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Treatment of Contaminated Waters with Petroleum by Moving Bed Biofilm Reactor (MBBR)

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Abstract. The study ahead aims at treatment of waters around Tehran Refinery contaminated with petroleum compounds. Since, there are lots of villages around the Tehran Refinery and the majority of the villages provide their required drinking water from the wells. During study period a laboratory scale with a total liquid volume of 550 L was used. The reactor was filled with 85% Polyurethane elements, occupying 3% of the reactor's liquid volume. Pilot conditions are as follows, Temperature= 15 to 25 °C, pH= 6.7 to 7.5, dissolved oxygen = 4 to 5 mg/lit, MLSS= 1400 to 1700 mg/L Hydraulic Retention Time (HRT) = 240 minutes and unlimited Solid Retention Time (SRT), after suspended oil removal by oil separation system, COD, NO_3-N and PO_4-P removal efficiencies for the MBBR, filtration and activated carbon was 99, 94 and 58%, respectively. The results of the average effluent from each reactor show that denitrification process in the preceding the aerobic MBBR, filtration and activated carbon occurred and in predenitrification system in filtration, consumed most of the biodegradable organic matter. In case of formaldehyde, phenol and total petroleum hydrocarbon (TPH) parameters, they were removed in the pilot up to 96, 79 and 94%, respectively. With the exception of Formaldehyde All parameters in the pilot output are within the standard and this method can be known as an optimal method for treatment of water contaminated with oil.

Keywords: Contaminated water, Petroleum compounds, Moving Bed Biofilm Reactor.

1. Introduction

Industrial activities consume a huge amount of natural water, utilizable resources and energy thereby discharging enormous wastewater to the natural environment. It is therefore necessary to analyse any industrial wastewater to determine its reuse potential and the degree of treatment required prior to its ultimate disposal or to device suitable measures for the recovery of useful products [1]. Petroleum refining utilizes large quantities of water for desalting, distillation, thermal cracking, catalytic and treatment processes to produce useful products. Refining process generates wastewater, 0.4 – 1.6 times the volume of crude oil processed. Discharge of untreated petroleum refining wastewater in to water bodies results in environmental and human health effects due to release of toxic contaminants (hydrocarbons, phenol and dissolved minerals). Hydrocarbons (Benzene, Toluene, Ethyl benzene and Xylenes (BTEX)) are of serious concern due to their toxicity and as carcinogenic compounds. High exposure for long periods to these compounds can cause leukaemia and tumours in multiple organs. Phenol and dissolved minerals are also toxic to aquatic life and lead to liver, lung, kidney and vascular system infection [2].

Biological treatment processes are economical and efficient methods that can be used for treating wastewater from oil industry [3]. In the last years more attention was paid to the biological treatment, in this regards, Petroleum refineries are looking for an alternative wastewater treatment method to ensure that they will meet the regulatory limit of effluent set by Environmental Quality Regulations (COD= 100 mg/L for

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discharge into the surface water and wells, COD= 200 mg/L for agricultural consumptions [4]). During the past decade the MBBR process has been successfully used for the treatment of many industrial effluents including pulp and paper industry waste, poultry processing wastewater, cheese factory wastes, refinery and slaughter house waste, phenolic wastewater, dairy wastewater and municipal wastewater [5].The MBBR process is based on the bio film principle that take advantage of both activated sludge process and conventional fixed film systems without theirs disadvantages. Reactor can be operated at very high load and the process is insensitive to load variations and other distributances. Unlike most bio film reactors, the reactor volume in the MBBR is totally mixed and consequently there is no dead or unused space in the reactor. In addition, this system has a small head loss and no need for recycling of biomass or sludge [6].

