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Chapter 5

Biological Treatment of Petrochemical Wastewater

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Abstract

Petrochemical wastewater is inherent to oil industries. The wastewater contains various organic and inorganic components that need to be well managed before they can be discharged to any receiving waters. The complexity of the wastewater and stringent discharge limit push the development of wastewater treatment by combinations of different methods. Biological wastewater treatments that have been well developed for organic and inorganic wastewater treatment are thus a potential method for petrochemical wastewater management. This chapter summarizes the commonly applied petrochemical wastewater pretreatment methods prior biological treatments and compares different biological treatment systems' performance such as biological anaerobic, aerobic and integrated systems. Two case studies are presented for a high chemical oxygen demand (COD) contents petrochemical wastewater treatment in full-scale by applying Biowater Technology's biofilm system continuous flow intermittent cleaning (CFIC) and a pilot-scale study by an integrated anaerobic and aerobic biofilm system hybrid vertical anaerobic biofilm (HyVAB). Both processes showed substantial (over 90%) COD removal, while the HyVAB system produced high methane content biogas that can be potentially used as an energy source. Studies of degradation of certain toxic chemicals, such as aromatic compounds in petrochemical wastewater, by the advanced treatment systems incorporating specific organisms can be of good research interest.

Keywords: petrochemical wastewater, anaerobic digestion, aerobic digestion, biofilm reactor, integrated system

1. Introduction

Increasing consumption of oil in modern society has led to more oil/oil refinery waste generation. The oil processing wastewater/waste has high concentrations of aliphatic, aromatic petroleum

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hydrocarbons, etc. Direct discharge of this will affect plants and aquatic life of surface and ground water sources. Due to its organic origination, complex nature, and toxic effects, wastewater treatment prior to discharge is obligatory. The biological treatment process is normally applied to reduce the effects of petrochemical waste.

Stringent regulations have motivated researchers to design advanced treatment facilities to give high treatment efficiency, low maintenance, footprint, and operational costs. Biological anaerobic, anoxic, and aerobic digestion (or a combination of each other) have been implemented to treat petrochemical wastewater. Optimizing pretreatment process using physicochemical processes is also important for getting suitable pretreatment wastewater for efficient biological secondary treatment. An overview and update of the petrochemical wastewater treatment processes will contribute to the knowledge development both theoretically and practically.

In this section, the petrochemical wastewater treatment by biological processes is shortly reviewed and discussed. Section 2 introduces the petrochemical wastewater sources and their components in general. Section 3 introduces the normally applied pretreatment process prior to biological treatment processes. Section 4 presents the commonly applied anaerobic, aerobic, and combined anaerobic and aerobic biological systems for petrochemical wastewater treatment. Section 5 shows two case studies on the petrochemical wastewater treatment using Biowater Technology AS's continuous flow intermittent cleaning (CFIC) and hybrid vertical anaerobic biofilm (HyVAB) processes. Section 6 summarizes challenges and further studies in the petrochemical wastewater treatment.

2. Petrochemical wastewater

Petrochemical wastewater is a general term of wastewater associated with oil-related industries. The sources of petrochemical wastewater are diverse and can originate from oilfield production, crude oil refinery plants, the olefin process plants, refrigeration, energy unities, and other sporadic wastewaters [1, 2]. The compositions of wastewater from different sources consist of varying chemicals and show different toxicity and degradability in terms of biological treatment. In this chapter, to better compare the treatment efficiency with varying pretreatment processes, the petrochemical wastewater has been categorized to oilfield-produced wastewater, petrochemical refinery, and oily wastewater based on the originates.

Oilfield-produced wastewater is generated in crude oil extraction from oil wells that contain high concentrations of artificial surfactants and emulsified crude oil characterized of high COD and low biodegradability [3]. It is produced during oil extraction in oil fields and contains complex recalcitrant organic pollutants such as polymer, surfactants, radioactive substances, benzenes, phenols, humus, polycyclic aromatic hydrocarbons (PAHs), and different kinds of heavy mineral oil [4, 5]. **Table 1** presents the commonly found compositions of wastewater obtained from oilfield production.

Petroleum refinery wastewater is generated in oil refinery processes that produce more than 2500 refined products. The wastewater can be from cooling systems, distillation, hydrotreating, and

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Parameter	Values	Heavy metal	Values (mg/L)
Density (kg/m^3)	1014–1140	Calcium	13–25,800
Surface Tension (dynes/cm)	43–78	Sodium	132–97,000
TOC (mg/L)	0–1500	Potassium	24–4300
COD (mg/L)	1220	Magnesium	8–6000
TSS (mg/L)	1.2–1000	Iron	<0.1–100
pH	4.3–10	Aluminum	310–410
Total oil (IR; mg/L)	2–565	Boron	5–95
Volatile (BTX; mg/L)	0.39–35	Barium	1.3–650
Base/neutrals (mg/L)	<140	Cadmium	<0.005–0.2
(Total non-volatile oil and grease by GLC/MS) base (g/L)	275	Chromium	0.02–1.1
Chloride (mg/L)	80–200,000	Copper	<0.002–1.5
Bicarbonate (mg/L)	77–3990	Lithium	3–50
Sulfate (mg/L)	<2–1650	Manganese	<0.004–175
Ammoniacal nitrogen (mg/L)	10–300	Lead	0.002–8.8
Sulfite (mg/L)	10	Strontium	0.02–1000
Total polar (mg/L)	9.7–600	Titanium	<0.01–0.7
Higher acids (mg/L)	<1–63	Zinc	0.01–35
Phenols (mg/L)	0.009–23	Arsenic	<0.005–0.3
VFA’s (volatile fatty acids) (mg/L)	2–4900	Mercury	<0.001–0.002
		Silver	<0.001–0.15
		Beryllium	<0.001–0.004

Table 1. Wastewater parameter form oilfield production [6].

desalting. The compositions of the refinery wastewater can vary depending upon the operational units for different products at specific time and locations. Different concentrations of ammonia, sulfide, phenols, Benzo, and other hydrocarbons are normally present in such wastewater [7, 8].

The oily wastewater is defined here to be any wastewater that does not clearly belong to the two categories mentioned earlier. This wastewater can be from petrochemical-related industries such as from oil transportation tank, garage oil wastewater, etc. The composition of such wastewater is diverse with high COD that can be over 15 g/L [9].

