# Biological treatment of fuel wastewater generated from a thermal power plant by continuous and discontinuous aeration

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# **ABSTRACT**

The National Electricity Office of Mohammedia (Morocco) is an electricity production plant with the aid of boiler cells using coal and fuel oil as energy source. The operation of this process consumes a large quantity of water for washing the fuel oils to feed and heat the boilers, which could have a significant production of pollutant-laden wastewater. Wastewater must be treated before discharge into the marine environment. In this study, the process of biodegradation of organic materials by continuous or discontinuous aeration was carried out. The fuel oil washing wastewater is too loaded with pollutants with a chemical oxygen demand (COD) of 7.5 kg/m<sup>3</sup> and biochemical oxygen demand  $(BOD<sub>5</sub>)$  around 4 kg/m<sup>3</sup>. After 9 d of operation, the continuous and discontinuous aeration resulted in an elimination of 96%, 97% and 86% respectively for turbidity, BOD<sub>5</sub> and COD. In addition, both treatment methods showed removal rates of pollutants such as phenol, nitrate, total phosphorus and total Kjeldahl nitrogen, 82%, 86%, 83% and 47% respectively. No significant difference was observed between continuous and discontinuous aeration. This shows that discontinuous or continuous aeration could be very interesting for the decontamination of fuel oil washing water.

*Keywords:* Wastewater; Biological treatment; Fuel wastewater; Continuous aeration; Discontinuous aeration

# **1. Introduction**

Economic development has contributed to the increase in the amount of water used and therefore the amount of wastewater generated. Thus, in recent years, the problem of water and wastewater management has become a very important issue for both developed and developing countries. The priority issues for local governments

are those linked to ecology, and therefore to the quality of wastewater discharged into the environment [1,2].

The water and wastewater treatment industry has experienced significant progress over the past decades [3,4]. However, there is no doubt that water contamination has also increased sharply due to uncontrolled industrial development [5,6]. As a result, the available water resources have been contaminated with a wide range of contaminants generating various health problems [7,8].

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The production technology of electricity by the National Office of Mohammedia, is based on boilers using fuel oil as an energy source after washing to remove impurities such as suspended matter and catalysts with a high production of wastewater, since the thermal power station operates 24/7. Wastewater washing is generally laden with various contaminants and must be treated before it is released into the environment. Thus, the study on the treatment of wastewater from fuel washing is very important and requires special attention.

The power station is located on the coast and the wastewater produced should not be discharged into the marine environment without treatment. Indeed, Moroccan regulations require treatment of the effluent before discharge. This fuel wash water can have a considerable impact on the environment especially on the marine environment, as it can contain large amounts of organic contaminants high concentrations of heavy metals and inorganic salts and inorganic compounds. Hydrocarbons are the main constituents of fuel oil wash water. Pollutants can be thought of as a mixture of several acidic, basic and neutral compounds. Acidic components include acids and phenols, basic components include nitrogen compounds, and neutral components include polyaromatic compounds. The main component of inorganic residues is ammonia and low concentrations of H<sub>2</sub>S and chlorides. Considering the high content of biodegradable organic compounds, pollutant-laden wastewater (FWW) appears to be a very promising raw material for microbial degradation. However, biological treatment of wastewater from fuel plants is difficult because its composition is not suitable for microbial growth due to the high concentrations of hydrocarbons. Wastewater has a high pH and is poor in nutrients necessary for microbial growth and changes over time except for the carbon source (residual oil, methanol and glycerol), therefore minimum amounts of important nutrients should be added. Methanol is a good substrate for microorganisms because of the high concentrations in wastewater, which promotes rapid microbial growth [9]. This can be useful in a biological treatment of FWW containing slowly degradable residual oils. If not treated and safely disposed of, FWW could be a potential source of contamination of seawater, surface water and groundwater, as it could percolate through soils and basements, causing thus pollution. FWW treatment would be required prior to discharge to the sea. Due to changes in the composition of drinking water over time, wastewater control systems would have to adapt to these changes. FWW treatment is necessary to remove all contaminating components from FWW and bring it to a standard that allows it to be released into the marine environment. Thus, the wastewater generated must be treated and/or regenerated in the most economical and ecological way possible to save both energy and the environment [10].

Recently, some countries in the Near East region (TNS) have limited the discharge of effluents laden with pollutants into the marine environment. The efficiently treated wastewater is directly used in the irrigation of green spaces. Several treatment techniques have been used, such as chemical and biological treatments, to reduce the polluting nature of the effluents of several wastewaters have been used. Studies [11,12] show that biological treatments are effective methods for the degradation of organic pollutants in wastewater with high concentrations of pollutants [13]. Aerobic systems, such as aerated lagoons or activated sludge units, are frequently used to remove pollutants from hydrocarbon-rich industrial wastewater, despite the generation of large amounts of sludge that must be treated and disposed of. Anaerobic digestion represents a less expensive alternative in terms of energy consumption for the treatment of sludge, which makes it possible to produce biogas (methane) which could cover part of the energy required by the plant [14].

However, anaerobic digestion has certain drawbacks in the case of sludge waste rich in pollutant which is difficult to biodegrade, such as the presence of phenolic compounds toxic for methanogenic bacteria and inhibiting the efficiency of this anaerobic process.