The study ahead aims at treatment of waters around Tehran Refinery contaminated with petroleum compounds. Since, there are lots of villages around the Tehran Refinery and the majority of the villages provide their required drinking water from the wells, the villagers' health is threaded due to water pollution caused by penetration of petroleum compounds into the soil layers as well as leakage into the underground water. Hence, the contaminated water must be somehow retreated to reach at standard level of drinking water. The main objective of this research was to evaluate the organic, NO_3, PO_4, TPH, Formaldehyde and Phenol removal by applying a lab-scale oil separation, MBBR, Bagfilter and activated carbon process without return sludge in MBBR system, continuously operated and filled with polyurethane. The objectives of this work include: Characterization of contaminated waters with petroleum generated at the Tehran refinery wells, Evaluation of the current treatment process performance, Design, development and evaluation of alternative treatment processes and Laboratory scale tests on the most promising treatment process with a view to improve the current Process and enable recycling of contaminated waters for uses required by the end user.

2. Material and Method

In this study, once the existing aeration process with changing flow is applied to the completely mixed reactor in which, mobile media is added to convert it into the MBBR. The system consists of MBBR, filtration and Activated carbon. The overall control such as influx into the system, the oil separation, MBBR, filtration, activated carbon, and opening and closing the valve is automatically done using PLC.

Petroleum refinery effluent wastewater COD concentration ranged from 1568±340 mg/L during study period. The pH of the wastewater was in the range of 7.1±0.4. The average wastewater characteristics are given in Table 1. The research methodology was conducted on the basis of pilot studies.

Table 1: Physical and chemical analysis results of water contaminated by petroleum compounds

No.	parameter	unit	value
1	pH	---	7.1±0.4
2	NO_3-N	mg/L	1.5±0.7
3	PO_4-P	mg/L	9±2.4
4	COD	mg/L	1568±340
5	TPH	mg/L	55.3±10
6	turbidity	NTU	63±5
7	Formaldehyde	mg/L	372±200
8	Phenol	mg/L	0.66±0.66
9	TN	mg/L	19±2
10	NH_4-N	mg/L	16±3

A laboratory scale polyethylene reactor with a total liquid volume of 550 L was used in the study. Media added into the reactor was Biocube of Polyurethane and the Physical characteristics of packing media are shown in Table 2. The reactor was filled with 85% Polyurethane elements, occupying 3% of the reactor's liquid volume. Pilot conditions are as follows, Temperature= 15 to 25 °C, pH= 6.7 to 7.5, dissolved oxygen = 4 to 5 mg/lit, MLSS= 1400 to 1700 mg/L Hydraulic Retention Time (HRT) = 240 minutes and unlimited Solid Retention Time (SRT). The total cycle for MBBR and the combined system was 4 hours and 2 hours, respectively. A scheme of the pilot is illustrated in Figure.1. Mixing and aeration were provided by pressurised air through four membrane disk aerators in the bottom of the reactor. The reactor was covered in order to minimise stripping and evaporation. Oxygen concentration in the reactor was kept at 4 to5 mg O_2 L^{-1}.

Table 2: Physical Characteristics of the packing media

parameters	Biocube
Materials	Polyurethane
Specification(cm)	1.5*1.5*1.5
Volume (cm3)	3.37
Weight (g)	0.15
Density (g/cm3)	0.044
Porosity (%V)	95

The current study was lasted six months. Within early two months, the pilot was commissioning constantly until it comes to consistency conditions. Then, the sampling from the pilot was continuously performed through three months. At the end of each month, the measured parameters were recorded which results obtained from every three months were almost too close together. However, given the specific nature of this research, multi-point sampling manner was selected and results in each stage of the treatment were recorded separately, every week. The first sampling station was placed after the Oil Separator Unit, in this unit, the bulk composition of the suspended oil compounds as well as the contaminated water is conducted in to the microbial treatment section. The second station was situated just after the biological Treatment Unit, in this unit, nutrients for growth and activity of microorganisms is prepared and placed at the disposal of them. The wastewater after passing this stage is entered into the Adsorption Unit in which there are special filters to absorb oil-soluble compounds. While the third and forth station was located after the Bag filter and activated carbon where the purified water was driven out, respectively. Table 1 shows the amount of pollutants in contaminated and untreated water.

