52-57% of the TKN in the wastewater.

The performed evaluation indicated that the average O&G removals in both API separators were of 91%. The TSS removals were 87 and 78% in API 1 and API 2 respectively. The COD removals were 49 and 67% respectively. Hardness, TDS and chloride removals (22-36%) were observed in the API separator for discharge 1, which can be attributed to precipitation caused by the high water temperature. The sulphide removals in both API separators can be

Parameter	Oily discharge D1	Oily discharge D2	Effluent from API discharge 1	Effluent from API discharge 2	Effluent from the final CPS
Flow, L/s	116±55	108±72	113±46	107±69	220±109
Temperature, °C	44±7	32±2	41±4	32±1	38±3
O&G, mg/L	624±728	474±464	55±54	40±21	48±40
COD, mg/L	586±212	591±214	311±73	318±56	314±61
CODsoluble, mg/L	217±63	159±48	192±52	141±45	167±46
BOD <sub>5</sub> , mg/L	144±54	146±84	108±26	102±60	105±52
TSS, mg/L	185±65	195±64	24±2	42±24	33±6
TDS, mg/L	1,583±250	828±167	1,076±155	733±109	883±165
Sulphates, mg/L	111±8	253±52	98±14	214±88	164±77
Chlorides, mg/L	782±39	241±86	545±83	222±89	388±85
Sulphides, mg/L	50±37	18±9	40±33	14±5	27±18
Fluorides, mg/L	0.50±0.08	0.36±0.14	0.39±0.14	0.35±0.16	0.37±0.11
Phenols, mg/L	0.95±0.65	1.29±0.82	0.82±0.61	1.21±0.90	1.01±0.72
NH <sub>4</sub> -N, mg/L	28±22	35±32	25±21	33±36	29±23
TKN, mg/L	49±25	67±29	36±24	58±38	46±31
Ptotal, mg/L	0.70±0.17	0.87±0.22	0.63±0.16	0.72±0.13	0.66±0.15
Alkalinity, mg/L	123±21	102±30	105±38	100±25	104±40
Hardness, mg CaCO <sub>3</sub> /L	389±126	224±35	249±38	207±45	225±34
pH	7.13±0.34	7.06±0.15	7.09±0.12	7.05±0.10	7.09±0.11
Conductivity, µS/cm	2,570±419	1,340±436	1,840±151	1,170±240	1,790±110

Table 3. Characteristics of the oily effluents in refinery R2

attributed basically to desorption. The evaluation indicated that the API separators were correctly designed; there was 40% additional capacity for safety reasons. However, the oil recollection and recovery, as well as the sludge extraction were deficient and reengineering project of the pretreatment facilities was developed, based on the wastewater characterizations and on the results of the performed treatability tests. The existing CPS did not provide any O&G, COD and TSS removal. The plate modules, after a complete cleaning, got saturated with oily sludge in few months. The constant cleaning and sludge extraction was too complicated operationally.

The obtained characterizations and the pretreatment performance evaluation indicated that additional treatment is required after the API separators for reaching the appropriate water quality for reuse. The emulsified and dissolved oil remain in the water after the physical separation. Therefore, as it had been indicated in previous publications (Eckenfelder, 2000; Galil & Wolf, 2001; Al-Shamrani et al., 2002), destabilization of the oil-water emulsions and separation by dissolved air flotation, followed by biological and advanced treatment are needed for an effective water reuse implementations.

### 3.2 Water management options

With the proposal to achieve a complete wastewater reuse and increase the fresh water saving in each one of the studied refineries, new water management options were suggested. The option development was based on the current water usage and management data, on the performed wastewater measurements and characterizations, as well as considering the results of the evaluation of the existing treatment systems.

The water management option for refinery R1 considered the treatment for reuse of the two effluents that are currently discharged to the sea. This refinery has already constructed sequential batch reactors, lime softening reactors, rapid sand filters and reverse osmosis system with a capacity of 86 L/s. These facilities require adjustment for the processing of all the pretreated wastewater. Currently only 50 L/s of the pretreated effluent are submitted to the biological treatment. The effluent is mixed with fresh water and then submitted to the advanced treatment. Performance problems in the separators frequently cause reductions of the influent to the biological treatment for avoiding biomass intoxication.

The current and the proposed new water management systems for the refinery R1 are presented on Fig. 1. Currently the refinery reuses only 30% of the generated wastewaters, which allowed 13% reduction of the fresh water consume. The proposed water management system considers complete reuse of the treated wastewater which will provide an increase of the fresh water save to 39%. Recently, a new municipal wastewater treatment facility was constructed next to the refinery with a capacity of 45 L/s. This facility included nitrification-denitrification activated sludge system with the objective to use the treated water in the cooling tower make-up in the refinery. This way 51% fresh water consume reduction will be reached.

The refinery R2 has already constructed nitrification-denitrification activated sludge system, followed by ultrafiltration and inverse osmosis systems. Currently this facility provides treatment to only 40-50% of the generated wastewater because of the high O&G concentrations in the effluent from the pretreatment system. The industrial effluent is mixed with 30 L/s domestic wastewater before to be submitted to the biological treatment. The obtained water use reduction was only 26%.

The current and the proposed new water management systems for the refinery R2 are presented on Fig. 2. The reengineering project for the pretreatment wastewater treatment system will provide a complete wastewater reuse and this way 59% fresh water consume reduction will be reached.