The physical, chemical, physico-chemical, electrochemical, biological and integrated treatment processes of wastewater rich in toxic compounds and the performance of biological processes are improved by the pretreatment of wastewater [15]. In addition, many physical and chemical separation processes such as coagulation [16], acidification [17] and membrane processes [18] physico-chemical [19,20], physical, chemical, electrochemical treatment, biological [11,21], anaerobic digestion [22] had been used for the reduction of toxic pollution of wastewater laden with hydrocarbons and heavy metals. Various technologies of wastewater treatment by biological means have recently been adopted for depollution of discharges loaded with hydrocarbons remains ineffective [22]. In addition, among the most effective treatment methods is adsorption which has been proposed as the most reliable technology compared to other methods [23,24]. Activated carbons (ACs) have been widely used as adsorbents due to their surface properties such as extended area, porosity, and favorable surface characteristics [25]. These processes alone do not produce treated water that meets oil refinery discharge standards [26,27]. The proper method which gives the best permeate requires a series of pre- and post-treatment operations to remove various contaminants [28]. Pretreatment involves separation techniques such as removal of oil, grease, suspended solids, microfiltration, ultrafiltration, direct osmosis, etc. The post-treatment focuses on the elimination of organic compounds by electro flocculation, adsorption, and bioreactors [28]. The objective of this work is to simulate the reduction of pollution linked to hydrocarbons by biological means by the efficiency of continuous and discontinuous aeration processes in order to reduce turbidity, total suspended solids (TSS), biochemical oxygen demand (BOD<sub>5</sub>), chemical oxygen demand (COD), phenol, nitrate, total Kjeldahl nitrogen (TKN) ammoniac nitrogen, total phosphorus (TP) and surfactant, and compare the efficiency between continuous and discontinuous aeration. In addition, the operating conditions of this inexpensive technique are optimized to effectively reduce pollution.

## **2. Materials and methods**

#### *2.1. Presentation of the National Electricity Office*

The Mohammedia Thermal Power station (TPP) is the second largest electricity production unit at the national level after that of Jorf Lasfar. The TPP consists of four 150 MW units for each unit, two of which run on coal and two more on fuel (oil). The plant produces 3,000 GWh, of which 46% compared to ONE production, and 15% compared to national production.

# *2.2. Sample collection and experimental procedure*

The wastewater used for the study was collected for 48 h at a rate of 2 L/h. Several sampling campaigns were carried out during a year. The samples were stored in a cold room at 4°C before being analyzed. To examine the aerobic process, the FWW was placed in two 10 L glass reactors labeled R1 and R2 (Fig. 1). A magnetic stirrer was then placed under each reactor. The samples were stirred continuously until the end of the experiment.

The FWW in reactor R1 was aerated continuously, while the FWW in reactor R2 was aerated batch wise (30 min aeration per hour) using a time controller. Aeration was carried out using air pumps with diffusers, with a flow rate of 160 L air/h. Samples were taken for microbiological enumeration and analysis of the various physicochemical parameters such as dissolved oxygen (DO), turbidity, COD elimination, TSS elimination,  $BOD<sub>5</sub>$  elimination, ammoniacal nitrogen, nitrate, phenol, TP, pH and conductivity.

#### *2.3. Analysis methods*

The pH was measured using a pH meter OHAUS STARTER 3100. Turbidity was measured using a HACH  $2100$ N Turbidimeter.  $BOD_5$  was determined by incubating the samples in the dark for 5 d at 20°C using a Velp Scientifica sensor system according to the APHA standard [29]. The COD was determined by the potassium dichromate method according to the AFNOR standard NF T90-101. The determination of TSS was conducted by the centrifugation method according to the AFNOR standard NF T 90-105-2. The phenolic compounds were analyzed using the Folin-Ciocalteu assay, after leaving the sample for an hour in the dark the absorption was measured at 725 nm by a UV-visible spectrophotometer [30]. The nitrate ion  $(NO<sub>3</sub><sup>-</sup>)$  was determined with sodium salicylate by quantifying the formation of yellow sodium paranitrosalicylate which was analyzed at 415 nm by UV-visible spectrophotometry [31]. The concentration of ammonium



Fig. 1. Experimental setup.

(NH<sub>4</sub>) was measured by a spectrophotometric method with blue indophenols according to AFNOR NF T 90-015-2. The oil and grease were determined according to standard method 1164, EPA. The anionic surfactant concentration was analyzed by using solvent extraction and spectrophotometric quantitative determination with ethyl violet method. The removal efficiency of pollutant concentrations was calculated accordingly using the formula given below [32]:

$$
Removal\% = \left(1 - \frac{C}{C_0}\right) \tag{1}
$$

where  $C_0$  and  $C$  are concentrations of wastewater before and after coagulation–flocculation in NTU or mg/L.

#### **3. Results and discussions**

# *3.1. Physico-chemical characterization of the effluent*

The characterization of the FWW is shown in Table 1.

The results of the characteristics showed that the FWW is highly loaded with pollutants, in particular COD,  $BOD_{5'}$ TSS, etc. which had values of 7200, 3821 and 535 mg/L respectively. It should be mentioned that FWW has a pH value varying around 8.17, compatible with the biodegradability of organic materials since the  $BOD<sub>5</sub>/COD$ ratio > 0.53 (Table 1).

In addition, the concentration of phenol and surfactant show values of 83.3 and 188.5 mg/L respectively, which could pose enormous problems for the marine environment, knowing that the wastewater at the level of the TPP of the company is released into the marine environment without any prior treatment. In addition, the  $NH<sub>4</sub><sup>+</sup>$  concentration value varies around 107.6 mg/L while the total phosphate shows a concentration of 102 mg/L. This could have a considerable impact on the marine environment.

