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Improring the performance of Pars Oil Refinery Wastewater Treatment System

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ABSTRACT: This study aims to inspect the performance of the wastewater treatment system of the Pars Oil refinery. Quantity and quality of wastewater are determined through samplings and measurements. The performance of system is evaluated considering total suspended solids, total dissolved solids, phosphate, chemical oxygen demand, biochemical oxygen demand, ammonia nitrogen, furfural, oil and pH. For precise comparing the qualitative and quantitative parameters, the wastewater entering the refinery is sampled four times from different places like boilers and from their channels, oil wastewater channels, and solvent wastewater channels. Despite some reforms that has been applied to the treatment system in order to reach the environmental standards, the system cannot treat the wastewater to the discharge standards. From the results of this research the advanced Membrane Bioreactor system for complementary refining along with optimized oil elimination system from wastewater is suggested.

Key words: Oil Refinery, Membrane Bioreactor, Treatment, Optimization

INTRODUCTION

One of the main sources of many industrial contaminations is the wastewater produced by industries which must be treated in order to achieving local effluent discharge standards. Oil refinery, as one of the most important industries worldwide, especially in Middle East, produces a huge amount of poisonous and oily wastewater which needs complicated treatment systems. Wastewater treatment depends on many interdependent factors which should be carefully considered when selecting and designing integrated treatment systems (Daigger and Nolasco, 1995; Eckenfelder and Wesley, 2000). In spite of these considerations, developing plans of industries may result in failure of existing wastewater treatment systems from their design effluent. In such cases, optimization plans are applied and some extra treatment units may be added. Wastewater treatment through new methods usually includes three stages: physical treatment (primary level), biological or bio-chemical treatment (secondary level), and supplementary treatment, including clarifiers, and chemical processing on the wastewater (last level) (Romano, 1990). Among the various technologies which have been developed to guarantee an acceptable quality in wastewater treatment plant effluent, membrane technologies such as membrane bioreactor (MBR) are of particular interest (Arévalo *et al.*, 2009). The MBR is a technology that combines an activated sludge reactor with a membrane filtration unit to purify wastewater (Wei-sheng *et al.*, 2000). The MBR has several advantages over the conventional activated sludge system. Compactness, production of reusable water, and trouble-free operation make the MBR an ideal

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process for recycling wastewater where water and space are both limited. (Daigger, and Nolasco, 1995; Arévalo *et al.*, 2009). The MBR has been widely used in water reuse systems in buildings, industry, sanitary treatment and municipal wastewater treatment. (Eynsham Hall, 2007; Chang *et al.*, 2008; Weiss and Reemtsma, 2008; Dialynas and Diamadopoulos, 2009).

Pars Oil Refinery, as one of the biggest refineries in Iran, uses a series of physical and chemical processes for producing lubricating oil, antifreeze, grease and break liquid. The processes used in such industries, which are special refineries in producing lubricating oil, entails effects and consequences on environment. The main cause of these problems is poisonous materials in the refinery's wastewater. The most important poisonous materials are furfural, methyl-ethyl-ketene, and toluene. Besides, Pars Oil Refinery produces and paints the barrels of products at the refinery which causes some amounts of substances for washing barrels and paint to enter into the wastewater. It is clear that painting substances and detergents make wastewater treatment complicated. Furthermore, supplementary materials and paints used in the refinery causes heavy metals to enter into wastewater. Elimination of heavy metals from wastewater needs special processes and a considerable finance (Horan, 1990). Contaminating wastewater enters into the environment and seepages into the soil levels of the region. In long term, it spoils soil and makes it unsuitable (Metcalf and Eddy, 2000). The same object was experienced on the roundabout grounds of Tehran's refinery. Regarding the organic base of oily wastewater, it provides an appropriate place for microorganisms to grow and reproduce (Lessard and Beck, 1991). Many of these microorganisms cause disease and endanger human health (Reed, 1995). Same problems have been observed in other refineries. Kangan Gas Refinery is one of the greatest gas refineries in Iran. Environmental affects of this refinery should be assessed because of its high economic importance, as well as its considerable revenue. The results show that although pollution of the refinery wastewater is within world permissible limits (EPA), since the area is affected by the wastewater and surrounding area is confined with river basin it could be concluded that pollutants, which are discharged to the echo environment, are not in the permissible limits of the similar Industries (Sadatipour, 2004).

