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Combining dissolved air flotation (DAF) and modified moving bed biofilm reactors (MMBBR) for synthetic oily wastewater treatment

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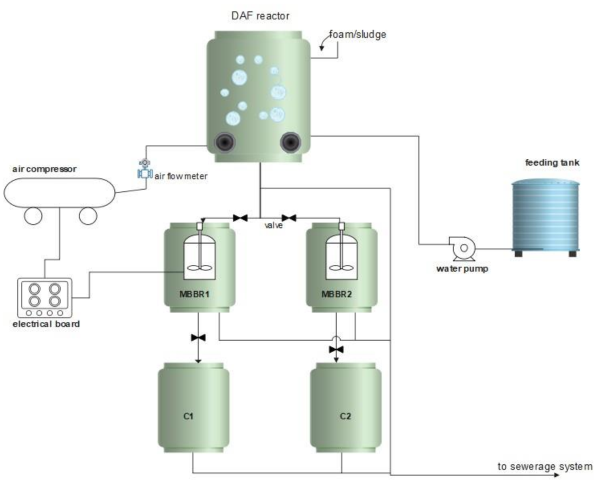
Graphical abstract



Abstract

Numerous industrial processes, including petroleum refining, food production, car washes, leather manufacturing, and slaughter houses, generate significant volumes of wastewater due to their substantial water consumption during processing. The presence of oily wastewater has detrimental effects on surface and ground water resources, Human health and aquatic ecosystems. This study aims to integrate dissolved air flotation (DAF) and moving bed biofilm reactors (MBBR) for the treatment of oily wastewater. For this reason, a synthetic oily wastewater was prepared by utilizing commercially available powdered starch as an organic source, along with diesel oil and a finely ground soil. In addition, the experiments were designed and analysed using Response Surface Methodology (RSM). DAF reactor factors were flotation time and air flow rate. While the MBBR reactor variables were mixing time and hydraulic retention time (HRT). The responses were chemical oxygen demand (COD), oil and grease(O&G), ammonia (NH_3-N) and total suspended solids (TSS). Optimum results obtained by RSM for the DAF were 10 min for the flotation time and air flow rate of 72 L/min and gave the high removal efficiency and high desirability of COD, oil and grease, NH3-N and TSS were 61.30%, 97.57%, 45.93% and 75.98% respectively. in addition, HRT for both MBBRs was 23.5 hr and mixing time of 13 min and 23 min for MBBR1 and MBBR2 respectively. Since they provided high removal efficiencies and high desirability of COD, oil and grease, NH_3-N and TSS were 47.41%, 73.96%, 94.85% and 95.37% respectively for MBBR1. Similarly, removal of COD, oil and grease, ammonia and TSS were 45.59%, 85.48%, 97.98% and 98.56% respectively for MBBR2.