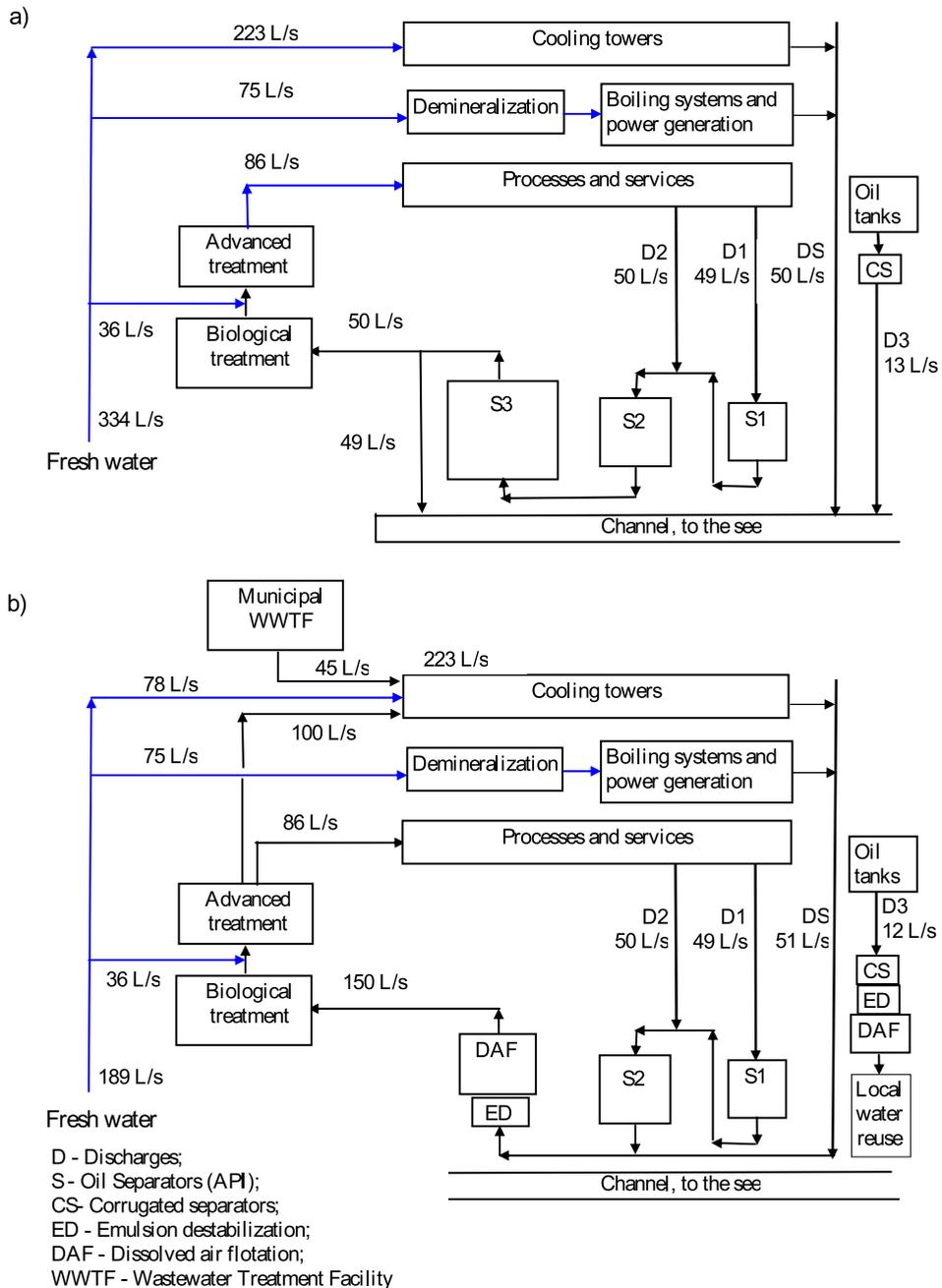


Fig. 1. Water management systems in the refinery R1: *a)* current management; *b)* proposed water management.

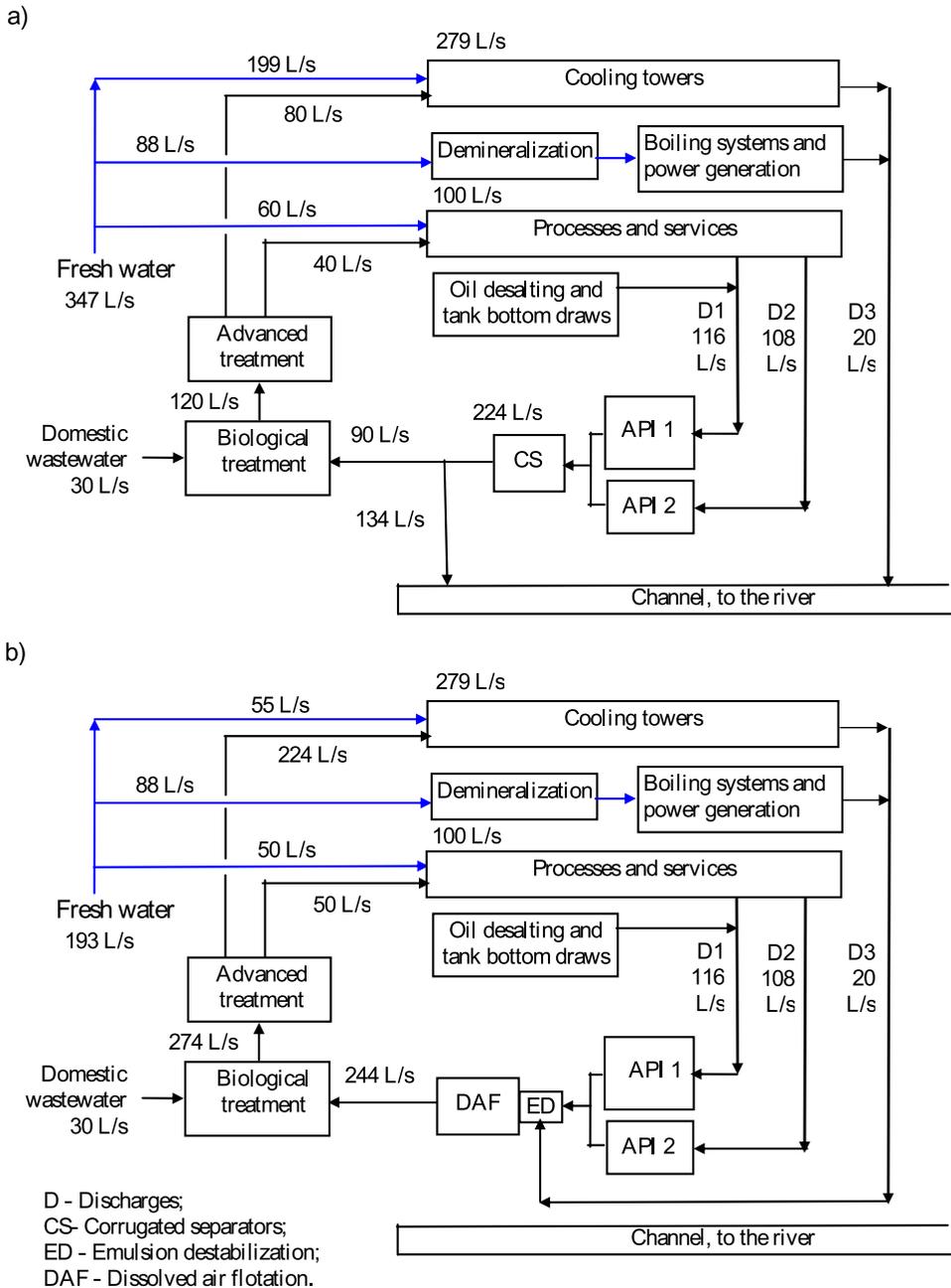


Fig. 2. Water management systems in the refinery R2: a) current management; b) proposed water management.

### 3.3 Results of the treatability tests

Treatability tests for natural oil flotation were performed in both refineries. For refinery R1 water samples for the tests were taken from the oily discharge 1 (influent to the first stage separator) and from the influent to the secondary stage separators which is a mixture of the oily discharge 2 with the effluent from the first stage separator. For refinery R2 water samples were taken from both oily discharges D1 and D2. The obtained removal-surface loading rate relationships for the refinery R1 are presented on Fig.3. As it can be seen, 90% O&G removal was obtained in the first and second stage separators with surface loading rates of 3.43 and 4.60  $\text{m}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  (floatation velocity of 0.10 and 0.13 cm/s) respectively. The simultaneous TSS removal was of 59% and 60% respectively with 30-40 min hydraulic retention time (HRT). Higher O&G removals, of 95% were obtained with surface loading rates of 1.15 and 1.53  $\text{m}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  (0.03 and 0.04 cm/s) respectively. The TSS removal did not increase substantially, 62% were obtained for both kinds of wastewater with HRT of 1.5-2.0 hours.

The results of the tests for natural oil flotation performed in refinery R2 are presented on Fig.4. O&G removals of 90% were obtained in D1 and D2 with surface loading rates of 2.77 and 2.30  $\text{m}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  (floatation velocity of 0.08 and 0.06 cm/s) respectively. The TSS removals were 68% and 59% respectively with 50-60 min HRT. The COD removals were relatively low, 34% and 32% respectively. O&G removals of 95% were obtained with the water of both discharges at surface loading rates of 1.15  $\text{m}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  (0.03 cm/s). The TSS and COD removals increased at this rate when the HRT of 2 h was used. TSS removals were 72% and 63% for D1 and D2 respectively; COD removals reached 39 and 34% respectively. The experimentally obtained floatation velocity was two times lower than the theoretically calculated for D1. Both velocities were similar in the case of D2. The tests indicated also that after the natural flotation the COD values remain in the range 340-460 mg/L, in spite of the low O&G concentrations (47-62 mg/L). The optimal separator depth was also obtained in the tests, it was 0.8-1.3 for the best O&G and COD removal and it could be up to 2.3 m considering as criteria the TSS removal.