Table 1

Physicochemical characteristics of fuel wastewater

Physico-chemical parameters		Literature data <sup>a,b,c</sup>
Turbidity (NTU)	4,000.00	$17.36 - 98.00$ a,c
Conductivity $(\mu S/cm)$	628.00	$1,680$ <sup>d</sup>
Temperature $(^{\circ}C)$	19.80	
pH	8.20	$9.20 - 7.60^{a,b}$
$BOD5$ (mg/L)	3,821.20	270.00-4,047.00a,b
$COD$ (mg/L)	7,200.00	$550.00 - 8,100.00^{a,b}$
BOD <sub>5</sub> /COD	>0.5	
TSS (mg/L)	535.00	$19.50 - 231.50^{a,b}$
Phenol $(mg/L)$	83.30	$2.44 - 238.09$ a,d
Surfactant (mg/L)	188.50	
Ammoniacal nitrogen (mg/L)	107.60	$9.80 - 15.00$ <sup>b,c</sup>
Nitrate $(mg/L)$	7.40	
Total phosphorus (mg/L)	102.07	$8.00^{b}$
$TKN$ (mg/L)	202.50	40.00 <sup>b</sup>
OD (mg/L)	1.04	

*a* [16]; *<sup>b</sup>* [33]; *<sup>c</sup>*

# *3.2. Variation of pH, T°C, conductivity and O<sub>2</sub>*

In this study, the pH of the FWW is mainly in the 8.17. However, during aeration the pH decreases in some cases up to 7.7 (Fig. 2a). The effect of the initial wastewater pH on the pollutant removal was evaluated over a pH of 7.7 using the continuous and discontinuous aeration, time of 15 d. As clearly seen in (Fig. 2a), the aeration capacity changed significantly as a function of initial pH of wastewater, indicating that the pollutants in fuel wastewater were significantly removed in either acid or basic environments. Degradation in biological systems can be significantly affected by temperature fluctuations and microbial metabolism may even be altered if temperatures exceed 39°C. Optimum temperature for microbial growth is therefore between 15°C and 39°C [36]. On the contrary,

Prachand stipulated that anaerobic treatment systems can operate at temperatures ranging between 10 and 60°C [37]. However, there are two main types of microorganisms (i.e., acidogens and methanogens) present during wastewater treatment. In addition, the pH of the wastewater solution affects not only the treatment biological of the aeration but also the chemistry of the pollutants in the fuel wastewater [38]. The optimum pH for methanogenesis (i.e., production of methane by methanogenic bacteria) is between 7.8 and 8.2, while the optimum pH for acidogenesis (i.e., production of acid by acidogenic bacteria) is between 5.5 and 6.5. The optimum pH for the co-existence of methanogens and acidogens is between 6.8 and 7.4 [38].

The explanation of this is that, under acidic environment, the hydrogen atom  $(H<sup>+</sup>)$  in the solution could



Fig. 2. Variation of (a) pH, (b) oxygen concentration, (c) temperature and (d) conductivity in the effluent during operating period.

protonate the amine groups  $(-NH_2)$  of chitosan (Eq. (2)), resulting to the increase of pH [39].

$$
R' \_NH_2 + H^+ \to R' \_NH_3^+
$$
 (2)

In addition, these effluents are rich minerals, the electrical conductivity that reflects ionic concentration of around 628 uS/cm (Table 1) and reach 391 uS/cm (Fig. 2d). These important values of conductivity are due to the use of large quantities of salts for the manufacturing process. These high levels are due, in particular, to the presence of the heavy metals in the effluent.

The variation of oxygen  $(O_2)$  concentration for continuous and discontinuous aeration is illustrated in Fig. 2b. The oxygen concentration varies between 3.8 and 2.4 mg/L.

This variation is accompanied by the biomass development, which varies between 5.7 and 2.3  $log_{10}$  CFU/ml in both cases (Fig. 9). This change is accompanied by the growth of microorganisms that are naturally found in the FWW; these microorganisms consume  $O_2$  necessary for their growth. The degradation of the organic matter present in the wastewater is carried out by heterotrophic bacteria.

The variation of temperature during the period of study is given in Fig. 2c.

The temperature during continuous and discontinuous aeration varies from 19.5°C to 21.8°C. The temperature can strongly influence the development of biomass and subsequently the biodegradation of organic pollutants, whereby the metabolic activity of organisms (heterotrophic bacteria) accelerates when the temperature of the FWW increases.

During the 15 d follow-up, the highest values of conductivity were observed at the beginning and at the end of aeration (768.1 uS/cm in the case of continuous aeration and 720.9 uS/cm in the case of discontinuous aeration). While between 4 day and 9th day of aeration, it was observed that the conductivity decreased to 390.3 uS/cm (Fig. 2d). These values may imply that the decrease in conductivity is influenced by the presence of microorganisms naturally

present in the FWW of the biomass, indicating a strong correlation between electrical conductivity and biomass.

# *3.3. Variation of turbidity removal*

Continuous and discontinuous aeration were used as design factors for search of the optimum via statistical design of experiments. Turbidity was selected as optimization parameters.

The separator constructed for this purpose proved to be suitable for fast and reliable investigation of multivariable systems and for search of the optimum via statistical design of experiments. It is deduced that the turbidity depends strongly on time of aeration.