Keywords

Refinery, car wash, DAF, MBBR, treatment, RSM

1. Introduction

The qualities of oily wastewater typically differ depending on the economic makeup of a nation. Crude oil quality is another factor affecting the composition of the effluent in refinery wastewater which varies in operating conditions (Yavari *et al.* 2015). Petroleum refineries generate large volumes of wastewater containing a variety of pollutants, both organic and inorganic. These pollutants include hydrocarbons, heavy metals, and toxic organic compounds. When these wastewater streams are discharged into natural aquatic environments, they can have detrimental effects on the ecosystem (Sperling 2007). Insufficient treatment of oily wastewater can harm the environment due to the presence of hydrocarbons and other contaminants. Various methods have been developed in recent years to remove oil and other pollutants efficiently from wastewater. A technique that combines dissolved air flotation (DAF) and modified moving bed biofilm reactors (MMBBR) has been proposed. The DAF technique floats oil droplets to the surface of water by using fine air bubbles, forming a layer of scum that can be easily removed (Palaniandy *et al.* 2017). While MMBBR is a biological treatment process that degrades organic compounds by attaching a biofilm to a moving carrier material. The treatment efficiency of oily wastewater can be improved by integrating these two processes. Oil and suspended solids are effectively removed by the DAF process, while organic contaminants are removed more effectively by the MMBBR process. Combining physical and biological treatment mechanisms helps to achieve a higher level of oil and pollutant removal. Studies and applications may require different modifications to the MMBBR process (Dong *et al.* 2011). As part of these modifications, the carrier material can be adjusted, operating conditions optimized, or additional treatment stages incorporated to enhance overall system performance. In general, a variety of methods and treatment approaches have been employed for the remediation of oily wastewater, including techniques such as flow anaerobic sludge blanket (UASB), up-flow anaerobic fixed bed (UAFB) reactors, membrane bio-reactors (MBR), the activated sludge process (ASP), moving bed bio-reactors (MBBR), anaerobic-aerobic-biofilm reactors (A/O-BR), membrane filtration, catalytic ozonation, and more. In order to reuse treated water, a variety of integrated physical and chemical treatment systems have been developed. An aeration system was used as a pretreatment for oil removal via flotation in a previous study. This pretreatment step took 90 minutes to achieve 96.3% O&G removal efficiency. According to Fayed *et al.* (2023) an integrated treatment process for car wash wastewater involves aeration, alum addition, and waste hydrogen peroxide addition to oxidize COD. This integrated treatment process reduced O&G by up to 99%, COD by 96% and turbidity by 86%. Most conventional methods of treating MOW are limited by their variations in composition and properties. There are several physical techniques available, including scavenging, flotation with soluble air, adsorption, and membrane filtration. Furthermore, chemical methods include electrochemical oxidation, chemical oxidation, and coagulation. Due to the high cost of chemicals, equipment, and the need to remove excess sludge, physical and chemical methods are expensive. As a result, biological methods combined with physical methods are preferred because they are simple, affordable, and environmentally friendly (Majid and Mahna 2019). This study aims to treat synthetic oily wastewaters from Kewrgosk refinery and car wash wastewater by combined DAF and MMBBR. RSM was used to optimize parameters such as flotation time and air flow rate for DAF. Consequently, mixing time and hydraulic retention time (HRT) for MMBBR. The responses of the experiments were COD, oil and grease, ammonia (NH_3-N) and TSS.

2. Materials and methods

2.1. Synthetic wastewater

In order to simulate oily wastewater and to avoid variations in wastewaters quality, synthetic oily wastewater was prepared. The experimental wastewater was artificially prepared to simulate the real wastewaters (car wash and refinery). There were three main components including organic source as starch, oil diesel and a very fine soil were used. Starch was used to provide COD; car oil diesel was used to obtain oil and grease (O&G) and sieved soil was used to provide total suspended solids (TSS). In addition, tap water was used for the preparation of synthetic wastewater solution. To obtain the optimum COD value for synthetic wastewater, each time the COD value was verified with the HACH spectrophotometer DR3900. The optimal COD value for a 1.5 g/L starch dosage was 1500±50 mg/L. in addition, Different car oil diesel of 0.1, 0.2, 0.3, 0.5, 1, 1.5 and 2 ml were added to the solution to get optimum oil and grease value. As a result, 1.5 ml/L was selected for 1500±150 mg/L oil and grease value. Moreover, for optimum TSS value, sieved soil (pass NO. 0.075μm) was used. The optimal TSS value of 2 g/L sieved soil was 10,000±100 mg/L.

2.2. Study area

Wastewater from a big car wash service location called (Diyari) located in Erbil city and situated at 36° 9′ 23′′ N 44° 0′ 43′′ E. and wastewater from Kewrgosk oil refinery located in Khabat District, near Kewrkosek Sub-District situated at 36° 8′ 8′′ N 43° 47′ 23′′ E were collected for 8 months. A large amount of fresh water was used for each car washed by hand by a full hand service. Cars were washed daily with fresh water brought by tankers. The refinery is 40 Km far from west of Erbil. And has been occupied by a land of 2.5 km^2. It is the largest oil refinery in the Kurdistan Region of Iraq, located in Erbil. Kewrgosk refinery has a daily capacity of 185,000 barrels. As a result of plant operations and the extraction of oil products such as kerosene, benzene, gasoline, and fuel oil, wastewater is composed of oil and grease as well as heavy metals. Figure 1 shows the location of study area.