3. Pretreatment process for biological stabilization

Wastewater from petrochemical industries consists of different chemicals. The treatment processes depend and are specialized by wastewater sources, discharge requirements, and treatment efficiencies. Normally, pretreatment processes are applied in the treatment of petroleum refinery wastewater before it is sent to biological process for organic elimination [8]. A primary treatment includes the elimination of free oil and gross solids; elimination of dispersed oil and solids by flocculation, flotation, sedimentation, filtration, microelectrolysis, etc.; increasing the biodegradability of wastewater, etc. [8]. This chapter lists a few commonly applied methods for petrochemical wastewater pretreatment.

3.1. Physical treatment

Depending on the wastewater characteristics, physical treatment such as adsorption by active carbon, copolymers, zeolite, etc. can be used for removing hydrocarbons in the petrochemical wastewater [6]. Evaporation is proposed to remove oil residuals in saline wastewater. Dissolved air flotation (DAF) is commonly used for wastewater containing oil/fat as well as suspended solids, which can also be applied for petrochemical wastewater.

Microfiltration (MF) and ultrafiltration (UF) are also applicable for pretreatment before the wastewater passes through, for example, reverse osmosis (RO) process for reusing purposes [10].

3.2. Chemical treatment

Enhancing hydrolysis by adding chemicals for removing the long-chain organics, toxic material, or suspended solids can increase the Biochemical Oxygen Demand (BOD) ratio of the wastewater. Three chemical treatment processes are listed here.

Micro-aeration breaks down high hydrocarbon content components from wastewater, which leads to easily biodegradable organic generation. At a dissolved oxygen (DO) concentration from 0.2 to 0.3 mg/L, the hydrolysis of wastewater organics is enhanced. The BOD/COD ratio is increased and SO_4- reduction in wastewater is inhibited. Low H_2S generation due to SO_4- reduced reduction can benefit subsequent biological treatment by lowering inhibitory effects. Benzene ring organics', such as benzene, toluene, ethylbenzene, and xylenes, treatability in the biological stage can be improved [11].

Coagulation-flocculation for specific petrochemical wastewater treatment, such as purified terephthalic acid (PTA) production wastewater; the wastewater contains aromatic compounds such as p-toluic acid, benzoic acid, 4-carboxybenzaldehyde, phthalic acid (PA), and terephthalic acid (TA), etc. Ferric chloride is found to be the most effective coagulant with COD removal efficiency at 75.5% at wastewater COD of 2776 mg/L and dose of pH 5.6. Adding cationic polyacrylamide improves the sludge filtration [12]. Certain streams that combine coagulation and flocculation as pretreatment followed by MF and UF achieved significant suspended solid removal [10].

Ozonation for wastewater that contains phenol, benzoic acid, aminobenzoic acid, and petrochemical industry wastewater containing acrylonitrile butadiene styrene (ABS) at 30 min and 100–200 mg O_3/h showed an increased BOD/COD ratio from 20 to 35% [13].

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3.3. Other treatment

Microelectrolysis of petrochemical wastewater has been tested with positive effects on the COD removal as well as increasing the BOD-to-COD ratio levels [14].

4. Biological treatment of petrochemical wastewater

Biological treatment incorporates actions of different microbes to eliminate organics and stabilize hazardous pollutants in petrochemical wastewater. Stringent environmental standards and recycling of water for reuse have shifted focus to biological treatments because of its cost and pollutant removal efficiency. As the nature of petrochemical wastewater is very complex, biological treatment to remove pollutants still has challenges despite immense potentials. Complex structures of aromatic, polycyclic, and heterocyclic ringed chemicals are known to be restraint to biological degradation [15]. However, recent research activities have produced notable removal percentages of pollutants from petrochemical wastewater [16].

Anaerobic digestion (AD), aerobic digestion, or an integration of both methods is commonly applied in biological processes to treat petrochemical wastewater.

4.1. Anaerobic process

Anaerobic digestion has the advantages of producing methane as a renewable energy, requiring less space and having lower sludge generation than aerobic process. A literature review of anaerobic digestion on the petrochemical wastewater is given in **Table 2**. Petrochemical wastewater treated in anaerobic baffled reactor (ABR), sequence batch, and up-flow sludge blanket reactor (UASB) was commonly applied. It shows that organics in the petrochemical wastewater could be partially anaerobic digested at a removal efficiency depending on the chemical constituents, reactor type, operational conditions (temperature, loading rate, etc.), and wastewater sources [24].

COD removal efficiency is used here as a general parameter to assess the performance of different systems. Crude oil extraction of light, medium, and heavy petroleum wastewater treatment by different anaerobic digestion systems at mesophilic or thermophilic conditions showed that in batch test over 56–71% COD removal was achievable at thermophilic condition [1, 18] (**Table 2**), while UASB system can achieve over 93% COD removal at mesophilic conditions for wastewater from light petroleum extraction (**Table 2**). It seems light petroleum extraction wastewater was generally easily degradable (over 71–93% removal) compared to the medium and heavy oil extraction wastewater. The setup of plug flow pattern and granular sludge application in UASB might also enhance the interaction between wastewater and organisms, giving higher efficiency. The removal efficiency decreases as the loading rate increases, indicating the inhibition effects to the organisms.

Medium- and heavy oil-produced wastewater treatment efficiency was relatively low. Batch system gives generally a better treatment efficiency for these two wastewaters at about 50–60%

NO.	Types of wastewater	Treatment system	Operating conditions	Pollutants monitored	Removal efficiencies (%)	References
1	Crude oil extractions*	Batch reactors	Thermophilic conditions (55 ± 1°C)	COD	70.7 59.9 62.1	[1]
		UASB	Mesophilic	COD	81.7 23.5 35.7	[17]
2	Crude oil extractions**	Batch reactors	Thermophilic conditions (55 ± 1°C)	COD	68.2–69.2 55.9–50.4	[18]
3	Crude oil extractions***	UASB	Mesophilic 1.06 kg COD/m^3.d 0.78 kg COD/m^3.d	COD	93 26	[19]
4	Crude oil extraction of light petroleum	UASB	Mesophilic 4.7 kg COD/m^3.d 0.78 kg COD/m^3.d	COD	23.8 86.1	[20]
		UASB	Mesophilic 5.6 kg COD/m^3.d Thermophilic 5.6 kg COD/m^3.d	COD VSS COD VSS	40–80 42–73 67–84 52–67	[21]
		UASB	Thermophilic 1.1 kg COD/m^3.d	COD	78	[22]
		UASB	4.1 kg COD/m^3.d	COD	82	[23]
5	Heavy oil refinery	UASB	3.4 kg COD/m^3.d	COD Total oil	70 72	[9]
		ABR	0.5 kg COD/m^3.d	COD Oil	65 88	[24]

*Water from light petroleum, medium petroleum and heavy petroleum, respectively.
**Water from medium petroleum and heavy petroleum, respectively.
***Water from light petroleum, medium petroleum, respectively.