With regards to turbidity, the results obtained showed that continuous and discontinuous aeration resulted in a decrease in turbidity 85% on day 1 (Fig. 3b), changing from initial characterization the fuel 4,000 to 577 and 160 NTU (Fig. 3a) after treatment by continuous and discontinuous aeration, and 88% after 5 d. This shows that aeration has an effect on the reduction of the average particle size by degradation of organic. The aeration appears to be the most important factor in the removal of turbidity. The results obtained showed that the time plays an interesting role in the reduction of turbidity (96%) for the both aeration process on day 15 corresponding a decreases of concentration to 154 and 160 NTU by continuous and discontinuous aeration, respectively. However, in other study of tannery wastewater the initial turbidity (332 NTU) was reduced by 97% [40].

# 3.4. Removal of COD, BOD<sub>5</sub> and TSS

Biological treatment is the one of the good solution important advanced process have recently using for several organic pollutants in wastewater [41,42].

The results of COD are illustrated in (Figs. 4a and b). It can be observed that the value of COD decreases from



Fig. 3. Variation of (a) turbidity concentration and (b) turbidity removal, in the effluent during operating period.

7,200 to 960 mg/L (Fig. 4a), with a removal efficiency of 86% (Fig. 4b) on day 8. The high COD removal is explained by high levels of biodegradable organics in the reject water. However, the percentage removal of the COD in the case of continuous aeration remains almost the same thing that in the case of discontinuous aeration. In addition, it was observed low COD removed using the hybrid vertical anaerobic biofilm reactor (HyVAB) for reject water which



Fig. 4. Variation of (a) COD concentration, (b) COD removal, (c) BOD<sub>5</sub> concentration, (d) BOD<sub>5</sub> removal, (e) TSS concentration and (f) TSS removal, in the effluent during operating period.

was just 20%, explaining this reasonable is because the Knarrdalstrand wastewater treatment plant (KWWTP)'s anaerobic digestion (AD) reactors utilize most of the BOD for biogas production [43].

The results of removal of  $BOD<sub>5</sub>$  by continuous and discontinuous aeration are illustrated in (Figs. 4c and d). It is observed that the value of  $BOD<sub>5</sub>$  changes from 3821.2 to 105.6 mg/L on day 7 until the end of treatment (Fig. 4c), with a removal efficiency of 97% (Fig. 4d). The percentage of removal of  $BOD_5$  in case of continuous aeration is the same as for discontinuous aeration.

Aeration has allowed the introduction of oxygen into the FWW, facilitating the intensification of bacteria activity.

However, in other study of malt whisky wastewater, the batch aerobic reactors were operated for 15 d. Effluent COD was measured on days 0, 1, 2, 6, 15, and  $BOD_5$  was measured on days 0, 10, 15. On day 15, the effluent COD concentrations were 649 mg/L, as opposed to the influent 1,476 mg/L. The  $BOD_5$  effluent concentrations were 90 mg/L at this day vs. 323 mg/L on day 1. The experimental results by electrochemical-oxydation of the reactor for 16 d show that the integrated treatment process could reduce COD and  $\mathrm{BOD}_5$  levels by 79% and 71%, respectively [44]. Such a quick removal of easily biodegradable substrates in the reactor due to storage of polymers in microbial cells or absorption of organics on granules in the feeding phase favors stable granulation [45].

This enables the degradation of the biodegradable organic material present in the FWW, which results in decreased values of  $BOD_5$  (Fig. 4c).

It is important to note that after 8 d of aeration, the redox potential is reduced (reduction of the bacterial environment), thus constituting a limiting factor of the bacterial activity. It then becomes increasingly difficult to transform the organic biodegradable material; therefore, the  $BOD_5$  value is stabilized. As shown in (Fig. 9), the bacterium bounces and begins a new cycle of DO consumption, resulting in the degradation of remaining organic matter (decreased  $\mathrm{BOD}_5$  values).

The results of the removal of TSS in FWW are as presented in (Figs. 4e and f). The results showed that both continuous and discontinuous aeration process provides removal more effective with time. Percentage removal of TSS is 53% of continuous aeration and 61% of discontinuous aeration (Fig. 4f) after 4 d. Results showed that the removal increased until 5 d and reached an optimum value, the removal started to decrease.

#### *3.5. Removal of total phosphorus*

Large differences in the TP removal of the FWW were observed between continuous aeration water in reactor R1 and discontinuous aeration in reactor R2.

Figs. 5a and b represent the TP concentration in the FWW obtained during the operating period. The TP concentration decreased from initial concentration 40.83 to 6.6 mg/L (Fig. 5a) on day 6 corresponding to 83% removal in the case of continuous aeration (Fig. 5b). In the case of discontinuous aeration the concentration decreased from initial total phosphorus 40.83 to 7.53 mg/L on day 7 (Fig. 5a) corresponding to 64% (Fig. 5b) of total phosphorus removal. Consequently, the removal efficiency of the continuous aeration is 19% higher than the discontinuous one.

A higher removal for phosphorus it is essential to attain almost complete removal of nitrate by aeration. It could be concluded that the TP removal mainly depended on biological assimilation in this period.

Other study by screening microalgae native to Quebec for wastewater treatment and biodiesel production, most of the strains removed only around 20%–30% of the phosphate [46].