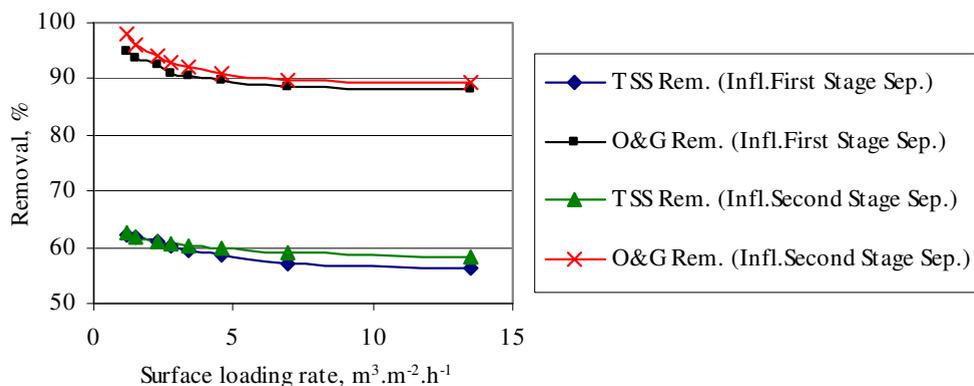


Fig. 3. Results of the treatability tests for natural flotation performed in Refinery R1.

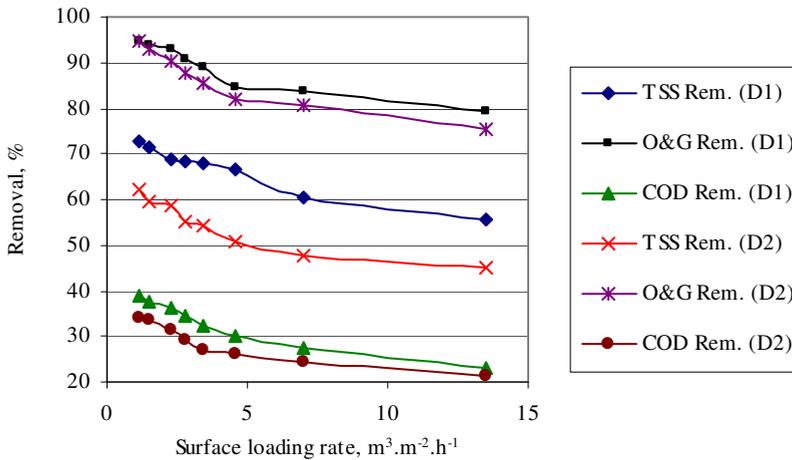


Fig. 4. Results of the treatability tests for natural flotation performed in Refinery R2.

The emulsion destabilization study began with preliminary tests applying only acidification and alcalinization of the wastewater. Fig. 5 shows the effect of the final pH on the O&G and COD removal in effluents from API separators. The average initial pH in the three effluents was  $7.3 \pm 0.1$ . The effluent from the second stage separator of the refinery R2 had O&G and COD of 95 and 1,513 mg/L respectively. The effluents from the API separators of the refinery R2 had lower concentrations. The effluent API-D1 had O&G and COD of 58 and 518 mg/L respectively, the effluent API-D2 had 48 and 487 mg/L respectively. The results showed different compartment in the wastewater from refinery R1 and R2. The removals decreased gradually with the pH increase in the wastewater from refinery R1, which means an increase of the emulsion stability and this can be attributed to the adsorption of hydroxyl ions at the oil-water interface. This indicates that the oil droplets are stabilized mainly by ionic surfactants present in the wastewater. The inverse tendency was observed in the wastewater from refinery R2, the removals increased gradually with the pH increase. Consequently the emulsion stabilization can be attributed basically to non-ionic substances in this case. The results showed also that the pH variation had very low effect of on the removals in the range pH of 6-8. That is why the test with the different coagulants and flocculants were performed at the natural pH of the wastewater. As it can be observed on Fig.5 a drastic increase of the COD removal was obtained at pH of 12. This can be attributed to the intense precipitation of Ca and Mg compounds which contribute to the emulsion destabilization. This phenomenon had a very strong effect in the effluent API-D1 which had the highest hardness and salinity.

The emulsion destabilization was obtained satisfactorily using combinations of mineral coagulant and polymers, as well as applying only cationic polymer of high molecular weight. The obtained results when using different mineral coagulants for the emulsion destabilization in the effluent API-D1 are illustrated on Fig.6. It can be observed that the polyaluminium chlorides had better behavior compared with the conventional coagulants. COD removals higher than 65% were reached with doses 30% lower than the required for the conventional coagulants. The best results were obtained with PAX-16S. Both aluminium and ferric sulphates proved to be effective destabilizing agents. The pH optimization tests

indicated that the optimum pH for Al and Fe coagulants was 7.8 and 7.1 respectively. This is expected because the maximum neutralization of the oil droplets surface charge by hydrolyzed aluminium and ferric cations occurs in the pH range of 7-8 (Al-Shamrani et al., 2002). Similar optimal doses for each chemical product were obtained in the three studied effluents.

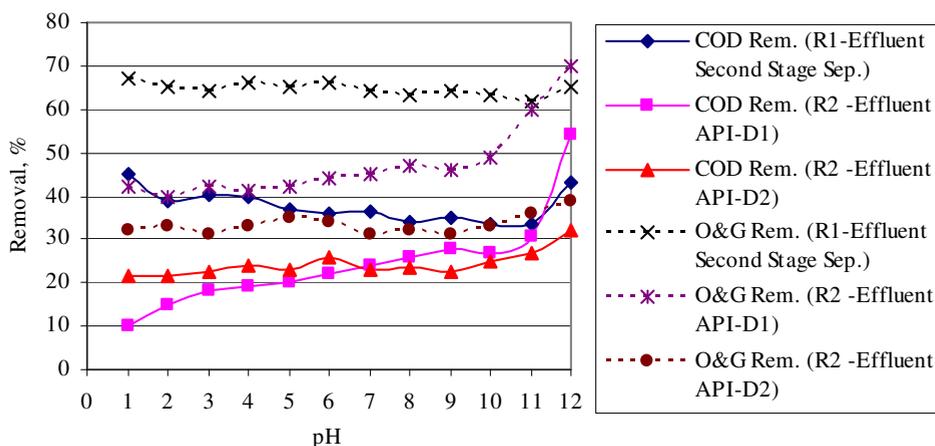


Fig. 5. Removals of O&G and COD before flocculation as a function of pH.