Table 2. Overview of anaerobic treatment of petrochemical wastewater.

removal (**Table 2**), while UASB shows low efficiency at around 20–30% removal efficiency. The effects of toxic chemicals in the wastewater and high content of large organic molecules can be the reason for low efficiency.

4.2. Aerobic process

Aerobic process has been applied widely in petrochemical wastewater treatment attributed to its features of easy operation, less sensitiveness to toxic effects, higher organisms' growth rate, etc. than the anaerobic system. Different aerobic reactors such as traditional active sludge, contact stabilization active sludge, sequence batch reactor (SBR) that applies active sludge and biological aerated filter (BAF), membrane bioreactor (MB), moving bed biofilm reactor (MBBR), aerobic submerged fixed-bed reactor (ASFBR) that applies biofilm, etc. have been

S. N	Types of wastewater	Treatment system	Operating conditions	Pollutants monitored	Removal efficiencies (%)	References
1	Petroleum refinery	Contact stabilization	F/M 0.38	COD BOD NH_3-N H_2S TSS	97.9 95.8 87.5 97.5 98.6	[25]
		Activated sludge		COD BOD NH_3-N H_2S TSS	93.4 94.4 83.3 95 97.6	
		Activated sludge		COD TOC TSS	94–95 85–87 98–99	[8]
		SBR		COD TOC	80 84	[26]
		MSBR	SRT: 20 days HRT: 8 h	COD Oil and grease TPH	80 82 93.4	[27]
		HF-UF MBR	HRT: 25–36 h	COD TSS Turbidity	82 98 98	[28]
		CF-MBR	DO: 4 mg/L F/M: 0.2–1.15	COD	93–94	[29]
		BAF	1.9 kg COD/m^3.d	COD Oil SS	84.5 94 83.4	[30]
		ASFBR	2.4 kg COD/m^3.d HRT: 12 h	COD TSS	70±7 65±16	[31]
2	Oilfield	BAF with immobilized carriers	1.1 kg COD/ m^3.d	TOC Oil	78 94	[5]
		MBBR with Activated sludge	4.2 kg COD/ m^3.d	COD	74	[32]
		Activated sludge	SRT: 20 days MLSS: 730 mg/L	THP	98–99	[33]
		Airlift reactor	HRT: 12 days	COD TOC Phenols NH4 + -N	65 80 65 40	[34]
3	Oily wastewater	Activated sludge	Temperature: 25–37°C	COD Ethylene dichloride Vinyl chloride Total hydrocarbons	89 99 92 80	[35]
		Activated sludge and contact oxidation	1.1 kg COD/ m^3.d	COD $NH4^+$-N	84.9 60	[36]

S. N	Types of wastewater	Treatment system	Operating conditions	Pollutants monitored	Removal efficiencies (%)	References
		UF Membrane bioreactor	Temperature–35°C	COD TOC Oil	97 98 99.9	[37]
		RBC	Diesel concentration: 0.6%	TPH COD	98.1 97.2	[38]
		CFIC	Temperature–35°C	COD	92	Case study in chapter 5

Table 3. Overview of aerobic treatment process of petrochemical wastewater.

tested to treat petrochemical wastewater from varying sources and presented in **Table 3**. Generally higher COD and chemical removal efficiencies by aerobic process are achieved than the anaerobic processes (**Tables 2** and **3**). The sludge retention time, hydraulic retention time, dissolved oxygen level, feed to organism ratio, and temperature are some of the important factors that determine the treatment efficiency.

Petroleum refinery wastewater COD removal was generally high from 70 to 98% in the mentioned aerobic system (**Table 3**), which in anaerobic system is from 70 to 93%. The contact and extended active sludge process can achieve high COD removal rate of 89–95% (**Table 3**) at a feed to microorganism ratio of 0.38 [25]. The applied aeration to the mixed liquor and the sludge recycle rate was found to be critical parameters in the successful optimization of the contact stabilization process. The treatment efficiency of NH_4-N, H_2S, and TSS were also high [25]. Traditional SBR has relatively lower treatment efficiency at 80% COD removal (**Table 3**).

The membrane reactors such as BAF, cross-flow membrane bioreactor (CF-MBR), membrane sequencing batch reactor (MSBR), and hollow fiber ultrafiltration membrane bioreactor (HF-UF MBR) including ultrafiltration MBR systems treating higher OLR or food to organisms' ratio can achieve over 80% COD removal (**Table 3**). MBBR system applying biofilm can achieve 74% COD removal at a high OLR of 4.2 kg COD/m^3·d (**Table 3**). It also can be seen that NH_4-N and H_2S removal are above 60% that cannot be obtained in anaerobic system. The Total Organic Compounds (TOC) and oil removal are also better than the anaerobic system.

Oilfield wastewater is relatively reluctant to aerobic digestion due to the complex ingredient. The removal efficiency of such water has a COD removal at around 30–74% (**Table 3**) by BAF, MBBR, etc. Active sludge process seems to handle well the wastewater and achieve high total petroleum hydrocarbon (TPH) removal.

The oily wastewater COD removal is generally high by using different aerobic methods, indicating its easily degradable nature (**Table 3**). The case study in Section 5 presents the advanced biofilm technology named CFIC process by Biowater Technology AS. The full-scale plant data show consistently high COD removal efficiency over 90%.

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4.3. Integrated biological process

The treatment efficiencies of individual anaerobic and aerobic systems show good capability in treating certain petrochemical wastewater. An integrated system combining anaerobic and aerobic processes can possibly take the advantages of both and achieve even better removal efficiency for chemicals that are not easily degraded by either anaerobic or aerobic process. An integrated system that is focused in this chapter can be a hybrid reactor consisting of an anaerobic and an aerobic system in a vertical design, such as a hybrid vertical flow anaerobic aerobic biofilm reactor (HyVAB) [9], provided by Biowater Technology AS, or a combination of different treatment processes in series, for example, a system consists of traditional anaerobic reactor and an aerobic stage in series. The performance of integrated systems for petrochemical refinery, oilfield-produced wastewater, and other oily wastewaters is presented in **Table 4**. The integrated system could effectively remove easily degradable COD in the anaerobic stage first and convert it to biogas with the residual COD and other chemicals such as ammonium, sulfide, etc. degraded in the aerobic stage (**Table 4**).

Hybrid system combining UASB and aerobic stage treating oilfield wastewater showed good effects on COD removal by enabling acidification prior to the aerobic stage where organisms are actively reacting with organic chemicals. The COD removal rates were over 70–95%. Oil and ammonia removal was also recorded over 87% (**Table 4**).