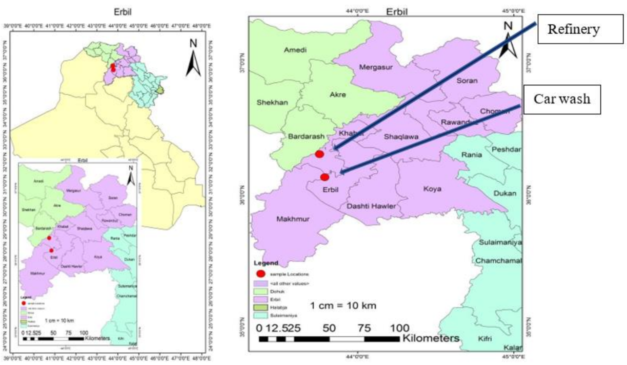


Figure 1. Map location of car wash and Kewrgosk oil refinery wastewaters

2.3. Pilot plant

2.3.1. Experimental setup

The laboratory scales of combined DAF, MBBR and clarifier were constructed in laboratory. The system consists of a feed container of 60L capacity for the daily storage and preparation of synthetic wastewater. Then the wastewater pumped into the DAF reactor by using a water pump. At the top of the pilot plant a DAF reactor of 55L was constructed with a free board of 10cm. Inside the DAF reactor, there are four disk diffusers to maintain flotation and make bubbles to push the impurities particularly oil and grease to the top of reactor which then removed and skimmed manually by an open space connected to a valve. The air supply for flotation maintained by air compressor connected to diffusers.

furthermore, the air flow rate was controlled by air flow meter device to ensure that DAF reactor operated under the required air flow rate. A valve was installed to control the air flow rate of DAF reactor. After flotation, the wastewater discharged by gravity into two identical MBBR reactors of 35L volume of each in parallel. In addition, each two reactors have different bio media i.e MBBR1 reactor consisted of polyethylene (PE) media and the MBBR2 reactor contained with water plastic bottle caps. The specification of the two biomedia were illustrated in Table 1. The MBBR reactors installed by mixers to provide appropriate mixing of bio media with wastewater and provide oxygen to grow biofilm at the surface of bio carriers. As well as to distribute bio carriers throughout the reactor. The MBBR reactors filled with %50 of bio media. In addition, after MBBR reactor the treated wastewater goes to two identical clarifier reactors, each with 35 L volume. Additionally, a control valve was installed for taking effluent samples in each reactor. Moreover, each reactor is equipped with a sludge discharge hole at the bottom, through which excess sludge can be removed. To transport the effluent from the work station to the sewerage system outside, a plastic pipe is connected. Also Figure 2 illustrates the specific aspects of the pilot plant.

Table 1. Properties of biocarriers used in this study

Descriptions	Aquaflex BIOAQUA for MBBR1	disposed plastic caps for MBBR2
Diameter	26 mm	31 mm
Length, Width	N/A, 10 mm	8 mm, N/A
No of inner departments	19 qty	N/A
Approximate dia. of inner deprt	5 mm	N/A
Surface Area	650 m^2/m^3	3686 m^2/m^3
Material	PE vigrin	plastic
Color	Natural white	blue
Media fill rate range % fill of Volume	%30-50	85%
Life Span	>15 year	
Density	0.92-0.96 g/cm^3 (bulk density)	0.92 g/cm^3

2.4. Adaptation phase of DAF-MBBR

During the first stage, the initial acclimation of reactors DAF and MBBRs were observed under appropriate conditions. Synthetic wastewater was fed to the rectors daily, and the start up operation of DAF reactor was initiated with duration of 35 aeration and with air flow rate of 60 L/min. Consequently, MBBR reactor was operated with 12 hrs HRT and 15 min mixing time. The process of adaptation was ongoing for more than 10 days, and in addition, the daily monitoring of biofilm media from MBBRs took place. Furthermore, COD, oil and grease NH3-N and TSS of effluent samples from DAF and MBBR reactors were assessed on a daily basis. Figure 3 shows the results of the adaptation phase. After 11 days of continuous operation of DAF-MBBRs, a steady state condition was reached, as the removal efficiency of parameters became approximately constant without any significant changes. Additionally, a thin yellowish layer of biofilm was also observed encompassing the media (Figure 4). The second phase is the full operation of DAF-MBBR. During this phase, the RSM design method was implemented for the reactors.