The present network for collecting the Pars Oil refinery's industrial wastewater has been designed and executed in three separated paths, including oily wastewater collecting network, solvents (furfural, methyl-ethyl-ketene, and toluene) wastewater collecting, and collecting network for underwater in cooling and boiling towers. Besides, the wastewater is gathered separately to be treated and processed. The refinery's wastewater show that there is no special network for gathering rain water streams, therefore they enter into this three-path network and are transfered to the treatment plant. Considering that human paths in this network are open-top, it is expected that most water streams enter into this network. In the future plan by the refinery, considering the results of analyzing industrial wastewater, and in order to solving the problem, wastewater network has been completed and adjusted. The treatment system consists of two oil-water separator unit, a dissolved air flotation unit, two monotonic tanks and a sand filter. This treatment system is not capable in reaching to the Iran department of environment (Iran DOE) effluent discharge standards.

With these considerations in mind, the objective of the present study is to analyze the treatment system problems and evaluate the effect of using MBR process as a tertiary treatment unit.

MATERIALS & METHODS

This research was carried out during six months from August 2006 to January 2007. Studies are conducted through two parts: determining the volume of consumed water, and assessing quality and quantity of the produced wastewater in Pars Oil Refinery. In order to determine the quantity of the wastewater entering into wastewater treatment system, there was volume measurement with containers of determined volume of 20 Liters. As the consequence of this measurement, the amount of wastewater produced by the refinery is estimated to be about 3 m^3/hr. Regarding the full-time activity of the refinery, 72 m^3 wastewater is produced daily. The average amount of mixed wastewater from solvents, cooling tower's underwater, boilers and oil pots were 12.1, 56.16, 9.7 m^3/hr, respectively. In order to examining the quality of refinery's wastewater, the sources of wastewater are identified at different units including furfural unit, severance unit, storage unit, blending unit, tin-making unit, barrel-producing and painting unit, dismounting materials and freighting unit, antifreeze unit, grease-producing unit, and boilers units. Thus, in order to compare the quality and quantity of wastewater entering into wastewater treatment system, three canals, includes; cooling towers' underwater and boilers, oily wastewater, and solvent wastewater canals, were sampled. These samplings were composite which were done at four stages on hourly basis in morning and 500cc each time. The exiting wastewater was sampled and each sample was placed in a separate container. Therefore, at each sampling stage, the samples were picked up for tests sampling of mixing. They were analyzed in the laboratories of Oil Industry Research Center, Pars Oil Laboratory, and the laboratory unit at Science and Research Campus, Islamic Azad University, Tehran, Iran. The parameters tested in this research are pH, BOD, COD, Oil, Furfural, NH_3, PO_4^-, TDS, TSS, and Detergent.

The method for testing each parameter is according to the standard method 1991 mentioned in Table 1. In order to evaluating the contaminated wastewater in this industrial unit, there were 5 determined points to be examined through necessary tests during a 4 months period. The places of these points are shown in Fig. 1. After necessary examinations, and also on the basis of the present possibilities for increasing the work functionality, the operation of MBR system in exiting wastewater treatment from the refinery was considered. Thus, to be informed of the system function, the determined parameters were examined and analyzed at several stages at the entrance and exit. The used MBR in this research is an active sludge reactor attached to an external pipe-shaped UF unit. The reareation reactor has a volume of 20 Lit. The reactor was reareation through a Membrane spray in a bioreactor. The non-soluble oxygen density was maintained within 2-3 mg/L throughout the test stages (Fig. 2).

RESULTS & DISCUSSION

The first step towards examining the capacity of wastewater in undergoing treatment is to determine its various pollutants. General indices were used, since determining each of pollutants is costly and difficult.