S. N	Types of wastewater	Treatment system	Operating conditions	Pollutants monitored	Removal efficiencies (%)	References
1	Oilfield produced	UASB coupled with immobilized biological aerated filters (I-BAFs)	HRT 12 h (Min)	COD NH_4^+-N SS	74 94 98	[39]
		UASB-two stage BAF	Temperature: 26–33°C	COD NH_4^+-N Oil PAHs	90.2 90.8 86.5 89.4	[3]
		hydrolysis, MBBR, O_3 and biological active carbon reactor		COD Oil Ammonia	95.8 98.9 94.4	[40]
2	Petroleum refinery	MBBR with anaerobic-aerobic (A/O)	HRT: 72 h HRT: 36 h	COD	<60 mg/L (effluent)	[41]
		UASB-aerobic packed bed biofilm reactor (PBBR)	0.5 kg COD/m^3.d Temperature: 35 ± 1 °C	COD PAHs	81.1 100	[42]
3	Oily wastewater	HyVAB reactor containing anaerobic and aerobic in vertical	To 23 kg COD/m^3.d	COD	86	[9]
		Bioaugmentation anoxic-oxic (A/O)	HRT 17.5 h	COD NH_4^+-N	91 89	[5]

Table 4. Overview of integrated treatment process of petrochemical wastewater.

For petrochemical refinery treatment, direct discharge of treatment effluents after combining anaerobic and aerobic MBBR system is possible. The PAH removal reached even 100% by combining the UASB and packed bed biofilm reactor (PBBL) at 0.5 kg COD/m^3·d (**Table 4**).

The pilot study of hybrid vertical flow anaerobic biofilm (HyVAB) treating oily wastewater had substantially high organic loading rate over 23 kg COD/m^3·d. The COD removal efficiency was consistently good over 86% [9]. A case study based on this HyVAB concept is followed in the next section with detailed performance data presentations and discussions.

5. Petrochemical wastewater treatment case study

Petrochemical wastewater of different sources, such as from manufacturing industries, auto repair shops, and washing water of oil tanks, is collected and delivered to a full-scale aerobic treatment plant at Bamble, Norway, for resource recovery and biological stabilization. The collected wastes are stored in storage tanks before being distilled to extract oil residuals. The wastewater after oil extraction still contains high COD and is therefore further treated by biological processes. The full-scale CFIC plant was designed and delivered by Biowater Technology AS and has been running continuously for 3 years. A pilot study of the integrated system HyVAB was also carried out on site of the full-scale plant running with the same feed water and the results showed good performance and can be referred to [9]. In this chapter, the full-scale CFIC operation data and a continuous study of HyVAB applying pure oxygen as aeration media are presented.

5.1. Full-scale CFIC treating petrochemical wastewater

The full-scale plant applies continuous flow intermittent cleaning biofilm (CFIC) technology. The CFIC technology is an advanced biofilm system based on MBBR concept. It is compact and is operated with alternating a normal and a washing mode while continuously feeding the reactor. CFIC contains highly packed biofilm carriers (over 90% filling ratio) to a degree that oxygen is utilized efficiently by enhancing gas transfer and limiting carriers' movement in the reactor. The biofilm grows in condition of sufficient oxygen, organic substrates, and nutrients. Excess aerobic sludge grown on the carriers' surface is washed off during the intermittent washing that helps maintain a thin and effective biofilm.

5.1.1. System layout

The full-scale plant layout is shown in **Figure 1**. Distilled wastewater is pumped to a conditioning chamber where nutrients are dosed and pH is corrected. Effluent from CFIC goes through chemical precipitation and DAF to remove solids before being discharged to the sea. Sludge is temporally stored and dewatered to be tanked away for specific treatment.

The full-scale system is treating wastewater of fluctuating concentrations with COD concentration ranging from 7 to 35 g/L at a designed daily flow rate of 240 m^3/d. The wastewater pH is around 5 and a total dissolved solid content of 4 g/L. BWTS® (Biowater Technology AS) with a surface area of 650 m^2/m^3 is applied as biofilm carriers in CFIC (**Figure 1**).

5.1.2. Operational results and discussion

Operational data of the full-scale plant in 2017 is summarized here. The COD feed to the reactor and the final effluent after DAF is shown in **Figure 2** together with removal efficiency. It shows that on average over 90% feed COD was removed by the system. At the early days of the year, sludge flocculation process chemical dosing was not well established; the total COD

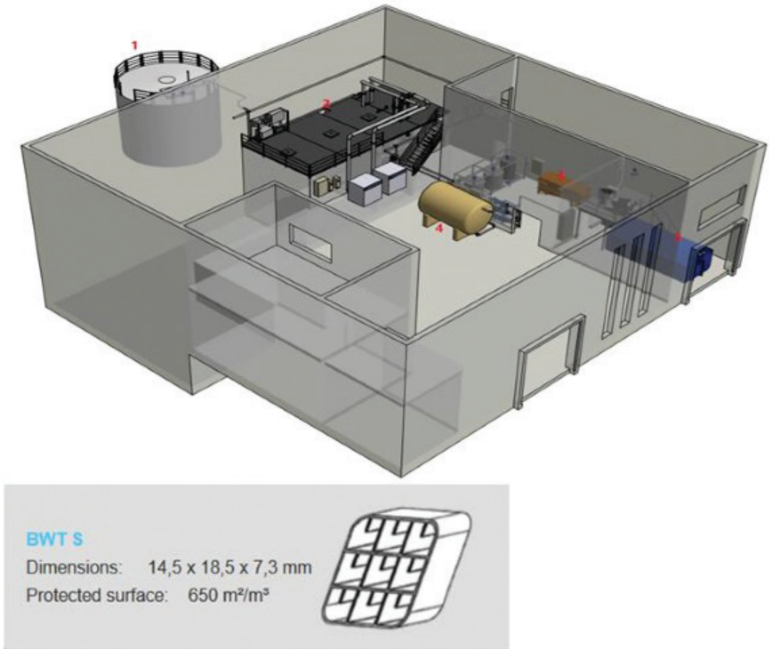

Figure 1. Up, layout of the full-scale CFIC plant with 1. Storage tank; 2. CFIC reactor; 3. DAF; 4. Sludge storage tank; 5. Dewatered sludge tanker. Down, applied BWTS® biofilm carriers.