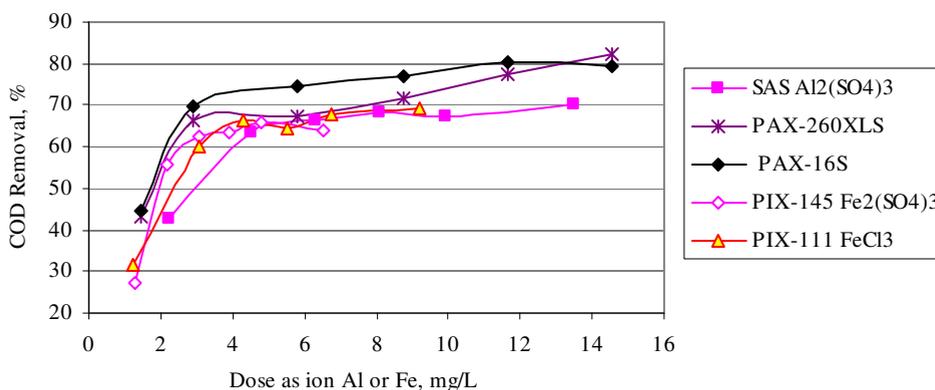


Fig. 6. Removals of COD using mineral coagulants (oily water with O&G, COD and TSS of 63-96, 503-566 and 65-74 mg/L respectively)

The removals obtained with the application of the different coagulants are summarized in Table 4. The results show that the addition of highly charged cations in the form of aluminium and ferric salts effectively induced the destabilization of the oil-water emulsions, leading to the significant oil separation (O&G and COD removal efficiencies of 61-79% and 61-70% respectively). TSS, turbidity and color were also successfully removed obtaining 69-85%, 92-97% and 87-89% efficiencies respectively. These results were expected, as the oil

droplets have negative values of zeta potential (Nalco, 1995; Al-Shamrani et al., 2002). However, the flocs formed in the coagulation process were small in size and their settling was very slow. Therefore combinations of mineral coagulants with different polymers were tested. In these tests the coagulants were added at doses equal to 70% of the optimal doses indicated in Table 4. The results obtained in the effluent API-D1 are presented on Fig.7 and Fig.8. Both kinds of polymers, cationic and anionic ones, improved the COD removal. Lower COD concentrations were reached with the cationic polymers compared with the obtained with the anionic ones. The COD removals were calculated in the ranges of 78-93% and 66-81% for the cationic and for the anionic polymers respectively. The O&G removals were of 94-97% and 89-92% for the cationic and for anionic polymers respectively. The TSS removal was also better, efficiencies of 89-92% and 86-89% were obtained for the cationic and for anionic polymers respectively. Since the oil droplets are negatively charged, the better performance of the cationic polymers can be attributed to the increase of the cationic charge added to the oily wastewater, which enhances the reduction of the zeta potential and improves this way the destabilization of the oil-water emulsion. The anionic polymers combined with the mineral coagulants had only flocculating effect. The flocks formed in these tests were much greater and heavier than the obtained when only coagulants were used. The sludge quantities were of 40-60 ml/L.

The best coagulant-flocculant combinations and their optimal doses are summarized in Table 5. The O&G and COD removal efficiencies of 93-96% and 89-95% respectively were reached, which is almost 24% higher than the obtained using only coagulants. TSS, turbidity and color removal efficiencies were 81-90%, 99% and 94-97% respectively, that is 5-8% higher than the efficiency using only coagulant. The obtained in the performed tests removal efficiencies are higher than the reported by Galil & Wolf, 2001 and the determined optimal doses are lower than the reported in Galil & Rebhun, 1992.

Coagulant	Optimal doses, mg/L	Removal efficiencies, %								
		R1-Effluent Second Stage Separator			R2-Effluent API-D1			R2-Effluent API-D2		
		O&G	COD	TSS	O&G	COD	TSS	O&G	COD	TSS
Aluminium sulphate (SAS)	50	62	67	83	62	63	69	61	62	76
PAX-XL60S	45	64	67	84	-	-	-	-	-	-
PAX-260XLS	30	-	-	-	64	66	80	66	67	78
PAX-16S	30	65	68	85	66	70	86	67	68	77
PAX-XL19	40	63	65	80						
Ferric chloride (PIX-111)	15	-	-	-	75	66	85	78	65	77
Ferric sulphate (PIX-145)	20	-	-	-	77	62	85	79	64	79
Ferric sulphate (Ferrix-3)	20	65	68	82	-	-	-	-	-	-

Table 4. Removals of O&G, COD and TSS obtained using only coagulants in the different API effluents (the doses are expressed in mg/L of chemical product)

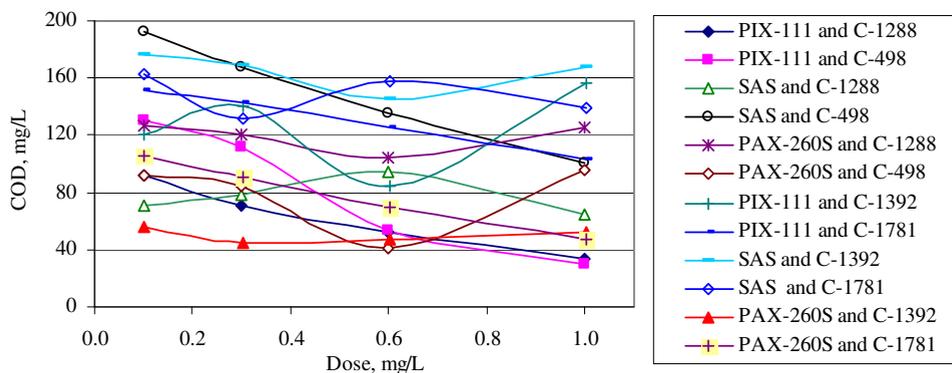


Fig. 7. Removals of COD using mineral coagulants and cationic polymers (oily water with O&G, COD and TSS of 96-120, 592-733 and 60-78 mg/L respectively)

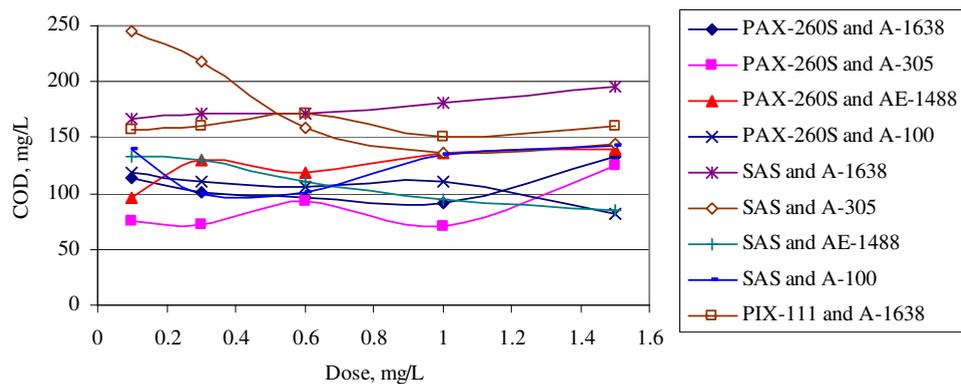


Fig. 8. Removals of COD using mineral coagulants and anionic polymers (oily water with O&G, COD and TSS of 96-110, 404-490 and 62-75 mg/L respectively)

Coagulant	Optimal doses, mg/L	Flocculant	Optimal doses, mg/L	Removal efficiencies, %								
				R1-Effluent Second Stage Separator			R2-Effluent API-D1			R2-Effluent API-D2		
				O&G	COD	TSS	O&G	COD	TSS	O&G	COD	TSS
SAS	45	ECOFLOC	0.4	96	93	87	-	-	-	-	-	-
PAX-260XLS	40	C-1288	0.6	95	91	88	-	-	-	-	-	-
PAX-260XLS	31	C-1392	0.3	-	-	-	96	94	85	93	92	84
SAS	35	C-1288	0.3	-	-	-	95	90	83	94	89	83
PIX-111	11	C-1288	1.0	-	-	-	93	95	81	93	93	83
PIX-145	14	C-498	1.1	-	-	-	96	95	90	94	93	88

Table 5. Removals of O&G, COD and TSS obtained using coagulants and flocculants in the different API effluents (the doses are expressed in mg/L of chemical product)

The results of the tests adding only cationic polymers for the emulsion destabilization and flocculation are presented on Fig.9. All studied polymers provided good COD, O&G and TSS removals, very similar to the obtained with coagulant and flocculant addition. The obtained COD, O&G and TSS removal efficiencies were of 81-94%, 83-96% and 78-95% respectively. The sludge generation adding cationic polymers was 20-30 ml/L, almost 50% lower than the obtained in the tests with the combinations of coagulant and polymers. The tests with pH variation indicated that the optimum pH was different for each polymer, the optimal pH values were in the range 6.9-8.5. The optimum pH were different for the three studied effluents. The removals obtained with the application of the different coagulants and the optimum pH values are summarized in Table 6. The flocculants ECOFLOC and C-1288 had the best performance for the oily effluent from the second stage separators of refinery R1 and C-5100 and C-1288 for both effluents of the refinery R2.