2.5. Design experiments using RSM

This study utilizes central composite design (CCD) and RSM techniques to assess the correlations among the key operational variables that hold the utmost significance. Out of the various variables considered, two primary factors were selected as key determinants impacting the reactor's efficiency. In this study, flotation time and air flow rate were chosen for DAF reactor as independent variables. Moreover, mixing time and hydraulic retention time were selected for MBBRs. Furthermore, each of the two operating variables was examined at three levels: low (-1), central (0), and high (+1). Their responses were COD, NH_3-N, oil and grease and TSS. The operating variables were optimized to determine the optimal value of the responses.

Table 2. Experimental range and levels of the independent variables

DAF					
Code	**Factors (variables)**	**Unit**	**Range and levels**		
			-1	**0**	**+1**
A	Flotation time	min	10	35	60
B	Air flow rate	L/min	35	60	85
MBBRs					
Code	**Factors (variables)**	**Unit**	**Range and levels**		
			-1	**0**	**+1**
A	Mixing time	min	5	15	25
B	HRT	hr	0.5	12	23.5

Table 3. Experimental variables and responses for DAF

Run	Factors		Responses			
	Flotation time(min)	Air flow rate (l/min)	Oil&Grease %removal	COD %removal	NH_3-N %removal	TSS %removal
1	60	85	97.57	46	8	4
2	10	60	97	58	53.42	71.76
3	10	35	97.15	22.80	36.05	26.47
4	35	60	60.46	68.18	10.63	42.42
5	35	60	94.11	46.74	65.21	73.33
6	35	85	94.65	43.08	10.3	9.37
7	35	60	90.65	30.95	3	6
8	60	60	97.16	17.27	8.31	43.07
9	35	35	95.54	35.29	23.84	25.53
10	35	60	66.15	43.42	15	11.56
11	35	60	64.60	55.58	13.68	77.83
12	60	35	85.95	38.21	4.33	70.18
13	10	35	81.50	30.17	15.56	17.24

3. Results and discussions

After adaptation phase of DAF-MBBR, the RSM experiments were directly conducted. Table 3, 4 and 5 show the results of the experiments.

3.1. Performance of DAF

After 11 days of operation, representing more than 10 days adaptation phase for each filter media type, the RSM experiments were directly carried out on the DAF to evaluate their performance. To determine the removal efficiencies of the responses for each experimental run, samples were collected from both the influent and effluent of DAF reactor.

Table 4. Experimental variables and responses for MBBR1

	Factors		Responses			
Run	Mixing time(min)	HRT (hr)	Oil&Grease %removal	COD %removal	NH_3-N %removal	TSS %removal
1	5	23.5	50	54.25	95.52	97.89
2	15	12	92.59	5.017	97.74	91.66
3	15	0.5	41.66	66.71	70.83	90
4	15	12	94.11	8.04	93.76	98.24
5	25	12	50	23.80	79.54	79.16
6	25	23.5	94.11	2.34	89.70	98.27
7	15	12	60	4.16	83.84	97.77
8	5	0.5	12.5	83.19	63.98	83.78
9	15	12	38.46	47.06	78.26	91.66
10	15	12	70	54.40	81.42	97.22
11	25	0.5	25	2	39.02	36.99
12	5	12	98.52	23	91.93	91.5
13	15	23.5	74.07	54.62	89.41	77.08