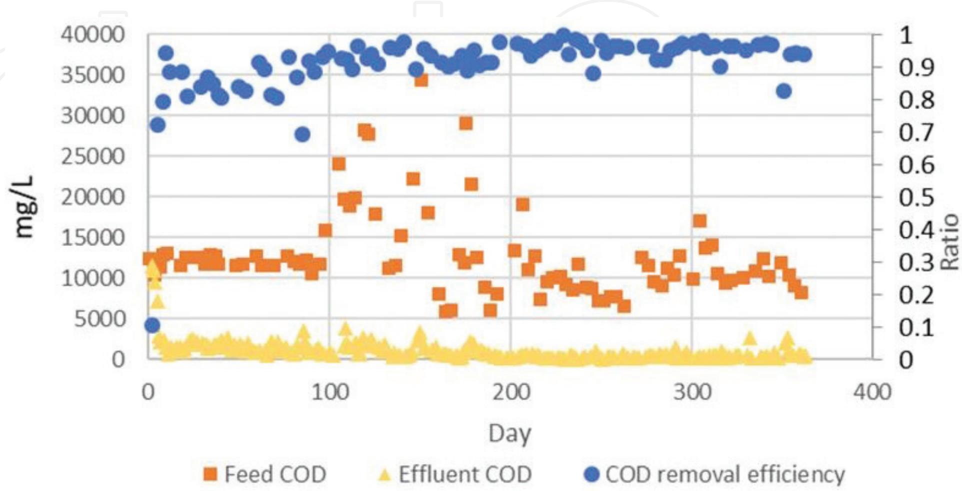

Figure 2. Feed and effluent total COD and COD removal efficiency.

removal was fluctuating around 80–90%. When the system was stabilized even high COD feed from 100 to 200 days did not reduce treatment efficiency. The high removal efficiency indicates that CFIC is a stable and robust system.

The suspended solid content of the final effluent shows that the average value was within 100 mg/L (**Figure 3**). The CFIC system running in normal mode generally worked as a filter bed which retains suspended solid in the reactor. When washing mode starts, raised water level in the reactor coupled with increased aeration induces a well-mixed moving bed biofilm system. The extra biofilm/sludge in carrier voids are washed off due to intensified shear force and are carried out of the system by continuous effluents. The washing washes away on average 30% of the total solids on the biofilm carriers.

5.2. Pilot study of HyVAB treating petrochemical wastewater using pure oxygen

The concept of the HyVAB system is illustrated in **Figure 4**. The system consists of a bottom anaerobic and a top aerobic biofilm stage in a vertical mode. Biogas generated from the anaerobic stage can be collected through the three-stage separator. Due to the close integration of two processes, the dissolved gases (methane, H_2S, etc.) in liquid that are generated in the AD stage will not be released to the atmosphere but captured and oxidized by aerobic organisms, avoiding a commonly observed emission problem in anaerobic treatment plants [43]. Returning of the excess aerobic sludge to the AD stage by gravity where the solids undergo stabilization simplifies the sludge treatment which also contributes to methane production. The detailed longer-term pilot study with reactor layout and performance can be referred to [9], where air was applied as aeration source.

This chapter presents the pilot study of pure oxygen effects on HyVAB performance. Oxygen aerations were known to be less energy intensive, high in efficiency, and give good biofilm development due to its close contact with biofilm layers. Results show that the HyVAB COD removal using air and pure oxygen reached similar ratios on average 94 and 85% for the soluble and total feed COD removal, respectively. Oxygen aeration minimized the flushing

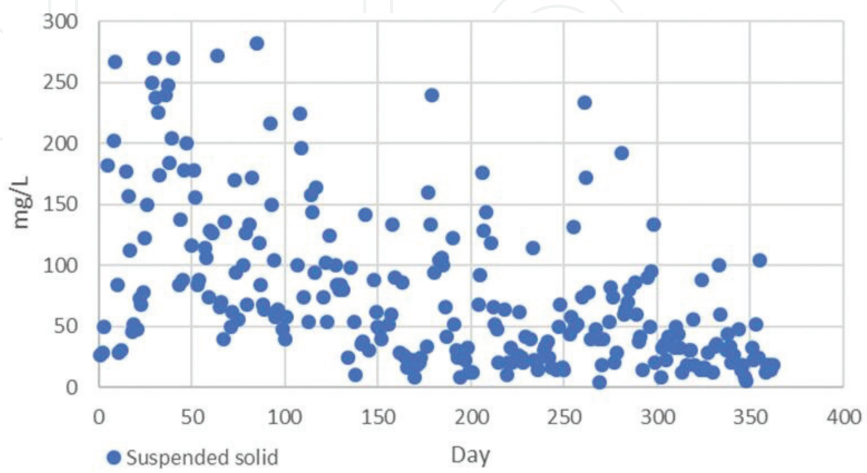

Figure 3. Effluent suspended solid concentration after DAF.

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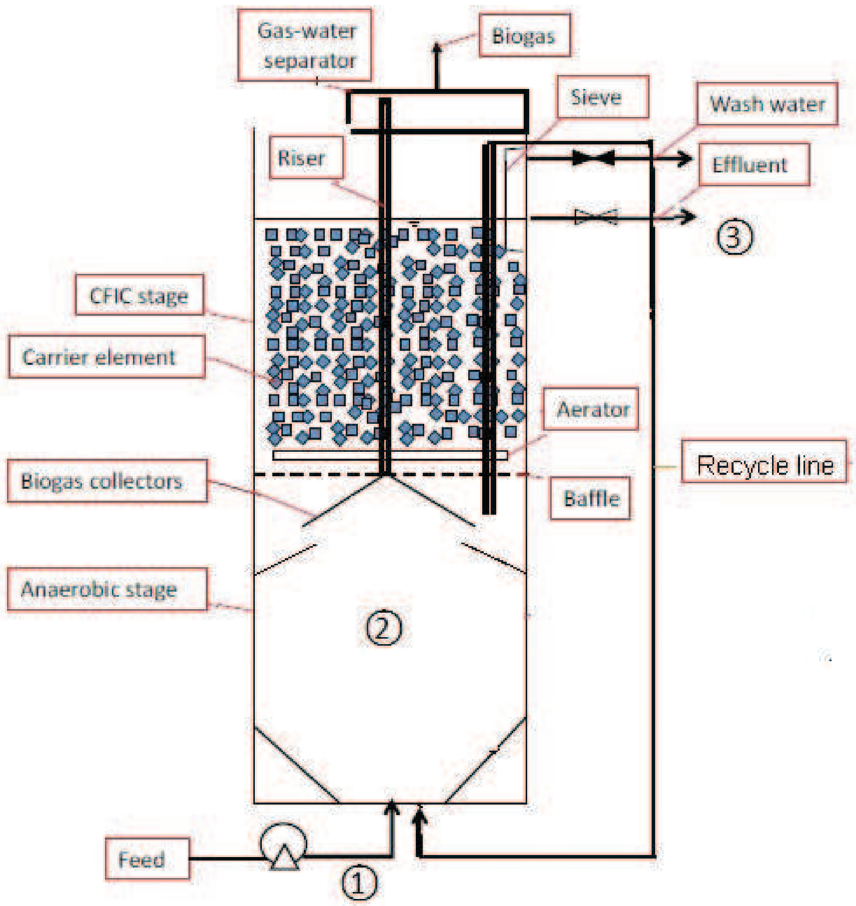

Figure 4. Sketch of the HyVAB (hybrid vertical anaerobic biofilm) bioreactor with the anaerobic stage at the bottom and a CFIC stage at the top. Numbers are sampling points.

effects on biofilm carriers and reduced the effluent suspended solid to 500 mg/L and effluent pH was overall 1.1 less than applying air aeration.