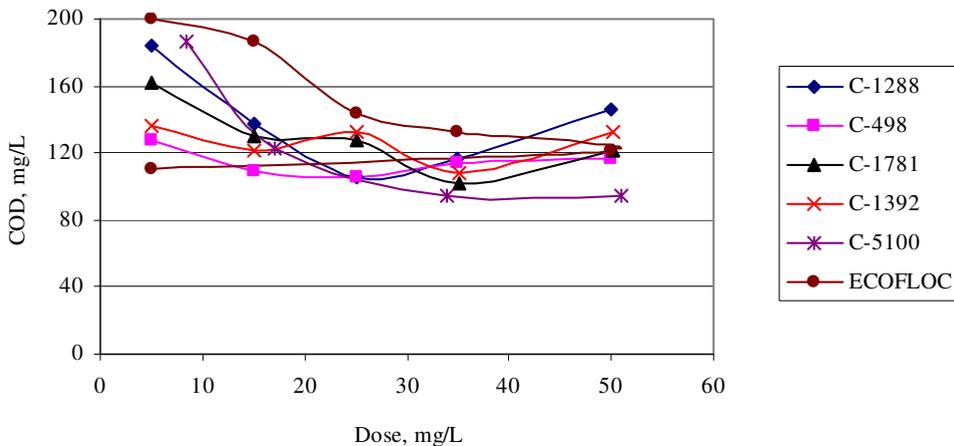


Fig. 9. Removals of COD using cationic polymers (oily water with O&G, COD and TSS of 142-164, 500-651 and 84-95 mg/L respectively)

Cationic polymers	Optimal doses, mg/L	Optimal pH	Removal efficiencies, %								
			R1-Effluent Second Stage Separator			R2-Effluent API-D1			R2-Effluent API-D2		
			O&G	COD	TSS	O&G	COD	TSS	O&G	COD	TSS
C-1288	30	7.4	94	85	94	-	-	-	-	-	-
C-1288	25	7.0	-	-	-	96	84	82	93	83	83
C-498	40	7.4	91	83	91	-	-	-	-	-	-
C-498	25	7.2	-	-	-	93	84	88	92	82	87
C-1781	35	7.2	92	85	93	-	-	-	-	-	-
C-1781	35	7.2	-	-	-	92	83	95	90	80	91
C-1392	40	7.2	92	83	90	-	-	-	-	-	-
C-1392	35	7.0	-	-	-	91	83	88	89	81	90
C-5100	34	7.6	-	-	-	95	94	91	92	90	92
ECOFLOC	30	7.4	95	86	95	-	-	-	-	-	-
ECOFLOC	50	7.2	-	-	-	83	81	78	82	82	80

Table 6. Removals of O&G, COD and TSS obtained using only coagulants in the different API effluents (the doses are expressed in mg/L of chemical product)

The combination of processes flocculation and dissolved air flotation was first performed in refinery R1. The used oily wastewater had O&G, COD and TSS concentrations of 286 mg/L, 1,390 mg/L and 207 mg/L respectively. The saturation pressure (P) was varied from 40 to 70 lb/in<sup>2</sup>, the recycling ratio (R) from 0.1 to 0.4. Both cationic polymers ECOFLOC and C-1288 were used in the tests. The results of the first experimental run indicated that the most important factor for the O&G, COD and TSS removal is the selection of the polymer, followed by the recycling ratio and finally the saturation pressure. ECOFLOC showed better performance than C-1288 in these tests. The effect of P and R variation on O&G concentration in the treated water using ECOFLOC is illustrated on Fig.10 (a). It can be observed that R values higher than 0.2 caused an increase of O&G concentration in the effluent. The increase of the O&G concentration was higher when high P values are applied. The values of the COD were between 111 and 309 mg/L. The determined O&C, COD and TSS removal efficiencies were of 74-99%, 78-92% and 73-89% considering all of the obtained results in this experimental run.

As the P reduction provided lower O&G concentrations in the effluent, the second experimental run considered P variation in lower range 35-55 lb/in<sup>2</sup> and R variation between 0.05 and 0.20. The initial O&G, COD and TSS concentrations varied in the ranges of 175-480 mg/L, 1,050-1,500 mg/L and 268-292 mg/L respectively. The effect of P and R variation on the O&G concentration in the treated water is illustrated on Fig.10 (b). The treated water O&G, COD and TSS concentrations were of 2-113 mg/L, 121-950 mg/L and 21-89 mg/L respectively considering all of the obtained results in this experimental run. ANOVA indicated that the most important factor for the O&G, COD and TSS removal was the recycling ratio, followed by a combined effect of R and the initial concentration. With minimum air/solid ratio of 0.10 a surface charge of 0.94-2.30 m<sup>3</sup>.m<sup>-2</sup>.h<sup>-1</sup> was obtained in the flotation cell. According to the obtained optimization model O&G, COD and TSS removals more than 97%, 89% and 91% respectively can be obtained using low pressures in the saturation tank, of 37-40 lb/in<sup>2</sup>, with 0.07-0.09 recycling ratio.

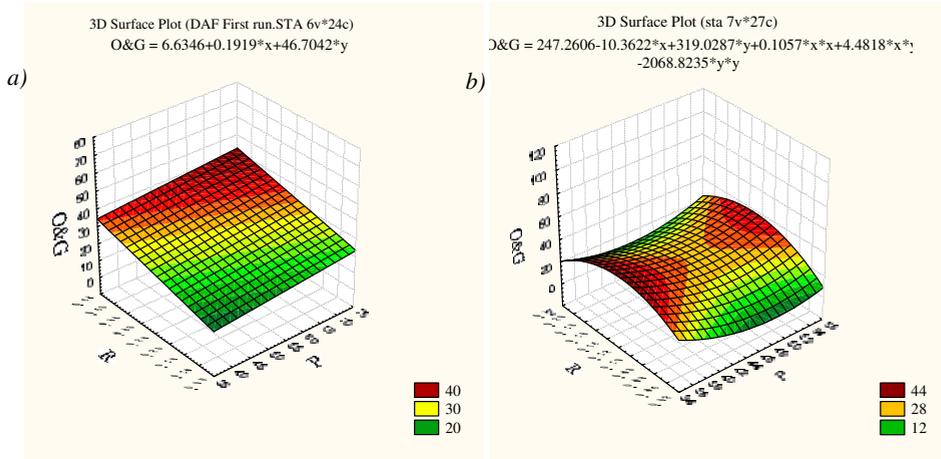


Fig. 10. Effect of P and R variation on O&G concentration in the treated water: a) first experimental run; b) Second experimental run (refinery R1)

The third run flocculation-flotation tests were performed using the cationic polymer C-5100 and wastewater from the API effluent D1. The initial O&G, COD and TSS were 54, 414 and 120 mg/L respectively, much lower than the values in the previous tests. Color and Turbidity were 2,630 PtCo and 379 NTU. The P, R and HRT were varied in the ranges of 14-28 lb/in<sup>2</sup>, 0.1-0.30 and 15-25 min. The effect of the HRT and R on the O&G concentration in the treated water using C-5100 is shown on Fig.11. The R had more significant effect on the removal of all the parameters compared with the one of the HRT. The best operational conditions were: P of 21 lb/in<sup>2</sup>, HRT of 25 min and recycling ratio of 0.2. The obtained removal efficiencies for O&G, COD and TSS were 50-85%, 47-61% and 56% respectively. The Turbidity and Color removals were determined of 83-85% and 85-92% respectively.