The efficiency of the reactor in phosphorus removal was evaluated in cold and warm seasons in order to assess the effects of environmental conditions (i.e., temperature as the most important parameter) between 10 and 50% in the warm season with a mean temperature of 21°C–28°C and the highest efficiency was reported for 21°C [44].



Fig. 5. Variation of (a) total phosphorus concentration and (b) total phosphorus removal, in the effluent during operating period.

## *3.6. Removal of nitrate and TKN*

The results of the removal of nitrates and TKN from FWW are given in (Figs. 7a and b).

By nitrification, ammonium ions are transformed into nitrites and then into nitrates, which makes it possible to increase the concentration of nitrates in the wastewater. In fact, nitrates in turn transform into N2, a gas that escapes into the air according to the following reactions [43].

Figs. 7a and b show the evolution of the nitrate concentration and the percentage of elimination over time. The results obtained show that the nitrate concentration decreases from 5 to 0.5 mg/L with an elimination percentage of almost 100%. Moreover, the TKN goes from 200 to 100 mg/L with a yield of 50% reduction after 7 d of operation to increase again in the medium. This can be due to the transformation of nitrogenous organic compounds into nitrates.

Based on the observation of various parameters during the Continuous and discontinuous aeration treatment, the TKN removal mechanism is proposed in the following

routes: (1) cleavage of  $R\text{-}NH_2$  bond in organic nitrogen by aeration hydroxylation (Eq. (5)), (2) oxidation of  $NH<sub>3</sub>$  by •OH and subsequent dehydration reaction (Eq. (6)) and/ or (3) oxidation of  $NH<sub>3</sub>$  by hydroxyl radical ('OH) formed during the photocatalytic process (Eq. (7)).



Fig. 6. Nitrification, denitrification, and the shortcut mechanism illustrated with oxidation states of nitrate [43].



Fig. 7. Variation of (a) nitrate concentration, (b) nitrate removal, (c) TKN concentration and (d) TKN removal, in the effluent during operating period.

$$
R\text{-}NH_2 + H_2O \xrightarrow{MW} R-OH + NH_3 \tag{3}
$$

$$
NH_3 \xrightarrow{\cdot \text{OH}} NH_2 \xrightarrow{\cdot \text{OH}} NH_2 \xrightarrow{\cdot \text{OH}} NH \xrightarrow{\cdot \text{OH}} N
$$
\n
$$
(4)
$$

$$
NH_3 \xrightarrow{\text{CH}} HONH_2 \xrightarrow{\text{CH}} NO_2 \xrightarrow{\text{CH}} NO_3 \qquad (5)
$$

## *3.7. Removal of phenol*

The results of the removal of phenol from FWW are given in Figs. 8a and b. Phenol is a highly toxic product for the environment, elimination of wastewater before discharge into the receiving environment is necessary

The result indicates that the percentage of phenol removal varied from day to day during continuous and discontinuous aeration.

The aeration could have a considerable impact on the degradation by chemical oxidation and by biological means by an active biomass capable of degrading the phenolic compounds. The biodegradation of the latter is function of the biomass and the concentration of phenolic compounds. During continuous and discontinuous aeration tests, it is observed that the biodegradation varies over time. During the 10th day, the elimination yield is zero and subsequently increases from 11 d. This floctuation is due to the biomass and can be inhibited by the phenol of the medium.

## *3.8. Bacteriological analysis*

The study of the sequential evolution of the heterotrophic bacteria of the FWW of reactor R1 (continuous aeration) and of reactor R2 (discontinuous aeration) is mentioned in Fig. 9.

When the aeration pumps were implemented, the DO in the FWW was consumed (aerobic decomposition) by heterotrophic bacteria. This shows that the activity of strict

aerobic bacteria which degrades organic matter develops efficiently.

Aeration allows the multiplication of microorganisms up to 5.70 log10 CFU/ml, while the count for discontinuous aeration is 4.89 log10 CFU/ml between 7–9 d, and thus explains the importance of the presence of oxygen by aeration in the development of microorganisms necessary for the degradation of the load of organic matter (Fig. 9).

# *3.9. Comparison literature data with obtained results*

Due to the high amount of wastewater (containing high COD, BOD, and TSS, etc) produced from FWW during water washing fuel, FWW should be treated effectively. Although the continuous and discontinuous aeration process is one of the attractive and efficient treatment methods, there is only one study which investigated the treatment of



Fig. 9. Sequential evolution during operating period of heterotrophic bacteria.



Fig. 8. Variation of (a) phenol concentration and (b) phenol removal, in the effluent during operating period.

fuel wastewater from petroleum refineries and few studies of petroleum refineries as biodiesel wastewater and petroleum refinery wastewater, etc by the biological treatment so far. Richard and Luthy investigated the biological treatment process by air activated sludge for the synthetic fuel wastewater treatment. The authors that ammonia stripped wastewater could be processed reliably at 33% strength at substrate removal rates less than approximately 0.6 mg COD removed/mg MLVSS-day. The wastewater when diluted to 33% strength contained highest reported concentration of organic contaminants in coal conversion effluents processed successfully by air activated sludge [47].

On the other hand, Grobbelaar examined the treatment of biodiesel wastewater by the biological treatment process using a hybrid anaerobic baffled reactor microbial fuel cell (ABR-MFC) system. The authors combined the conventional anaerobic baffle reactor (ABR) system with microbial fuel cell (MFC) technology, which resulted in an innovative technology used to treat high strength industrial biodiesel wastewater under conditions ambient. Numerous studies have reported effective treatment of biodiesel wastewater. ABR-MFC has been successful in reducing COD and TSS by 64.55% and 98.55% [38] of wastewater from petroleum refineries, respectively.