5.2.1. Experiment management

The anaerobic stage was filled with granular sludge, with relatively equal size (~2 mm) from an industrial wastewater treatment facility. Similar biofilm carriers (**Figure 1**) were used in the aerobic stage. Pure oxygen was applied as aeration oxygen source and air washing was introduced intermittently during the washing mode in the study. The pilot was running continuously for 115 days at 21 ± 2°C.

5.2.2. Operational results and discussion

With OLR increased gradually to close to 30 kg COD/m^3·d at lower HRT of 15 h, the HyVAB system still performed well with over 90% soluble COD removal when the oxygen aeration was introduced after 32 days (**Figure 5**). The air aeration was conducted before 31 days and the results were treated as reference. With oxygen aeration, the anaerobic stage generated high

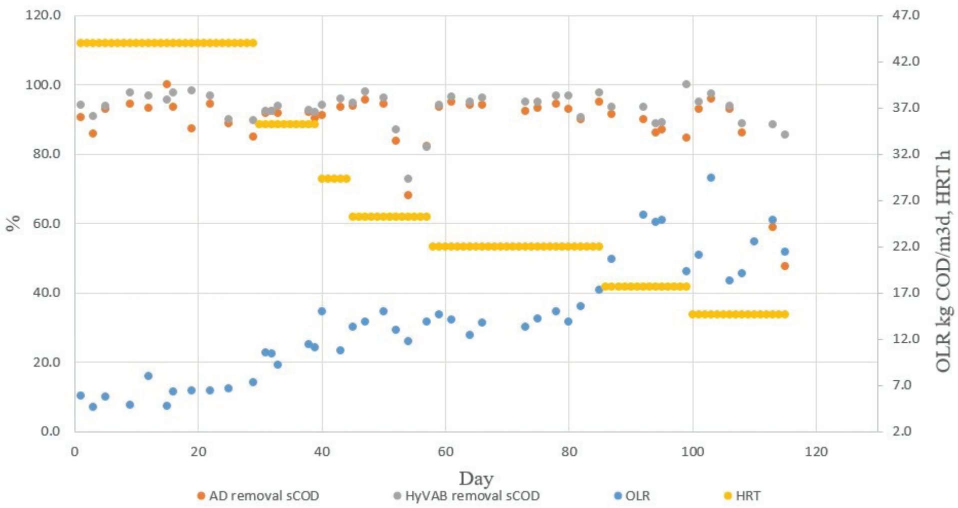

Figure 5. COD removal at different organic loading rate (OLR) and HRT.

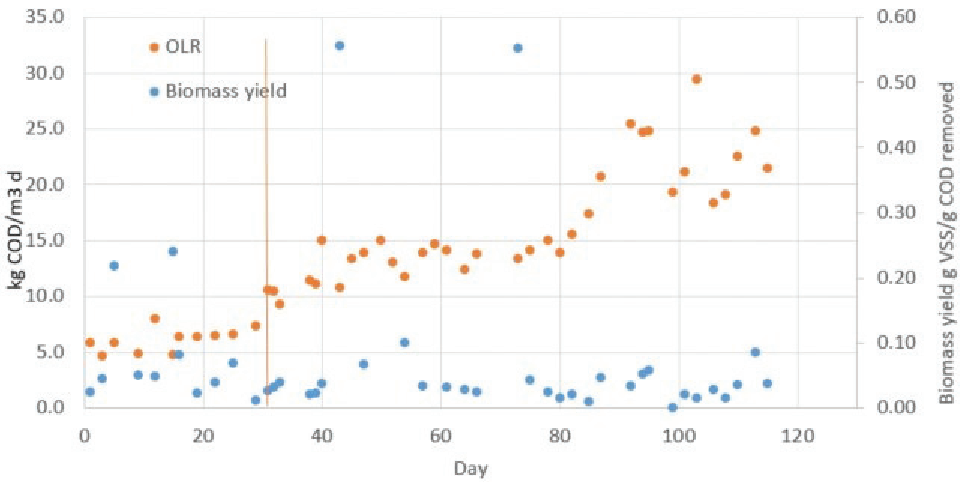

Figure 6. Biomass yield at different OLR and with/without oxygen aeration, vertical line separate air and oxygen aeration.

methane content biogas (82%) and the soluble COD removal efficiency was comparable with air aeration (**Figure 5**).

The sludge yield with oxygen aeration was at 0.04 g VSS/g $COD_{removed}$ and less variations showed comparing to the air aeration stage (**Figure 6**). The reasons can be that the fine bubbles of the aeration from oxygen did not give high shear force on the biofilm to scratch it off. The low mixing effects also retained the solids in the reactor. The low sludge yield at high organic loading rate indicates high efficiency of the HyVAB system in removing petrochemical organic substances. Consistently lower effluents of less than 500 mg/L were observed with oxygen aeration.

Some petrochemical wastewater contains high salinity and nutrients such as ammonia and phosphate, especially after anaerobic treatment. The high content of dissolved solids might

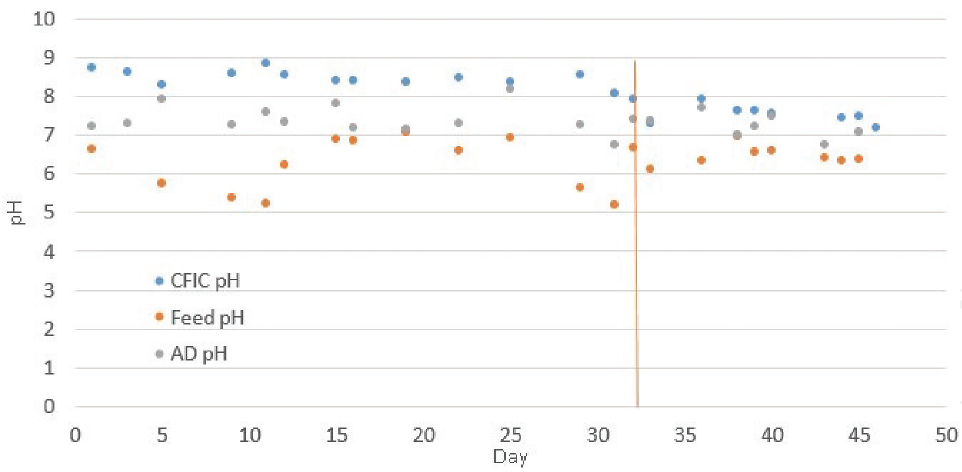

Figure 7. pH variations in different streams, vertical line separate air and oxygen aeration.