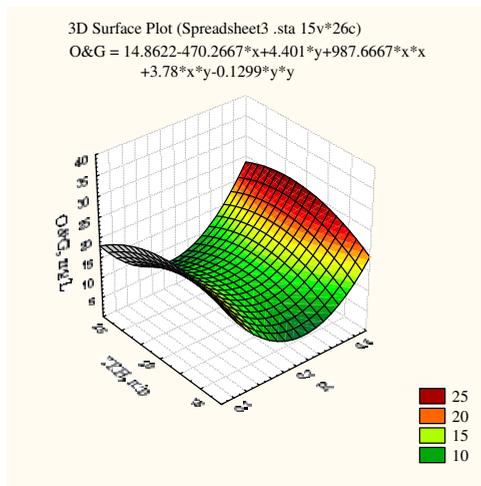


Fig. 11. Effect of HRT and R variation on O&G concentration in the treated water (R2)

The flocculation-floatation tests indicated that concentrations of O&G and TSS lower than 50 mg/L can be obtained in the treated oily wastewater. The O&G and TSS removal efficiencies were in agreement with the reported in Eckenfelder (2000) and Galil & Wolf, (2001), while the obtained COD removals were better than the reported in the literature. However, in spite of the obtained good COD removal efficiencies, the remaining values of the COD in the treated water were still high, in the range of 160-800 mg/L depending of the COD in the API effluents. These COD quantity, attributed basically to soluble organic matter, needs to be removed before the application of advanced treatment processes.

### **3.4 Evaluation of the biological and advanced treatment and analysis of the reclaimed water reuse feasibility**

Different biological treatment processes have been used for refinery wastewater treatment, and the biological treatment systems allow good organic matter degradation; however, inhibition problems may occur because of the presence of many recalcitrant and toxic hydrocarbons, as for example the phenols. Biological treatment systems were already implemented in the studied refineries. For protection of the process performance, they have established maximum permissible limits (MPL) for some parameters which have to be accomplished in the influents to the biological reactors. The phosphate concentration in the refinery wastewater is generally low, so phosphoric acid is frequently used to support the biomass growth. As it could be seen in the previous Tables 1 and 2, ammonia nitrogen concentrations are relatively high in the wastewater and their removal is frequently an additional object of the biological treatment. The refinery R1 has implemented sequential batch reactors (SBR) and refinery R2 a nitrification-denitrification activated sludge (AS) system. The refinery R1 has established the following MPL: 70 mg/L for O&G, 470 mg/L for COD, 30 mg/L for TSS, 6 mg/L for phenols, 560 mg/L for chlorides, 30 mg/L for sulfides and 6-9 units for pH. The MPL in refinery R2 are: 48 mg/L for O&G, 400 mg/L for COD, 5 mg/L for phenols, 560 mg/L for TDS, 8.5 units for pH and 35°C for temperature. The existing oily wastewater pretreatment facilities in the studied refineries normally accomplish these requirements due to their high retention capacity. However, the frequent operational problems made impossible the introduction of all the wastewater to the biological treatment systems. The reengineering project, considers design, construction and installation of new API separators and flocculation-DAF systems in both refineries. The obtained results of the treatability tests indicated that the suggested pretreatment systems provide the accomplishment of the established MPL for biological treatment. The averages of the physical-chemical parameters, obtained using one year operational data of the current biological systems are presented in Table 7. It has to be mentioned that the nitrification-denitrification AS reactor receive almost 30 L/s domestic wastewater which is treated in conjunction with the refinery effluent, while the SBR receive only pretreated refinery effluent. COD and NH<sub>4</sub>-N removal efficiencies of 65% and 96% respectively were obtained in both biological treatment systems. As it can be expected nitrification-denitrification AS provided higher TKN removal compared with the SBR, 86% and 68% respectively. The O&G and phenol removals were also higher in the AS system. The average O&G removal efficiencies were 94% and 86% in AS and SBR respectively, and the phenol removals were 82% and 70% respectively. Sulphide removal efficiencies were of 95-96%.

Parameter	SBR in refinery R1		Nitrification-denitrification AS in refinery R2		Quality for cooling water make up
	Influent	Effluent	Influent	Effluent	
O&G, mg/L	50.1±8.4	7.2±3.4	48.6±10.3	3.2±1.8	-
COD, mg/L	453±74	157±42	388±82.5	137±35	75
TSS, mg/L	39.3±9.2	54.1±15.3	44.4±12.1	57.6±19	100
NH <sub>4</sub> -N, mg/L	12.5±5.4	0.5±0.3	28.7±10.5	1.0±0.9	1
TKN, mg/L	20.3±3.4	6.4±2.5	45.2±5.3	6.2±2.4	-
Ptotal, mg/L	1.0±0.1	0.9±0.1	0.7±0.1	0.5±0.1	1
Phenols, mg/L	0.2±0.05	0.06±0.02	1.1±0.8	0.2±0.1	-
Sulphides, mg/L	11.3±7.1	0.5±0.3	27.0±10.3	1.3±0.8	-
Hardness, mg CaCO <sub>3</sub> /L	397±52	385±44	253±44	238±24	650
Alkalinity, mg CaCO <sub>3</sub> /L	125±12	105±33	103±27	84±15	350

Table 7. Performance of the biological treatment systems in the studied refineries

One of the reuse options in the refineries is in the cooling tower make-up. The most frequent water quality problems in cooling water systems are scaling, corrosion, biological growth, foaming, as well as fouling in the heat exchangers and condensers. To avoid these potential problems the reclaimed water used in cooling systems must not supply nutrients (nitrogen and phosphorus) or organics that promote the growth of biofilms. The cooling water must not lead to the formation of scale (calcium and magnesium precipitation). Mexican refineries use recirculating cooling systems and the quality of the water input is of big concern. The comparison of the water characteristics of the secondary effluents (Table 8) with the quality requirements for cooling water make-up (US EPA, 1980) indicated that the concentrations of TSS, NH<sub>4</sub>-N, P, Hardness and Alkalinity were lower than the suggested ones. The effluent COD was higher than the suggested value, however the organic matter present in the secondary effluent is constituted basically of compounds difficult for biodegradation. This organic matter could difficultly improve the biofilm growth. Therefore the secondary effluent could be used in the cooling system. Generally, all water reuse for cooling water make-up uses a lime clarification process prior to reuse (US EPA, 1989). This process can reduce hardness, phosphates, silicates and colloidal organics. Filtration is frequently recommended after the liming process.