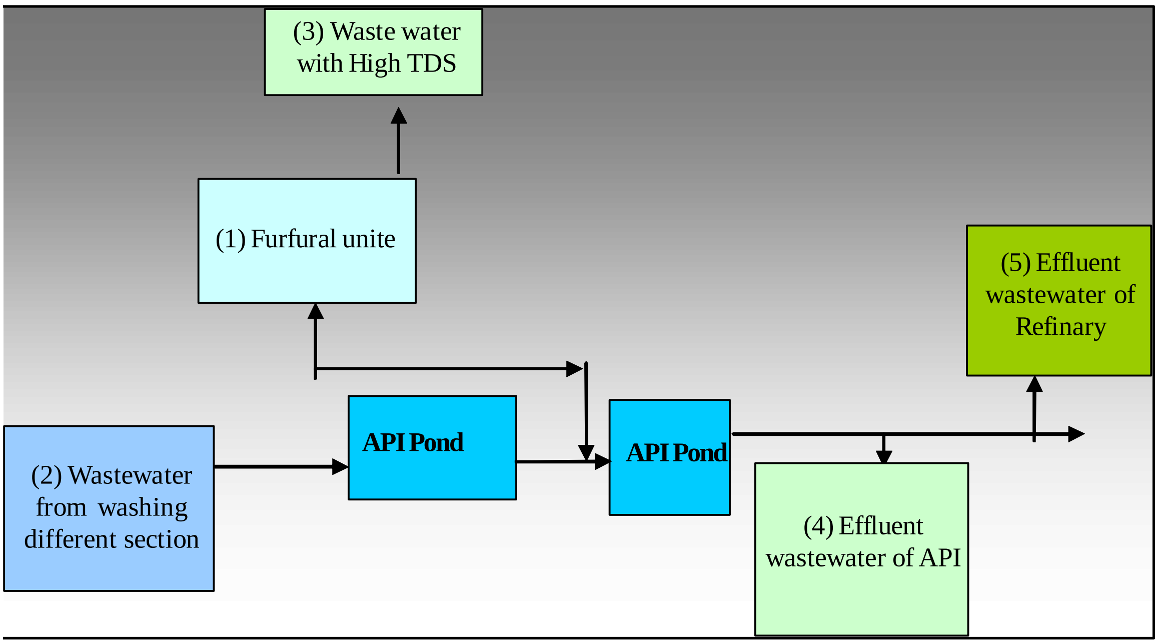

Fig. 1.The diagram of different section of refinery wastewater

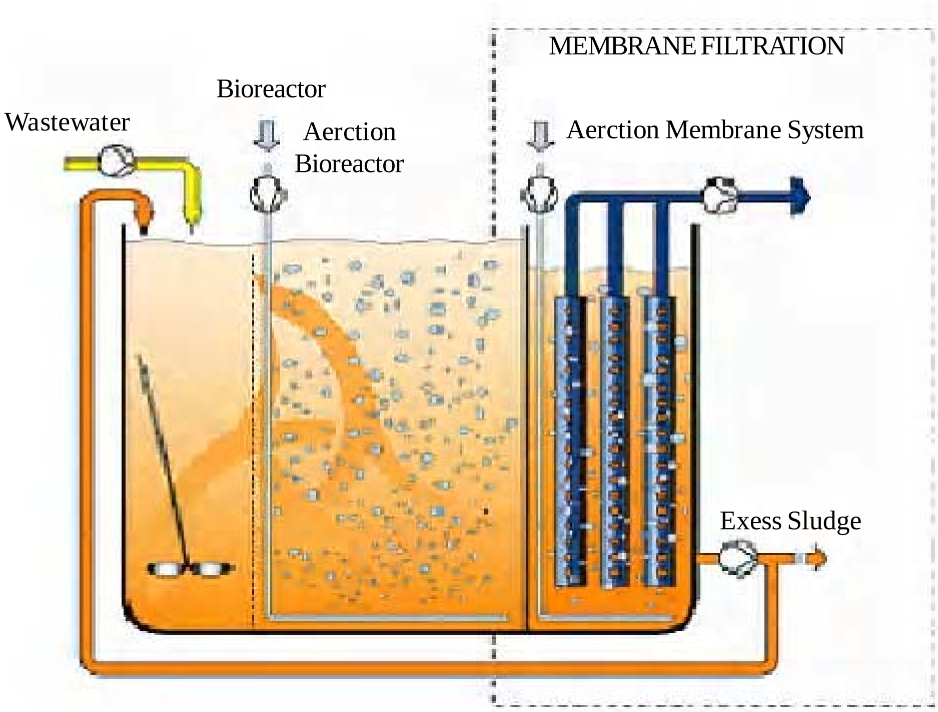

Fig. 2. Diagram of the pilot in a laboratory scale

Table 1. Standard method for the tests (Standard method, 1991)