Other studies using a membrane bioreactor have shown efficiency of COD (78%–98%), BOD<sub>5</sub> (96%–99%), SS (74%–99%) and turbidity (99%–100%) of refinery wastewater of petroleum [48].

These biological treatment results can be compared to other methods of physical and chemical treatment of wastewater from petroleum refining which have been carried out using different methods (electrocoagulation (63% COD removal) [49], electrochemical oxidation (92% for COD removal and low salinity of 84 uS/cm) [50] and dissolved air flotation (BOD and COD removal efficiency 76%–94% and 72%–92.5% respectively) [51].

# **4. Conclusion**

In this study, biological treatment was proposed as an alternative technology for the treatment of oil washing wastewater by continuous and discontinuous aeration. During treatment; a significant reduction in organic pollutants was obtained at pH 7.7 caused by continuous and discontinuous aeration. The results show that the pollutants are biodegradable since the BOD<sub>5</sub>/COD ratio varies around 0.5 which made it possible to achieve good elimination of the COD.

The percentage of pollutant removal varies around  $96\%$ ,  $97\%$  and  $86\%$  for turbidity,  $BOD_5$  and COD, respectively, after 9 d of continuous and discontinuous aeration. In addition, both treatment processes showed higher pollutant removal rates in fresh FWWs with 82%, 86%, 83% and 47% of phenol, nitrate, TP and TKN, respectively by continuous aeration, and 82%, 86% 64% and 47% of phenol, nitrate, TP and TKN, respectively by intermittent aeration for an aeration time of 3–6 d. This study aims to compare continuous and discontinuous aeration, establishing whether there is an optimal regimen that will increase the efficiency of FWW treatment while minimizing energy requirements. These results revealed that continuous aeration and discontinuous aeration were beneficial for the degradation of organic matter in the FWW effluent. However, the batch aeration process represents an efficient and energy efficient way to reduce organic matter and nitrate concentration and, in fact, for the general improvement of wastewater quality on fully aerated and non-aerated systems.

#### **References**

- [1] J. Boguniewicz-Zablocka, A.G. Capodaglio, Sustainable wastewater treatment solutions for rural communities': public (centralized) or individual (on-site) – case study, Econ. Environ. Stud., 17 (2017) 1103–1119.
- [2] L. Garfí, M. Flores, I. Ferrer, Life cycle assessment of wastewater treatment systems for small communities: activated sludge, constructed wetlands and high rate algal ponds, J. Cleaner Prod., 161 (2017) 211–219.
- [3] K.S. Hashim, P. Kot, S.L. Zubaidi, R. Alwash, R. Al Khaddar, A. Shaw, D. Al-Jumeily, M.H. Aljefery, Energy efficient electrocoagulation using baffle-plates electrodes for efficient *Escherichia coli* removal from wastewater, J. Water Process Eng., 33 (2020) 1–7.
- [4] D. Ghernaout, B. Ghernaout, M.W. Naceur, Embodying the chemical water treatment in the green chemistry—a review, Desalination, 271 (2011) 1–10.
- [5] N.H. Al-Saati, T.K. Hussein, M.H. Abbas, K. Hashim, Z.N. Al-Saati, P. Kot, M. Sadique, M.H. Aljefery, I. Carnacina, Iacopo, Statistical modelling of turbidity removal applied to non-toxic natural coagulants in water treatment: a case study, Desal. Water Treat., 150 (2019) 406–412.
- [6] G.V. Lombardi, G. Stefani, A. Paci, C. Becagli, M. Miliacca, M. Gastaldi, B.F. Giannetti, C.M.V.B. Almeida, The sustainability of the Italian water sector: an empirical analysis by DEA, J. Cleaner Prod., 227 (2019) 1035–1043.
- [7] V.L. Dhadge, C. Ranjan Medhi, M. Changmai, M.K. Purkait, House hold unit for the treatment of fluoride, iron, arsenic and microorganism contaminated drinking water, Chemosphere, 199 (2018) 728–736.
- [8] K.S. Hashim, N.H. Al-Saati, A.H. Hussein, Z.N. Al-Saati, An investigation into the level of heavy metals leaching from canaldreged sediment: a case study metals leaching from dreged sediment, IOP Conf. Ser.: Mater. Sci. Eng., 454 (2018) 012022.
- D. Phukingngam, O. Chavalparit, D. Somchai, M Ongwandee, Anaerobic baffled reactor treatment of biodiesel-processing wastewater with high strength of methanol and glycerol: reactor performance and biogas production, Chem. Pap., 65 (2011) 644–651.
- [10] T. Jafary, W. Ramli Wan Daud, S.A. Aljlil, A. Fauzi Ismail, A. Al-Mamun, M.S. Baawain, M. Ghasemi, Simultaneous organics, sulphate and salt removal in a microbial desalination cell with an insight into microbial communities, Desalination, 445 (2018) 204–212.
- [11] G.F. da Silva Brito, R. Oliveira, C. Koppe Grisolia, L.S. Guirra, I.T. Weber, F.V. de Almeida, Evaluation of advanced oxidative processes in biodiesel wastewater treatment, J. Photochem. Photobiol., A, 375 (2018) 85–90.
- [12] A.B. García, M.C. Cammarota, Biohydrogen production from pretreated sludge and synthetic and real biodiesel wastewater by dark fermentation, Int. J. Energy Res., 43 (2019) 1586–1596.
- [13] R. Changotra, H. Rajput, J.P. Guin, L. Varshney, A. Dhir, Hybrid coagulation, gamma irradiation and biological treatment of real pharmaceutical wastewater, Chem. Eng. J., 370 (2019) 595–605.
- [14] C.F. Wu, T. Shimaoka, H. Nakayama, T. Komiya, X.L. Chai, Y.X. Hao, Influence of aeration modes on leachate characteristic of landfills that adopt the aerobic–anaerobic landfill method, Waste Manage., 34 (2014) 101–111.
- [15] V.B. Veljković, O.S. Stamenković, M.B. Tasić, The wastewater treatment in the biodiesel production with alkali-catalyzed transesterification, Renewable Sustainable Energy Rev., 32 (2014) 40–60.
- [16] B. Singh, P. Kumar, Pre-treatment of petroleum refinery wastewater by coagulation and flocculation using mixed