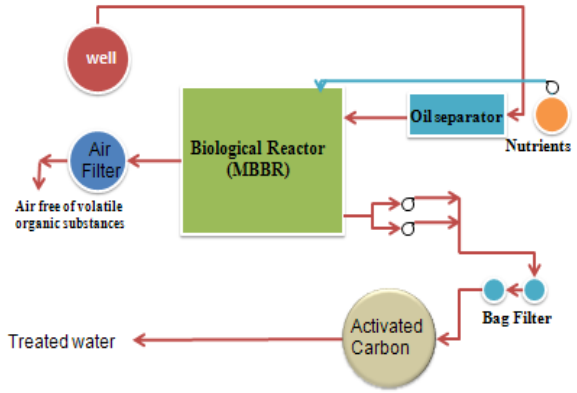

Fig. 1: Schematic diagram of combined oil separation, MBBR, infiltration and activated carbon

After sampling, the experiment of measuring parameters including TPH, COD, pH, nitrate, formaldehyde, and turbidity were conducted using methods recommended in standard Method as well as HACH digital device analysis. The pH measurements were conducted immediately after sampling, while dissolved oxygen was measured from the reactor, Unfiltered and filtered chemical oxygen demand, PO_4-P, NO_3-N and Phenol were determined according to Standard Methods [7]. Attached biomass was removed mechanically by scraping it off the Polyurethane, before MLSS analyses.

3. Result and Discussion

In this respect, the noted above manner were conducted four time within three consecutive periods i.e. in the months August, September and October, 2010 which the results obtained from the three-periods analysis are presented in Table 3 as follows; A major unit in Tehran refinery wastewater treatment plant is a biological treatment stage. In order to be able to reuse the treated wastewater, the dissolved oils, hydrocarbons and other constituents that sum up to the COD level must be removed. Biological treatment has proven to be the most economical and reliable tool after preliminary oil/water separation. Amongst hydrocarbons present in refinery wastewater, Phenol is one of the main dissolved components and it is also one of the toughest hydrocarbons to degrade biologically. The COD removal efficiency variation profile at this MBBR system is shown in Table 3. According to the experiments, the obtained results showed that, after suspended oil removal by oil separation system, during optimum conditions (599 mg COD L^{-1}, 2.55 mg

NO_3-N L^{-1} and 4.9 mg PO_4-P L^{-1}), COD removal with 62 % efficiency occurred in the MBBR system. As seen from the results, the average COD removal efficiency for the total MBBR and filtration system was 86 % and for the MBBR, filtration and activated carbon was 99.2 %. The results of the average effluent COD concentration from each reactor showed that denitrification process in the preceding the aerobic MBBR reactor, filtration and activated carbon occurred and in predenitrification system in filtration, consumed most of the biodegradable organic matter. Thus, in the filtration the average biodegradable COD load was considerably lower and did not interfere with the nitrification. According to table 3, degradation of organic matter will slow down or stop the nitrification process in filtration and activated carbon.

Table 3: the pilot results obtained from physical and chemical analysis of water contaminated by petroleum compounds