precipitate on biofilm carriers when pH is high and temperature is in good range. Oxygen aeration showed good pH control effects compared with air aeration which induced high pH (over 8.5) (**Figure 7**) in the aerobic stage. Good biofilm development was observed in the pilot test with such petrochemical wastewater and the scaling effects on carriers were minimal with oxygen aeration.

6. Conclusions and further study

Biological treatment of petrochemical wastewater is an economic and efficient waste stabilization method. The treatment of wastewater containing organic contaminants of refractory nature can be ineffective in biological treatments [44]. The challenges are as follows: (1) activated sludge method can fail while treating strong petrochemical wastewater with high COD concentration (>10 g/L) and contain some aromatic compounds (phenol and its derivatives, etc.); [45] (2) variations in the strength of the organic load due to various sources of petrochemical refinery can cause shock to the biomass; (3) petrochemical wastewater contains large amounts of volatile organic compounds (VOCs) and can cause odor and air pollutions around the biological treatments, and aerobic treatments like activated sludge should not be considered in this case; (4) oil, fat, and grease can cause floatation of the sludge and this can cause sludge washout ultimately failing the treatment system.

Application of certain organisms for specific wastewater components' treatment after secondary biological treatment can be a topic in the future. Isolation of specific bacteria to treat recalcitrant compounds can lead to effective removal, for example, the bacterium *Pseudomonas putida* to degrade phenolic compounds [7]. Integrated biological system showed general better performance for treating petrochemical wastewater; the synergistic effects of organisms of different originals such as from anaerobic combining aerobic might facilitate the recalcitrant organic removal. Also, reactor modification and microorganisms' isolation to handle complex petroleum wastewater treatment can be of great interest in coming days to reduce extra-treatment costs.

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Conflict of interest

There is no conflict of interest.

Notes/Thanks/Other declarations

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References

[1] Gutierrez E, Caldera Y, Fernandez N, Blanco E, Paz N, Marmol Z. Thermophilic anaerobic biodegradability of water from crude oil production in batch reactors. Revista Tecnica de la Facultad de Ingenieria Universidad del Zulia. 2007;**30**:111-117

[2] Llop A, Pocurull E, Borrull F. Evaluation of the removal of pollutants from petrochemical wastewater using a membrane bioreactor treatment plant. Water, Air, and Soil Pollution. 2008;**197**(1–4):349-359

[3] Zou XL. Treatment of heavy oil wastewater by UASB-BAFs using the combination of yeast and bacteria. Environmental Technology. 2015;**36**(18):2381-2389

[4] Tong K, Zhang Y, Liu G, Ye Z, Chu PK. Treatment of heavy oil wastewater by a conventional activated sludge process coupled with an immobilized biological filter. International Biodeterioration & Biodegradation. 2013;**84**:65-71

[5] Zhao X, Wang Y, Ye Z, Borthwick AGL, Ni J. Oil field wastewater treatment in biological aerated filter by immobilized microorganisms. Process Biochemistry. 2006;**41**(7):1475-1483

[6] Fakhru'l-Razi A, Pendashteh A, Abdullah LC, Biak DRA, Madaeni SS, Abidin ZZ. Review of technologies for oil and gas produced water treatment. Journal of Hazardous Materials. 2009;**170**(2–3):530-551

[7] Benyahia F, Abdulkarim M, Embaby A, Rao M. Refinery wastewater treatment: A true technological challenge. In: The Seventh Annual UAE University Research Conference; April 2006. UAE University

[8] Santo CE, Vilar VJP, Bhatnagar A, Kumar E, Botelho CMS, Boaventura RAR. Biological treatment by activated sludge of petroleum refinery wastewaters. Desalination and Water Treatment. 2013;**51**(34–36):6641-6654

[9] Wang S, Ghimire N, Xin G, Janka E, Bakke R. Efficient high strength petrochemical wastewater treatment in a hybrid vertical anaerobic biofilm (HyVAB) reactor: A pilot study. Water Practice Technology. 2017;**12**:501-513

[10] Vincent-Vela MC, Álvarez-Blanco S, Lora-García J, Carbonell-Alcaina C, Sáez Muñoz M. Application of several pretreatment technologies to a wastewater effluent of a petrochemical industry finally treated with reverse osmosis. Desalination and Water Treatment. 2015;**55**(13):3653-3661

[11] Wu C, Zhou Y, Wang P, Guo S. Improving hydrolysis acidification by limited aeration in the pretreatment of petrochemical wastewater. Bioresource Technology. 2015;**194**:256-262

[12] Verma S, Prasad B, Mishra IM. Pretreatment of petrochemical wastewater by coagulation and flocculation and the sludge characteristics. Journal of Hazardous Materials. 2010;**178** (1–3):1055-1064

[13] Lin CK, Tsai TY, Liu JC, Chen MC. Enhanced biodegradation of petrochemical wastewater using ozonation and BAC advanced treatment system. Water Research. 2001;**35**(3):699-704

[14] Li G, Guo S, Li F. Treatment of oilfield produced water by anaerobic process coupled with micro-electrolysis. Journal of Environmental Sciences. 2010;**22**(12):1875-1882

[15] Dai X, Chen C, Yan G, Chen Y, Guo S. A comprehensive evaluation of re-circulated biofilter as a pretreatment process for petroleum refinery wastewater. Journal of Environmental Sciences. 2016;**50**:49-55

[16] Jamaly S, Giwa A, Hasan SW. Recent improvements in oily wastewater treatment: Progress, challenges, and future opportunities. Journal of Environmental Sciences (China). 2015;**37**:15-30

[17] Diaz A, Rincon N, Martin J, Behling E, Chacin E, Debellefontaine H. Degradation of total phenol during biological treatment of oilfields produced water. Ciencia. 2005;**13**:281-291

[18] Gutierrez E, Caldera Y, Perez F, Blanco E, Paz N. Behavior of metals in water from crude oil production during thermophilic anaerobic treatment. Boletin del Centro de Investigaciones Biologicas. 2009;**43**(1):145-160