Test	Unit	Standard method
pH	-	ASTMD1293
T	°C	Standard Method 2550B
COD	mg/L	Standard Method 5220B
BOD	mg/L	Standard Method 5210B
Oil	mg/L	Standard Method 5520B
Furfural	mg/L	Polarography
NH_3	mg/L	ASTMD 1426
PO_4	mg/L	ASTMD 515
Cl	mg/L as $CaCO_3$	Standard Method 4500 Cl-E
TDS	mg/L	Standard Method 2540C
TSS	mg/L	Standard Method 2540D

The results of measuring PH, BOD, COD, Oil, NH_3, PO_4^-, Cl, TDS and TSS in wastewater sources, and also the results of comparing the influent and effluent of MBR system are shown in Tables 2 to 6 and Figs 3 to 9. Furthermore, the comparable graphs indicate the changing procedure of measured parameters at the sampling stations. In spite of some improvements in treatment system for achieving the environmental standards, the present systems are not able to eliminate the pollutants completely; i.e. since the treatment procedure is not complete, it could not treat the wastewater until reaching the effluent discharge standard of Iran DOE. During the survey, the function of MBR treatment system was introduced as an efficient system for treating the refinery's wastewater, because this system lowers the amount of pollution as much as possible.

Table 2. Result of the analysis of wastewater from Furfural Section

Parametr	Unit	sampling times							
		1	2	3	4	5	6	7	8
pH	mg/L	10.2	9.8	10.75	9.8	10.50	9.6	9.80	10
T	°C	75	68	56	73	70	66	59	61
COD	mg/L	687	97	86	697	876	753	310	488
BOD	mg/L	279	44	41	378	498	451	165	299
Oil	mg/L	150	130	138	212.1	256	80.20	119	295
Furfural	mg/L	21	28	26	28	34	51	44	31

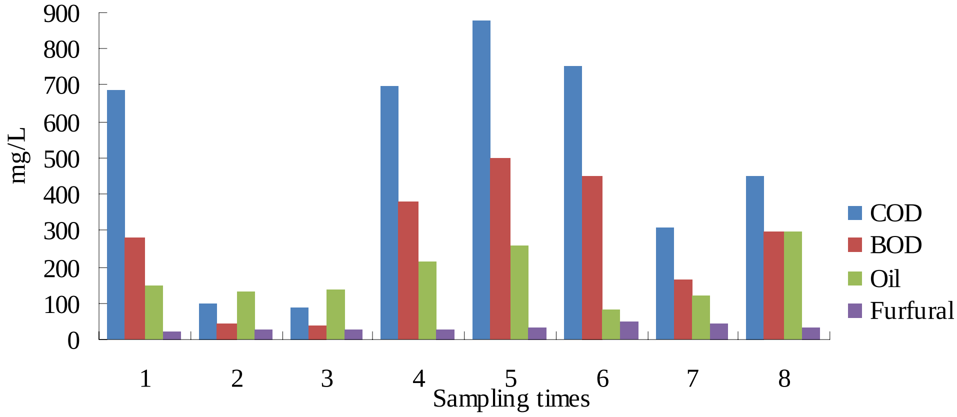

Fig. 3. Result of the analysis of wastewater from Furfural Unit

Table 3. Result of the analysis of the wastewater from washing different sections

Parametr	Unit	sampling times							
		1	2	3	4	5	6	7	8
pH	mg/L	9/20	8/70	7/80	8	8/10	7/40	8	7/90
T	°C	40	39	32	37	34	36	39	33
COD	mg/L	392	412	590	644	730	610	687	540
BOD	mg/L	148	205	265	325	342	295	349	225
Oil	mg/L	294	196	128	178	203	134	146	154
Furfural	mg/L	24	80. 33	35.40	35.20	26	28	30.10	22.10
N-NH3	mg/L	4.50	8.20	9.10	7.90	6.80	9.60	7.45	6.36
P-PO4	mg/L	0.09	0.07	0.24	0.26	0.14	0.18	0.17	0.13
Cl	mg/L	94	86	121	92	49	108	79	69