coagulant: optimization of process parameters using response surface methodology (RSM), J. Water Process Eng., 36 (2020) 101317, doi: 10.1016/j.jwpe.2020.101317.

- [17] J.H. Liang, C.M. Chen, B.A. Yoza, Y. Liang, J. Li, M. Ke, Q.H. Wang, Hydrolysis and acidification of activated sludge from a petroleum refinery, Pet. Sci., 16 (2019) 428–438.
- [18] I. Ratman, T. Djoko Kusworo, D. Puji Utomo, D.A. Azizah, W.A. Ayodyasena, Petroleum refinery wastewater treatment using three steps modified nanohybrid membrane coupled with ozonation as integrated pre-treatment, J. Environ. Chem. Eng., 8 (2020) 103978, doi: 10.1016/j.jece.2020.103978.
- [19] M.J.K. Bashir, L.P. Wong, D.St. Hilaire, J.H. Kim, O. Salako, M.J. Jean, R. Adeyemi, S. James, T. Foster, L.M. Pratt, Biodiesel fuel production from brown grease produced by wastewater treatment plant: optimization of acid catalyzed reaction conditions, J. Environ. Chem. Eng., 8 (2020) 103848, doi: 10.1016/j. jece.2020.103848.
- [20] G. Mannina, A. Cosenza, D. Di Trapani, M. Capodici, G. Viviani, Membrane bioreactors for treatment of saline wastewater contaminated by hydrocarbons (diesel fuel): an experimental pilot plant case study, Chem. Eng. J., 291 (2016) 269–278.
- [21] D.P. Myburgh, M. Aziz, F. Roman, J. Jardim, S. Chakawa, Removal of COD from industrial biodiesel wastewater using an integrated process: electrochemical-oxidation with IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anodes and chitosan powder as an adsorbent, Environ. Process., 6 (2019) 819–840.
- [22] T.R. Weiser Meier, P.A. Cremonez, T. Cintra Maniglia, S.C. Sampaio, J.G. Teleken, E.A. da Silva, Production of biohydrogen by an anaerobic digestion process using the residual glycerol from biodiesel production as additive to cassava wastewater, J. Cleaner Prod., 258 (2020) 120833, doi: 10.1016/j.jclepro.2020.120833.
- [23] T. Ahmad, M. Danish, Prospects of banana waste utilization in wastewater treatment: a review, J. Environ. Manage., 206 (2018) 330–348.
- [24] S.Q. Zhao, D. Chen, F.H. Wei, N. Chen, Z. Liang, Y. Luo, Removal of Congo red dye from aqueous solution with nickelbased metal-organic framework/graphene oxide composites prepared by ultrasonic wave-assisted ball milling, Ultrason. Sonochem., 39 (2017) 845–852.
- [25] M. Sharma, S. Hazra, S. Basu, Kinetic and isotherm studies on adsorption of toxic pollutants using porous ZnO@SiO2 monolith, J. Colloid Interface Sci., 504 (2017) 669–679.
- [26] L. de Oliveira Gonçalves, M.C.V.M. Starling, C. Dutra Leal, D.V.M. Oliveira, J. Calábria Araújo, M.M.D. Leão, C.C. Amorim, Enhanced biodiesel industry wastewater treatment via a hybrid MBBR combined with advanced oxidation processes: analysis of active microbiota and toxicity removal, Environ. Sci. Pollut. Res., 26 (2019) 4521–4536.
- [27] Z. Daud, N. Nasir, Ab.A.A. Latiff, M.B. Ridzuan, H. Awang. Treatment of biodiesel wastewater by coagulation–flocculation process using polyaluminium chloride (PAC) and polyelectrolyte anionic, ARPN J. Eng. Appl. Sci., 11 (2016) 11855–11859.
- [28] F. Ayub Khan, S. Hisham, M. Ghasemi, Oil field produced water recovery and boosting the quality for using in membrane less fuel cell, SN Appl. Sci., 1 (2019) 1–8, doi: 10.1007/ s42452-019-0523-3.
- [29] American Public Health Association, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 2012, 1360 pp.
- [30] V.L. Singleton, J.A. Rossi, Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents, Am. J. Enol. Vitic., 16 (1965) 144–158.
- [31] N. Rodier, Intégrabilité locale des caractères du groupe GL(n,k) où k est un corps local de caractéristique positive, Duke Math. J., 85 (1985) 771–792.
- [32] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters, J. Hazard. Mater., 129 (2006) 116–122.
- [33] S. Jafarinejad, Simulation for the performance and economic evaluation of conventional activated sludge process replacing by sequencing batch reactor technology in a petroleum refinery

wastewater treatment plant, ChemEngineering, 3 (2019) 45, doi: 10.3390/chemengineering3020045.