Advanced treatment facilities were already implemented in the studied refineries. The refinery R1 has lime softening (LS) reactors; pressure sand filters (F) and reverse osmosis (RO) system. Lime, soda ash and flocculant are used in the liming process. The effluent is acidified and then passed through the filters. Then the filtered effluent is submitted to a chlorine disinfection and send to a storage tank for its reuse in the cooling system of the refinery. Part of this water (86 L/s) is directed to the reverse osmosis system and the desalted water is supplied for use in different oil refining processes. The characteristics of the effluents from the advanced treatment processes are presented in Table 8. As it can be seen the liming process followed by filtration enhanced the water quality of the secondary effluent. This treatment allowed Hardness removal of 80%, TSS removal of 74%, Si removal of 71% and a complete P, O&G, S<sup>2-</sup> and phenol removals. Additionally, COD removal

efficiency of 48% was obtained and this way COD was reduced to 86 mg/L after liming and filtration. The obtained water quality is perfectly proper for their reuse in the cooling system. The reverse osmosis system provided 93% TDS removal and 82% hardness removal. COD was reduced to 31 mg/L and the rest of the characteristic pollutants were not detected in the effluent. The obtained water quality allows the use of the RO effluent in most of the production processes.

	Advanced treatment in R1				Advanced treatment in R2		
	Influent	LS	F	RO	Influent	UF	RO
O&G, mg/L	7.2±3.4	2.1±0.2	ND	ND	3.2±1.8	ND	ND
COD, mg/L	157±42	97±33	86±31	31±7	137±35	92±32	28±5
TSS, mg/L	54±15	45±8	14±6	ND	57±19	2±1	ND
NH <sub>4</sub> -N, mg/L	0.5±0.3	0.4±0.1	0.4±0.1	ND	1.0±0.9	1.0±0.2	ND
TKN, mg/L	6.4±2.5	5.3±1.8	5.1±1.1	ND	6.2±2.4	1.0±0.3	ND
Ptotal, mg/L	0.9±0.1	ND	ND	ND	0.5±0.1	0.3±0.1	ND
Phenols, mg/L	0.06±0.02	ND	ND	ND	0.2±0.1	0.1±0.1	ND
Sulphides, mg/L	0.5±0.3	ND	ND	ND	1.3±0.8	0.2±0.1	ND
TDS, mg/L	779±56	683±61	668±49	46±15	876±38	780±40	54±11
Hardness, mg CaCO <sub>3</sub> /L	385±44	75±23	67±22	12±3	238±24	221±19	39±7
Alkalinity, mg CaCO <sub>3</sub> /L	105±33	86±27	83±22	23±4	84±15	83±14	23±5
Si, mg/L	21±3	6±5	6±5	ND	24±4	23±4	14±2

ND-Not detected

Table 8. Performance of the advanced treatment systems in the studied refineries

The refinery R2 has ultrafiltration and inverse osmosis systems. The effluent from the nitrification-denitrification AS system is disinfected and then submitted to ultrafiltration. Most of the obtained effluent is directed to the cooling system of the refinery. Part of the filtered water ( 50 L/s) is submitted to reverse osmosis desalting and after that reused in the refining processes. The water characteristics after each treatment process are presented in Table 8. The ultrafiltration removed basically the TSS and O&G, as well as reduced the COD values and the concentrations of the rest of the water quality parameters. The effluent of the UF can be used in the cooling systems. The reverse osmosis allowed the same removals of TDS, hardness and COD as the one in the refinery R1 and the obtained water can be used in the production processes.

The performed analysis demonstrates that both refineries have the capacity to obtain two water qualities reclaimed water for reuse. The reengineering of the existing pretreatment systems will ensure the obtaining of water with proper quality to be submitted to the existing already biological and advanced treatment. This way all the wastewater could be treated and that will make feasible the implementation of the proposed new water management options in both refineries.

#### 4. Conclusions

Petroleum refining industry has a high potential for implementation of water conservation strategies. After a suitable treatment, the totality of the petroleum refining wastewaters can be reused, obtaining therefore the protection of the receiving water bodies and reducing the fresh water demand. The performed study of the water management systems in two refineries allowed the development of alternatives which could provide fresh water savings of 51-59%. It is possible to obtain high quality treated water not only for reuse in the cooling towers but also for the production processes and auxiliary services. The pretreatment of the oily wastewaters using primary oil gravitational separators and chemically enhanced separation processes allows a successful implementation of biological treatment, followed by advanced processes. The use of reclaimed municipal wastewater in the cooling towers make-up allows further fresh water saving opportunity. The waste management has to consider separate treatment of sour waters and for the spent caustics, as well as a pretreatment of all effluents whose main pollutants are oil, solids and sulfides. Cleaner production actions have to be implemented for the reduction of the pollutants in the wastewater.

The preliminary separation of the free oil by natural flotation allows 90-95% O&G removal efficiency with surface loading rates of 1.15-4.60 m<sup>3</sup>.m<sup>-2</sup>.h<sup>-1</sup>. As the floatation velocity of the oil droplets depend of the oil characteristics which are different for each refinery, the performance of experimental tests are highly recommended for the obtaining of reliable design parameters. The TSS and COD removals obtained in the performed treatability tests were of 62-72% and 34-39%. The increase of the hydraulic retention time in the range 0.5-2.0 h improves the TSS and COD removal in the separators. The effluents from the separators had low O&G concentration (47-62 mg/L), however the remained COD was higher than 340 mg/L. The further O&G and COD removal requires emulsion destabilization followed by separation process. The emulsion destabilization can be reached using combinations of mineral coagulants and polymers, as well as applying only cationic polymers of high molecular weight and high charge density. The addition of highly charged cations in the form of aluminium and ferric salts effectively induced the destabilization of the oil-water emulsions. Similar behavior was obtaining with Fe and Al salts. Polyaluminium chlorides had better behavior compared with the conventional coagulants. COD removals higher than 65% were reached with doses 30% lower than the required for the conventional coagulants. The combinations of mineral coagulants with cationic polymers provided O&G and COD removal efficiencies of 93-96% and 89-95% respectively, which is almost 24% higher than the obtained using only coagulants. Similar results were obtained applying only cationic polymers and the generated sludge was almost 50% lower than the generated with the combinations of coagulant y polymers. The characteristics of the oil-water emulsion may be different in each refinery. Therefore, the selection of the best chemical product for the emulsion destabilization, as well the determination of the optimal doses and pH, are crucial for the process success. The combination of flocculation and dissolved air flotation provides good O&G, COD and TSS removal efficiencies. Concentrations O&G and TSS lower than 50 mg/L can be obtained in the effluent. The COD removals vary in the range 47-92%. The experimental tests demonstrated that the most important factor for the O&G, COD and TSS removal is the selection of the polymer, followed by the recycling ratio. The effect of the saturation pressure, the hydraulic retention time were lower. The best results were obtained with relatively low pressures of 21-40 lb/in<sup>2</sup> and recycling ratio of 0.1-0.2. In spite of the obtained high COD removals, the remaining values in the treated water are still high. These

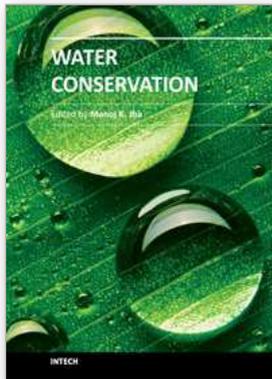
COD quantity, attributed basically to soluble organic matter, has to be removed before the application of advanced treatment processes.