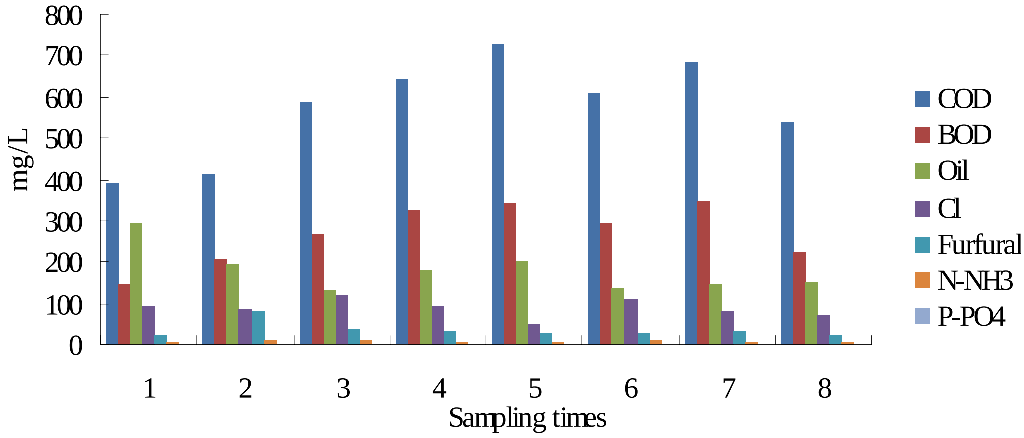

Fig. 4. Results of the analysis of the wastewater from washing different sections

Table 4. Results of the analysis of the effluent wastewater from API unit

Parameter	Unit	sampling times							
		1	2	3	4	5	6	7	8
pH	mg/L	7/90	8/10	8	8/50	8/20	7/90	8	8/30
T	°C	38	32	37	33	36	42	36	39
COD	mg/L	560	678	760	380	479	653	768	790
BOD	mg/L	270	340	355	190	225	345	376	376
Oil	mg/L	57	64	45	39	44	36	61	37
N-NH3	mg/L	13.41	12.72	8.12	9.20	8.30	9.12	8.21	11.20
P-PO4	mg/L	0.65	0.57	0.47	0.44	0.39	0.71	0.40	0.46
Cl	mg/L	112	109	119	98	121	97	89	78
TDS	mg/L	1120	890	769	870	908	768	1021	987
TSS	mg/L	56	49	56	64	53	44	33	49

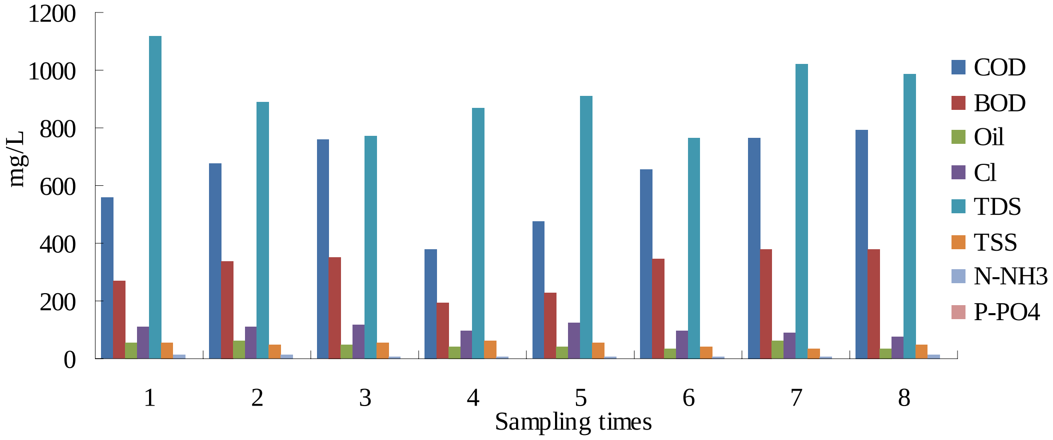

Fig. 5. Results of the analysis of the effluent wastewater from API unit

Table 5. Results of the analysis of the effluent wastewater from High TDS unit

Parameter	Unit	sampling times							
		1	2	3	4	5	6	7	8
pH	mg/L	7/30	8	8/12	7/50	8/10	7/90	8	7
T	°C	20	22	29	27	23	19	29	21
COD	mg/L	40	30	33	28	35	41	31	29
BOD	mg/L	19	13	14	11	17	21	15	10
N-NH$_3$	mg/L	0.45	0.62	0.35	0.29	0.42	0.82	0.37	0.91
P-PO$_4$	mg/L	0.20	0.35	0.99	0.15	0.18	0.19	0.26	0.16
Cl	mg/L	290	335	200	260	320	350	400	430
TDS	mg/L	1690	1900	2100	2095	1980	1850	1946	1840
TSS	mg/L	59	25	62	21	32	31	22	34