Table 5. Experimental variables and responses for MBBR2

	Factors		Responses			
Run	Mixing time(min)	HRT (hr)	Oil&Grease%	COD %	NH_3-N %	TSS %
1	5	23.5	75	59.31	97.89	98.95
2	15	12	96.29	41.37	97.18	91.67
3	15	0.5	33.33	78.07	72.57	94.00
4	15	12	94.11	2.64	92.63	98.25
5	25	12	50	4.60	64.77	91.67
6	25	23.5	94.11	12.40	93.69	98.28
7	15	12	30	26.35	83.85	97.42
8	5	0.5	50	79.10	61.22	83.78
9	15	12	76.92	46.51	65.22	93.33
10	15	12	90	57.15	88.21	97.37
11	25	0.5	40	25.70	39.94	37.80
12	5	12	97.05	15.66	97.98	91.98
13	15	23.5	33.33	40.71	76.45	70.83

3.1.1. COD removal

In wastewater, COD is a major pollutant that must be removed. Flotation time and air flow rate were found to have significant counter-interaction effects. A response surface is presented to visualize both the relationship between the input factors and the responses in 3D and contour plots, Figure 5. It was found that increasing the flotation time from 10 min to 60 min and air flow rate from 35 L/min to 85 L/min, the removal of COD pollutant in wastewater increased. By increasing the flotation time from 10 to 60 minutes, it allows more time for the attachment of COD particles to the air bubbles. This extended contact time enhances the chances of particle-bubble collisions and improves the removal efficiency of COD from wastewater. This is agreed with a study done by Sinaga *et al.* (2022), for a flotation time of 15 minutes the COD removal of 22.57%. while at 60 minutes of flotation time, the removal of COD increased to 33.50%. This indicates with longer flotation times leading to more substantial reduction in COD content. Because of the longer flotation times, bubbles and particles are more likely to be connected and larger bubbles are produced, therefore the bubble-particles are raised to a greater degree (Ahmadi and Mostafapour 2017).

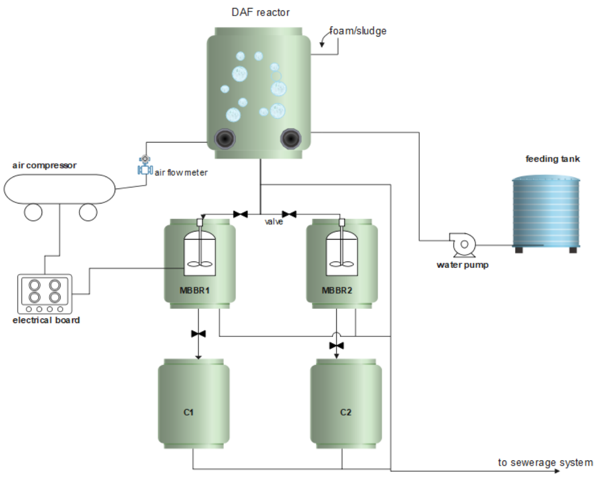


Figure 2. Experimental pilot plant of DAF-MBBR

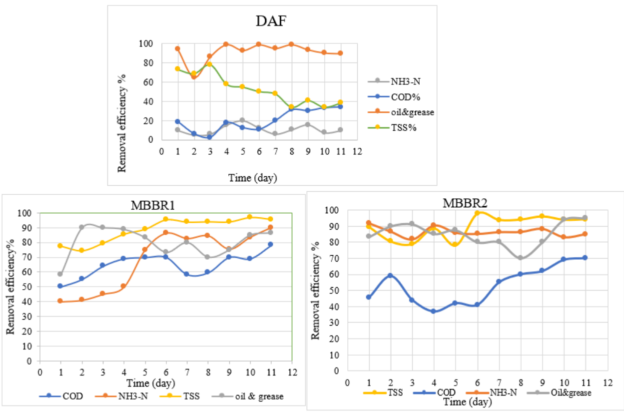


Figure 3. Adaptation phase of DAF-MBBRs

In addition, the air flow rate in a flotation system determines the size and distribution of air bubbles generated. Higher air flow rates result in smaller bubbles, which offer a larger surface area for particle attachment. This increased interfacial area facilitates the adsorption of COD pollutants onto the bubbles, leading to improved removal. Thus, by increasing the air flow rate from 35 to 85 L/min, it introduces more bubbles into the system, increasing the available attachment sites for COD particles and enhancing the overall removal efficiency. From the RSM plot, the maximum COD was 68% at 35 min of flotation time and 60 l/min of air flow rate. The same result was obtained by De Nardi et al. (2008) using DAF with chemicals for the treatment of industrial wastewater.