No.	Test	Month	Average influent	Monthly Average effluent			
				Oil separation	MBBR	filtration	Activated carbon
1	pH	August	6.9 ±0.3	6.9	7.3	8.2	8.0
		September		6.9	7.4	8.5	8.1
		October		6.8	7.1	8.3	8.1
2	NO_3-N (mg/L)	August	1.5 ±0.7	2.5	2.5	0.5	0.1
		September		1.5	2.3	0.7	0.1
		October		1.3	2.8	0.4	0.2
3	PO_4-P (mg/L)	August	9 ±2.4	9	7.6	-	3
		September		5.6	3.6	4.4	5.6
		October		8	3.5	3	2.7
4	COD (mg/L)	August	1568 ±340	828	590	216	10
		September		810	610	213	14
		October		1074	598	226	11
5	TPH (mg/L)	August	55.3 ±10	54	18.5	9	2.7
		September		50	20.9	8	3.1
		October		55.3	19.2	8	2.9
6	Turbidity (NTU)	August	63 ±5	52	18	5.6	3.1
		September		59.4	21	5.1	1.1
		October		55	17	6.1	1.8
7	Formaldehyde (mg/L)	August	372 ±208	195	47	30	10
		September		477	41	31	12
		October		372	53	33	13
8	Phenol (mg/L)	August	0.66 ±0.66	0.65	0.36	0.54	0.18
		September		0.07	0.06	0.08	0.04
		October		0.34	0.3	0.35	0.18

From the nutrients removal study results, it is shown that the wastewater from petroleum refinery is ultimately biodegradable. However, it is also found that wastewater treatment achieved better COD removals when MBBR coupled with filtration and adsorption by activated carbon. From the MBBR results, it is shown that the desired treatment level for wastewater can be achieved. MBBR reactor reported effluent COD concentration was upper than agricultural consumption Standards [4]. Lowest percentage COD removals were reported in the MBBR system and also in the combined MBBR and filtration system. Highest effluent COD concentration was recorded in the MBBR when the wastewater was treated by combined MBBR-filtration and activated carbon system. Based on the experimental results obtained from the lab-scale MBBR process behaviour, the following results can be made:

- The results of the average effluent soluble COD concentration from each reactor showed that denitrification process in the filtration may be consumed most of the biodegradable organic matter in filtration and activated carbon.
- Aerobic phosphate removal rate showed a good correlation to the filtration phosphate release rate
- During optimum conditions, close to complete nitrification occurred in the MBBR with average ammonium removal efficiency of 97% and Denitrification rate has increased with increasing NO_3-N loading in the filtration and the maximum denitrification rate was occurred.

- In overall, the lab-scale MBBR system coupled with filtration and activated carbon was a very effective process for close to complete organics and nutrients removal, with average COD, total nitrogen and phosphorus removal efficiencies of 99, 94 and 58%, respectively.

According to the results presented in Table 3 it is clearly that the treatment result of MBBR Method is successful and water contaminated with petroleum compounds can be treated using MBBR Method efficiently. The average of the obtained results showed that some parameters are within the treated potable water standards and some others are close to the standard limits. One of the benefits of treatment with the pilot is the fairly alkaline water which in addition to being in the range of environmental standards, in terms of health point of view, it improves gastrointestinal function and raises body immune factor. One of the problems of Tehran drinking water is high level of nitrate, the second advantage of MBBR filtration method is high removal of nitrate from the water. The turbidity of the water was removed as extent as drinking water standards. In case of formaldehyde, phenol and total petroleum hydrocarbon (TPH) parameters considered the most important chemical parameters of water contaminated with petroleum compounds; they were removed in the pilot up to 96, 79 and 94%, respectively. This elimination rate is so ideal. The only parameter that despite further reduction of 96% was not achieved the environmental standard limit is formaldehyde.

4. Conclusion

According to the average obtained for eight parameters analyzed in three months it is clear that:

- All parameters in the pilot output are within the standard determined by department of environmental protection to discharge into the surface water, wells and agricultural consumptions With the exception of Formaldehyde. Thus, this method can be known as an optimal method for treatment of water contaminated with oil.
- With regard to drinking water standards, it is considered that the most important qualitative parameters of water contaminated with petroleum compounds have been reduced with very tangible rate close to the standard limits while the other parameters are within the determined standard ranges.
- The removal efficiency of the pilot applied MBBR Method seems higher than 94% for TPH and formaldehyde and above 98% for turbidity, COD and nitrate. According to the results, we suggest that the moving bed biofilm process coupled with filtration could be used as an ideal and efficient option for the total nutrient removal from refinery wastewater

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