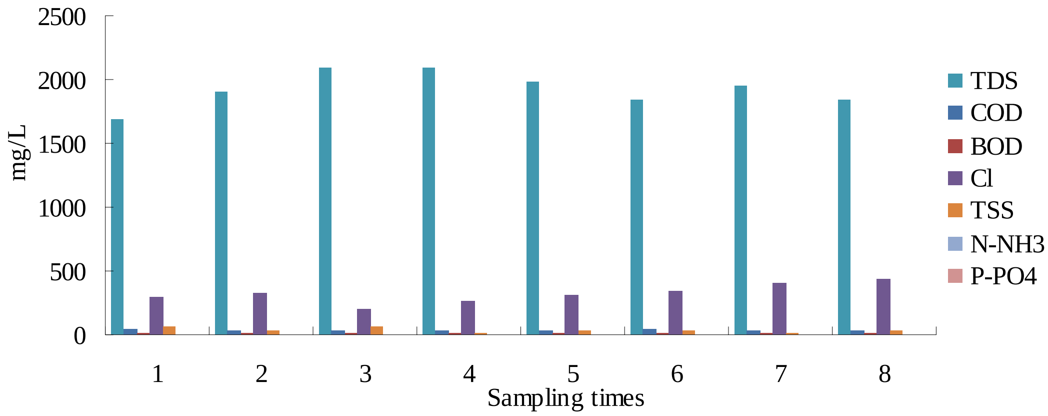

Fig. 6. Results of the analysis of the effluent wastewater from High TDS unit

Table 6. Results of the analysis of the effluent wastewater of treatment system

Parameter	Unit	sampling times							
		1	2	3	4	5	6	7	8
pH	mg/L	7/30	7/70	7/40	7/10	6/90	7/10	7/50	7/30
T	°C	30	32	28	27	38	32	29	30
COD	mg/L	197	168	148	154	151	132	142	178
BOD	mg/L	75	92	68	73	64	62	72	52
Oil	mg/L	7.90	8.20	9.20	6.80	7.40	8.30	7.40	8.20
Furfural	mg/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
$N-NH_3$	mg/L	2.30	1.40	2.10	1.90	2.20	1.60	2.40	1.80
$P-PO_4$	mg/L	0.24	0.18	0.10	0.09	0.11	0.09	0.08	0.10
Cl	mg/L	71	64	42	57	59	48	61	47
TDS	mg/L	1235	1320	1430	1150	1270	1360	1330	1040
TSS	mg/L	76	49	51	46	44	55	54	50