The performed evaluation of two real scale biological treatment systems, sequential batch reactors (SBR) and nitrification-denitrification activated sludge (AS) system showed COD and  $\text{NH}_4\text{-N}$  removal efficiencies of 65% and 96% respectively were obtained in both cases. Nitrification-denitrification AS provided higher TKN removal compared with the SBR, 86% and 68% respectively. The O&G and phenol removals were also higher in the AS system. The average O&G removal efficiencies were 94% and 86% in AS and SBR respectively, and the phenol removals were 82% and 70% respectively. Sulphide removal efficiencies were of 95-96%. The secondary effluents accomplish the required water quality for reuse in cooling system make-up. For better TSS control and additional enhancement of the secondary effluent water quality, filtration or ultrafiltration can be recommended. Lime softening of the secondary effluent can be implemented before filtration if the hardness of the wastewater is higher than the established limit for reuse or when the reverse osmosis system design establishes restrictions with respect of the Hardness in the water to be demineralized. The last one was the case of refinery R1. The obtaining of the second water quality of water for reuse in production processes is technically feasible using reverse osmosis systems.

## 5. References

- Al-Shamrani, A.A., James, A. & Xiao, H. (2002). Destabilisation of oil-water emulsions and separation by dissolved air flotation. *Water Research*, Vol. 36, No.6, pp.1503-1512.
- API, American Petroleum Institute. (1990). *Design and operation of oil-water separators*. API Publication. Washington D.C.
- Baron, C., Equihua, L.O. & Mestre, J.P. (2000). B.O.O. Case: water management project for the use of reclaimed wastewater and desalted seawater for the "Antonio Dovali Jayme" refinery, Salina Cruz, Oaxaca, Mexico. *Water Science and Technology*, Vol. 42, No.5-6, pp.29-36.
- Daxin Wang, Flora Tong & Aerts P. (2011). Application of the combined ultrafiltration and reverse osmosis for refinery wastewater reuse in Sinopec Yanshan Plant. *Desalination and Water Treatment*, Vol.25, No.1-3, pp.133-142.
- EC (European Commission). (2000). *Integrate pollution prevention and control: Reference document on best available technologies in common wastewater and waste gas*, Institute for Perspective Technological Studies, Seville.
- Eckenfelder, W.W. (2000). *Industrial Water Pollution Control*, 3<sup>rd</sup>.ed., McGraw-Hill.
- Elmaleh S. & Ghaffor N. (1996) Upgrading oil refinery effluents by cross-flow ultrafiltration. *Water Science and Technology*, Vol.34, No.9. pp. 231-238.
- Farooq, S. & Misbahuddin, M. (1991). Activated carbon adsorption and ozone treatment of a petrochemical wastewater. *Environmental Technology*, Vol.12, No.2, pp.147-159.
- Levine, A.D. & Asano T. (2002). Water reclamation, recycling and reuse in industry. In: *Water recycling and resource recovery in Industry*, Edited by P. Liens, L. Hulshoff Pol, P. Wilderer and T. Asano, IWA Publishing, p.29-52.
- Galil, N. & Rebhum, M. (1992). Waste management solutions at an integrated oil refinery based on recycling of water, oil and sludge. *Water Science and Technology*, Vol.25, No.3, pp.101-106.
- Galil, N. & Wolf, D. (2001). Removal of hydrocarbons from petrochemical wastewater by dissolved air flotation. *Water Science and Technology*, Vol.43, No.8, pp.107-113.

- Guarino C. F., Da-Rin B. P., Gazen A. and Goettems E. P. (1988). Activated carbon as an advanced treatment for petrochemical wastewaters. *Water Science and Technology*, Vol.20, No.10, pp. 115-130.
- IPIECA (International Petroleum Industry Environmental Conservation). (2010). *Petroleum refining water/wastewater use and management*. Operations Best Practice Series, London, UK.
- Lee, L.Y., Hu, J.Y., Ong, S.L., Ng, W.J., Ren, J.H. & Wong, S.H. (2004) Two stage SBR for treatment of oil refinery wastewater. *Water Science and Technology*, Vol.50, No.10, pp.243-249.
- Misković, D., Dalmacija, B., Živanov, Ž., Karlović, E., Hain, Z. & Marić S. (1986). An investigation of the treatment and recycling of oil refinery wastewater. *Water Science and Technology*, Vol.18, No.9, pp.105-114.
- Mukhetjee, B., Turner, J. & Wrenn, B. (2011). Effect of oil composition on chemical dispersion of crude oil. *Environmental Engineering Science*, Vol. 28, No.7, 497-506.
- Nalco Chemical Company (1995). *Manual del Agua. Su naturaleza, tratamiento y aplicaciones.*(The Nalko Water Handbook), Tomo I, II, III. Segunda edición. McGraw-Hill/Interamericana de México, S.A. de C.V.
- PEMEX (Mexican state-owned petroleum company). (2007). *Principales estadísticas operativas* (Basic operation statistics), México D.F..
- Powel, S. T. (1988). *Manual de aguas para usos industriales*. Vol. 1, 2, 3. Primera reimpresión, Ediciones Ciencia y Técnica, S.A. de C.V., México, D.F.
- Schneider, E.E., Cerqueira, A.C.F.P. & Dezotti, M. (2011). MBBR evaluation for oil refinery wastetreatment with post-ozonation and BAC, for water reuse. *Water Science and Technology*, Vol. 63, No.1, pp.143-148.
- Standard Methods for the Examination of Water and Wastewater*. (2005). 21<sup>th</sup> edition, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.
- Sastry, C A. & Sundaramoorthy, S. (1996). Industrial use of fresh water vis-a-vis reclaimed municipal wastewater in Madras, India. *Desalination*, Vol.106, pp.443-448.
- Teodosiu, C.C., Kennedy, M. D., van Straten, H.A. & Schippers, J.C. (1999). Evaluation of secondary refinery effluent treatment using ultrafiltration membranas. *Water Research*, Vol.33. No.9, pp.2172-2180.
- US EPA (U.S. Environmental Protection Agency). (1982). *Development Document for Effluent Limitations Guidelines and Standards for the Petroleum Refining Point Source Category*, Washington, D.C.
- US EPA (U.S. Environmental Protection Agency). (1980). *Treatability manual*, EPA 600/8-80-042E, Vol. 1, 2, 3, 4, 5. Washington, D.C.
- US EPA (U.S. Environmental Protection Agency) and US AID (US Agency for International Development). (1980). *Guidelines for Water Reuse*, EPA 625/R-92/004, USA.
- US EPA (U.S. Environmental Protection Agency). (1995). *Profile of the Petroleum Industry*. EPA/310-R-95-013. Washington, D.C.
- WB (World Bank). (1998). *Pollution Prevention and Abatement Handbook: Petroleum Refining*, Technical Background Document, Environment Department, Washington, D.C.
- WEF (Water Environment Federation). (1994). *Pretreatment of industrial wastes*. Manual of Practice FD-3, Alexandria, USA.
- Zubarev, S. V., Alekseeva, N. A., Ivashentsev, V. N., Yavshits, G. P., Matyushkin, V. I., Bon, A. I. & Shishova, I. I. (1990). Purification of wastewater in petroleum refining industries by membrane methods. *Chemistry and Technology of Fuels and Oils*, Vol.25, No.11, pp.588-592.



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Water is an essential and basic human need for urban, industrial and agricultural use. While an abundance of fresh water resources is available, its uneven distribution around the globe creates challenges for sustainable use of this resource. Water conservation refers to an efficient and optimal use as well as protection of valuable water resources and this book focuses on some commonly used tools and techniques such as rainwater harvesting, water reuse and recycling, cooling water recycling, irrigation techniques such as drip irrigation, agricultural management practices, groundwater management, and water conservation incentives.

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