[19] Rincon N, Cepeda N, Diaz A, Behling E, Marin JC, Bauza R. Behavior of organic fraction in water separated from extracted crude oil with anaerobic digestion. Revista Tecnica de la Facultad de Ingenieria Universidad del Zulia. 2008;**31**:169-176

[20] Rincon N, Chacin E, Marin J, Moscoso J, Fernandez L, Torrijos M, Moletta R, Fernandez N. Optimum time of hydraulic retention for the anaerobic treatment of light oil production wastewater. Revista Tecnica de la Facultad de Ingenieria Universidad del Zulia. 2002;**25**:90-99

[21] Gutierrez E, Caldera Y, Contreras K, Blanco E, Paz N. Anaerobic mesophilic and thermophilic degradation of waters from light crude oil production. Boletin del Centro de Investigaciones Biologicas. 2006;**40**:242-256

[22] Caldera Y, Gutierrez E, Madueno P, Griborio A, Fernandez N. Anaerobic biodegradability of industrial effluents in a UASB reactor. Impacto Cientifico. 2007;**2**:11/23

[23] Gasim HA, Kutty SRM, Isa MH, Alemu LT. Optimization of anaerobic treatment of petroleum refinery wastewater using artificial neural networks. Research Journal of Applied Sciences, Engineering and Technology. 2013;**6**:2077-2082

[24] Ji GD, Sun TH, Ni JR, Tong JJ. Anaerobic baffled reactor (ABR) for treating heavy oil produced water with high concentrations of salt and poor nutrient. Bioresource Technology. 2009;**100**:1108-1114

[25] Mirbagheri SA, Ebrahimi M, Mohammadi M. Optimization method for the treatment of Tehran petroleum refinery wastewater using activated sludge contact stabilization process. Desalination and Water Treatment. 2013;**52**:156-163

[26] Thakur C, Srivastava VC, Mall ID. Aerobic degradation of petroleum refinery wastewater in sequential batch reactor. Journal of Environmental Science and Health. Part A, Toxic/Hazardous Substances & Environmental Engineering. 2014;**49**:1436-1444

[27] Pajoumshariati S, Zare N, Bonakdarpour B. Considering membrane sequencing batch reactors for the biological treatment of petroleum refinery wastewaters. Journal of Membrane Science. 2017;**523**:542-550

[28] Razavi SMR, Miri T. A real petroleum refinery wastewater treatment using hollow fiber membrane bioreactor (HF-MBR). Journal of Water Process Engineering. 2015;**8**:136-141

[29] Rahman MM, Al-Malack MH. Performance of a crossflow membrane bioreactor (CF–MBR) when treating refinery wastewater. Desalination. 2006;**191**(1–3):16-26

[30] Xie W, Zhong L, Chen J. Treatment of slightly polluted wastewater in an oil refinery using a biological aerated filter process. Wuhan University Journal of Natural Sciences. 2007;**12**:1094-1098

[31] Vendramel S, Bassin JP, Dezotti M, Sant'Anna GL Jr. Treatment of petroleum refinery wastewater containing heavily polluting substances in an aerobic submerged fixed-bed reactor. Environmental Technology. 2015;**36**:2052-2059

[32] Dong Z, Lu M, Huang W, Xu X. Treatment of oilfield wastewater in moving bed biofilm reactors using a novel suspended ceramic biocarrier. Journal of Hazardous Materials. 2011;**196**:123-130

[33] Tellez T, Gilbert NK, Gardea-Torresdey J. Performance evaluation of an activated sludge system for removing petroleum hydrocarbons from oilfield produced water. Advances in Environmental Research. 2002;**6**:455-470

[34] Campos JC, Borges RMH, Oliveira Filho AM, Nobrega R, Sant'Anna GL Jr. Oilfield wastewater treatment by combined microfiltration and biological processes. Water Research. 2002;**36**(1):95-104

[35] Shokrollahzadeh S, Azizmohseni F, Golmohammad F, Shokouhi H, Khademhaghighat F. Biodegradation potential and bacterial diversity of a petrochemical wastewater treatment plant in Iran. Bioresource Technology. 2008;**99**:6127-6133

[36] Ma F, Guo JB, Zhao LJ, Chang CC, Cui D. Application of bioaugmentation to improve the activated sludge system into the contact oxidation system treating petrochemical wastewater. Bioresource Technology. 2009;**100**(2):597-602

[37] Scholz W, Fuchs W. Treatment of oil contamintaed wastewater in a membrane bioreactor. Water Research. 2000;**34**:3621-3629

[38] Chavan A, Mukherji S. Treatment of hydrocarbon-rich wastewater using oil degrading bacteria and phototrophic microorganisms in rotating biological contactor: Effect of N:P ratio. Journal of Hazardous Materials. 2008;**154**:63-72

[39] Liu G-h, Ye Z, Tong K, Zhang Y-h. Biotreatment of heavy oil wastewater by combined upflow anaerobic sludge blanket and immobilized biological aerated filter in a pilot-scale test. Biochemical Engineering Journal. 2013;**72**:48-53

[40] Zheng T. A compact process for treating oilfield wastewater by combining hydrolysis acidification, moving bed biofilm, ozonation and biologically activated carbon techniques. Environmental Technology. 2016;**37**:1171-1178

[41] Lu M, Gu LP, Xu WH. Treatment of petroleum refinery wastewater using a sequential anaerobic-aerobic moving-bed biofilm reactor based on suspended ceramsite. Water Science and Technology. 2013;**67**:1976-1983

[42] Nasirpour N, Mohammad Mousavi S, Shojaosadati SA. Biodegradation potential of hydrocarbons in petroleum refinery effluents using a continuous anaerobic-aerobic hybrid system. Korean Journal of Chemical Engineering. 2015;**32**:874-881

[43] Daelman MR, van Voorthuizen EM, van Dongen UG, Volcke EI, van Loosdrecht MC. Methane emission during municipal wastewater treatment. Water Research. 2012;**46**(11): 3657-3670

[44] Bahri M, Mahdavi A, Mirzaei A, Mansouri A, Haghighat F. Integrated oxidation process and biological treatment for highly concentrated petrochemical effluents: A review. Chemical Engineering and Processing Process Intensification. 2018;**125**:183-196. DOI: 10.1016/j.cep.2018.02.002

[45] Debellefontaine H, Chakchouk M, Foussard J, Tissot D, Striolo P. Treatment of organic aqueous wastes: Wet air oxidation and wet peroxide oxidation. Environmental Pollution. 1996;**92**(2):155-164

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