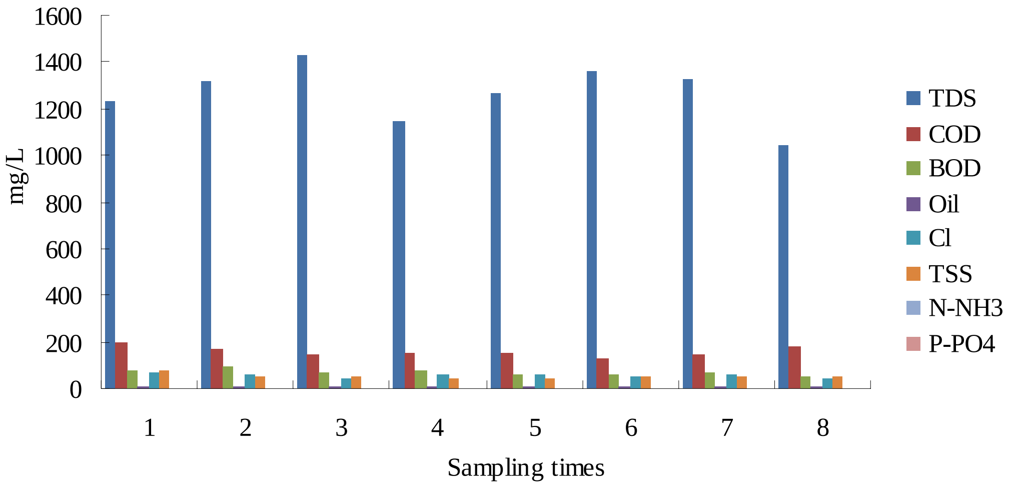

Fig. 7. Results of the analysis of the effluent wastewater of treatment system

Table 7. Results of the analysis of the influent and effluent from MBR pilot

Sample	Parameter	Unit	Samples Times					
Influent MBR	PH	-	8/5	8	7/8	7/6	8/1	7/6
	COD	mg/L	130	197	186	147	139	145
	BOD	mg/L	65	87	79	76	69	59
	OIL	mg/L	5.9	6.1	6.8	5.3	6.7	5.7
	TSS	mg/L	64	58	67	56	48	46
Effluent MBR	PH	-	8/3	7/7	8	7/7	7/9	7/1
	COD	mg/L	34	30	39	37	31	30
	BOD	mg/L	12	11	10	9	13	10
	OIL	mg/L	4.1	3.9	3.5	4	3.2	2.9
	TSS	mg/L	13	15	14	18	17	16

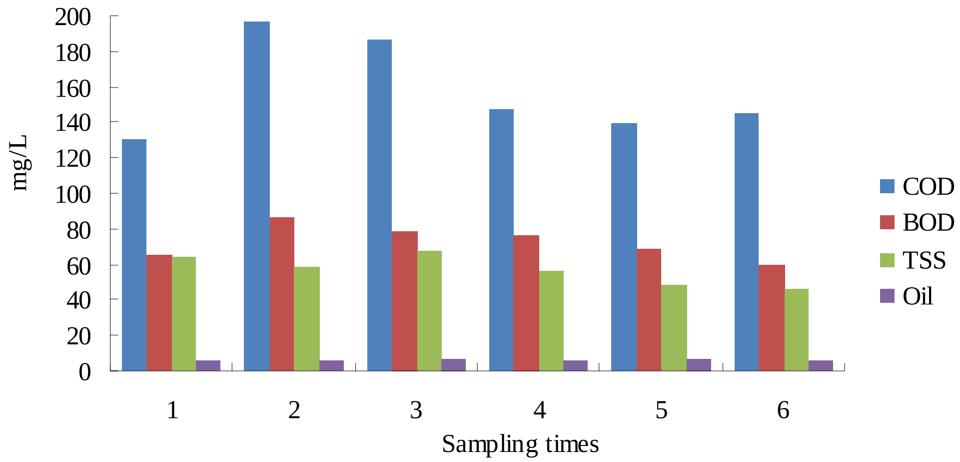

Fig. 8. Results of the analysis of the influent of MBR pilot

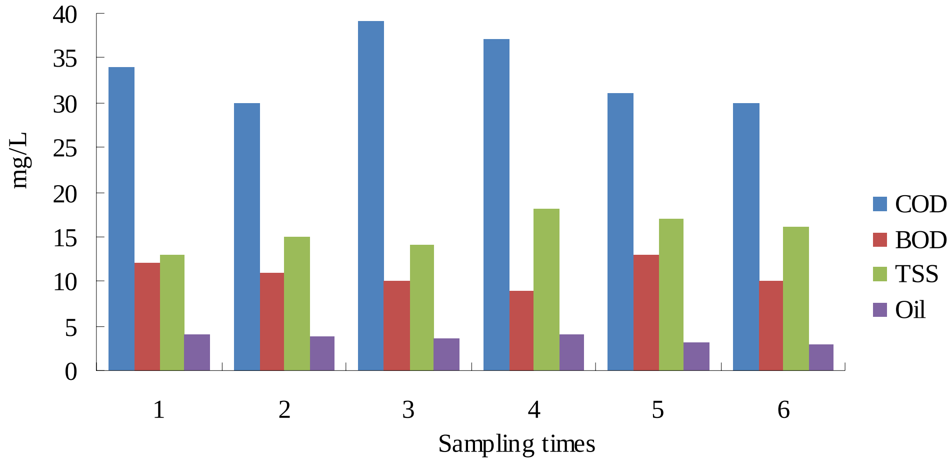

Fig. 9. Results of the analysis of the effluent from MBR pilot

According to results, the flowing and underground water resources of around the refinery are exposed to pollution. The wastewater of Pars oil refinery can be grouped by purification, and the process of treatment according to these six groups:

Toxic and solvent wastewater: This kind of wastewater is caused by furfural unit and the separation unit, and it contains furfural. *Oily wastewater:* This kind of wastewater is caused by several units of refinery. Treatment of this kind is by using DAF and API and then the active sludge and ultra filtration, excellently.

Flowing water and the wastewater caused by yard washing: The main part of this kind of wastewater is oil and can be treated by the mentioned system in the above. The main point of this kind is non-monotony and forcing the shock to treatment system while floodwater. For prevention, some preparations for monitoring the inflowing wastewater are done. *Wastewater containing heavy metals:* This kind of wastewater is from barrel making unit, painting unit and Blending unit.

Sanitary wastewater: This kind of wastewater is from health services, WC and the kitchen. It has a separated wastewater net system. *Saline wastewater:* Generates from blow-down and water treatment unit. This wastewater has no special pollution except high TDS that is diluted after mixing with other Wastewater and outflows.

As mentioned, the wastewater produced by the refinery inflows to the treatment system through three separated networks. Each network has its own pollution and its own treatment method. Here, the specifications of inflow wastewater were mentioned based on the tests which have been done on samples.

Oily wastewater network: The network which contains oil wastewater has all kind of wastewater inside. Pollutions like nitrates, phosphates, chlorides, heavy metals, sanitation wastewater, detergents, color materials, amines, and the most of it is the oil. The most part of the floodwater is carried by this net. The other oil wastewater sources like removed and leaked oil of instruments, washing of units, bottom of the tanks, restaurant wastewater, bathroom and health care services are transported by this network. The results of inspecting this network have been presented.

Solvent wastewater network: The main sources of this kind of wastewater are the Furfural unit, and a little part of it, washing of the separation unit. The chief pollutant of this network is furfural and then, oil, and toluene.

Saline water network: This network holds wastewater from the heat sink towers, boilers and the water treatment unit. The main pollution part in this network is TDS.

CONCLUSION

Wastewater treatment of the refinery is carried by one API unit and a DAF unit. For inspecting the quality of the wastewater, sampling and testing have been done at mentioned places. In these tests, the quality indexes of wastewater are experimented. Existence of detergents, colorful materials and heavy metals causes the treatment to be more complex and expensive. Considering the restaurant, bathroom, WC, etc. in the refinery yard and differences between this kind of wastewater and industrial wastewaters, the design and making a separated wastewater treatment system net for this kind of wastewater is necessary.

The main product of Pars Oil Refinery is grease which may exist in working places and around the yard beside the chemical materials. Not only the rain and yard washing makes this pollutants to flow, but also penetration out to environment cause the Environmental pollution. Managing and settling this kind of wastewater is very important. For qualifying the out flow of the wastewater, some basic reformation in the basic wastewater treatment system is needed. The inflow of the MBR system consists of sanitary wastewater and the outflow of DAF. The experiments shows that using MBR system has considerable influence on decreasing the expenses of membrane washing, energy, chemical materials, water usage and also increasing the efficiency of the system. The quality of the wastewater treated by this system is conformable to the wastewater offloading to the environment standards. Moreover, this treated wastewater, i.e. effluent of MBR, can be reused as makeup for cooling towers, and make minimize the wasting water from the system. This decreases the expense of raw water preparing, and has a positive influence on environment by decreasing the use of underground waters. It is should be mentioned that one of the main projects of Pars Oil Refinery, is to establishing an appropriate wastewater collection system for treating the wastewater of the refinery, in order to decreases the dangerous environmental impact. According to the research results in decomposing of furfural, it is possible to use negative gr bacteria, in a biological treatment. The problem of heavy metals due to the activity of coloring and blending is solved by replacing of the instrument by advanced system. By applying MBR system, it is possible to solve the problem of refinery industrial wastewater treatment system.

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