- [34] C.P.M. de Oliveira, M.M. Viana, M.C.S. Amaral, Coupling photocatalytic degradation using a green  $\text{TiO}_2$  catalyst to membrane bioreactor for petroleum refinery wastewater reclamation, J. Water Process Eng., 34 (2020) 101093, doi: 10.1016/j.jwpe.2019.101093.
- [35] S.H. Ammar, N.N. Ismail, A.D. Ali, W.M. Abbas, Electrocoagulation technique for refinery wastewater treatment in an internal loop split-plate airlift reactor, J. Environ. Chem. Eng., 7 (2019) 103489, doi: 10.1016/j.jece.2019.103489.
- [36] C.-J.G. Jou, G.-C. Huang, A pilot study for oil refinery wastewater treatment using a fixed-film bioreactor, Adv. Environ. Res., 7 (2003) 463–469.
- [37] P. Shrestha, M. Rasmussen, S.K. Khanal, A.L. Pometto, J.H. van Leeuwen, Solid-substrate fermentation of corn fiber by phanerochaete chrysosporium and subsequent fermentation of hydrolysate into ethanol, J. Agric. Food Chem., 56 (2008) 3918–3924.
- [38] L. Grobbelaar, Treatment of Biodiesel Wastewater in a Hybrid Anaerobic Baffled Reactor Microbial Fuel Cell (ABR-MFC) System, Thesis (Master of Engineering in Chemical Engineering)—Cape Peninsula University of Technology, 2019.
- [39] N. Sakkayawong, P. Thiravetyan, W. Nakbanpote, Adsorption mechanism of synthetic reactive dye wastewater by chitosan, J. Colloid Interface Sci., 286 (2005) 36–42.
- [40] M. Assou, A. Madinzi, M.A. Aboulhassan, S. Souabi, Removal of turbidity in tannery waste water: modelling by the experimental design, 36 (2014) 1290–1296.
- [41] F. Masi, A. Rizzo, R. Bresciani, N. Martinuzzi, S.D. Wallace, D. Van Oirschot, F. Macor, T. Rossini, R. Fornaroli, V. Mezzanotte, Lessons learnt from a pilot study on residual dye removal by an aerated treatment wetland, Sci. Total Environ., 648 (2019) 144–152.
- [42] V. Gomes de Barros, C.S.D. Rodrigues, W.A. Botello-Suárez, R.M. Duda, R. Alves de Oliveira, E.S. da Silva, J.L. Faria, R.A.R. Boaventura, L.M. Madeira, Treatment of biodigested coffee processing wastewater using Fenton's oxidation and coagulation/flocculation, Environ. Pollut., 259 (2020) 113796, 10.1016/j.envpol.2019.113796.
- [43] V. Sivalingam, C. Dinamarca, E. Janka, S. Kukankov, S. Wang, R. Bakke, Effect of intermittent aeration in a hybrid vertical anaerobic biofilm reactor (HyVAB) for reject water treatment, Water, 12 (2020) 1151, doi: 10.3390/w12041151.
- [44] A.A.R. Sarmazdeh, L. Mostafa, Investigation of the efficiency of phosphorus removal using anionic resins from the continuous flow in the waste stabilization pond outlet: a case study of Kaboodrahang Wastewater Treatment Plant, Avicenna J. Environ. Health Eng., 6 (2019) 16–23.
- [45] M. Pronk, M.K. de Kreuk, B. de Bruin, P. Kamminga, R. Kleerebezem, M.C.M. van Loosdrecht, Full scale performance of the aerobic granular sludge process for sewage treatment, Water Res., 84 (2015) 207–217.
- [46] A.E.M. Abdelaziz, G.B. Leite, M.A. Belhaj, P.C. Hallenbeck, Screening microalgae native to Quebec for wastewater treatment and biodiesel production, Bioresour. Technol., 157 (2014) 140–148.
- [47] R.G. Luthy, J.T. Tallon, D.J. Sekel, Biological treatment of synthetic fuel wastewater, Environ. Eng. Div., 106 (1980) 609–629.
- [48] Z.J. Yaopo F, Jusi W, Treatment of petrochemical wastewater with a membrane bioreactor, Acta Sci. Circumstantiae, (1997).
- [49] M.H. El-Naas, S. Al-Zuhair, A. Al-Lobaney, S. Makhlouf, Assessment of electrocoagulation for the treatment of petroleum refinery wastewater, J. Environ. Manage., 91 (2009) 180-185.
- [50] L. Yan, H.Z. Ma, B. Wang, Y.F. Wang, Y.S. Chen, Electrochemical treatment of petroleum refinery wastewater with threedimensional multi-phase electrode, Desalination, 276 (2011) 397–402.
- [51] M.L. Hami, M.A. Al-Hashimi, M.N. Al-Doori, Effect of activated carbon on BOD and COD removal in a dissolved air flotation unit treating refinery wastewater, Desalination, 216 (2007) 116–122.