Figure 4. Observing biofilm formation during the adaptation phase

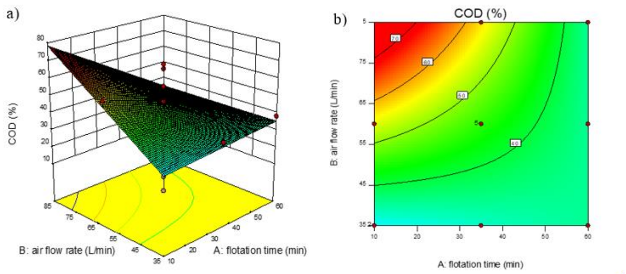


Figure 5. Effect of input factors on removal of COD: a) 3D plot b) Contour plot

3.1.2. Oil and grease removal

The 3D response curves illustrated in Figure 6 indicate the interaction effect observed between the flotation time and air flow rate in removing oil and grease pollutant. A high removal efficiency of 97.57% was achieved at 60 minutes of flotation time and 60 L/min air flow rate. The graph illustrates that flotation time with air flow rate were increasing linearly in removing oil and grease pollutant. In other words, increasing the flotation time and air flow rate independently may have an impact on the removal efficiency, but their combined effect does not exhibit any notable synergistic or interactive behavior. With a contact time of 60 minutes, oil and fat were removed more effectively because the air bubbles dissolved the molecules and caused them to float to the surface. Rattanapan *et al.* (2011) recorded the oil and grease efficiency to be in the range of 85-95% from treated biodiesel wastewater using DAF with alum and acidification. Meanwhile, Sinagata *et al.* (2022) studied that it can be seen that as the flotation time increases, namely 15, 30, 45, 60, and 75 minutes. the removal of oil and fat increases too for a time 75 min the highest removal efficiency of 21.22% was recorded.

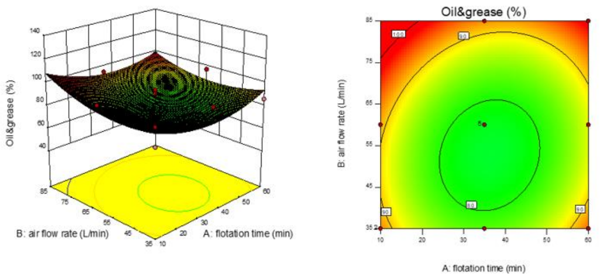


Figure 6. Effect of input factors on removal of oil and grease: a) 3D plot b) contour plot

3.1.3. Ammonia removal

From Figure 7, it was indicating that increasing in flotation time leads to decrease in removal efficiency of ammonia. While increasing in air flow rate did not have significant changes. However, the highest removal of %65 was recorded at 60 min. further studies recorded 43% removal of ammonia by using coagulation/DAF process with RSM tool (Adlan et al. 2011). A longer flotation time may cause more air bubbles to contact wastewater. In this process, volatile compounds, including ammonia, can be stripped from the water and released into the atmosphere. However, DAFs are not typically designed with ammonia stripping as a primary consideration. The primary purpose of DAF is to remove suspended solids, fats, oil and greases from wastewater.

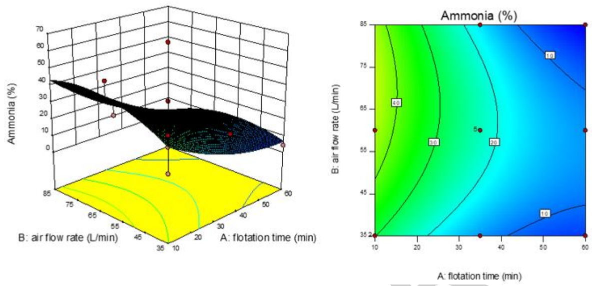


Figure 7. Ammonia (NH3-N) removal efficiency a)3D plot b) contour plot

3.1.4. TSS removal

The surface plot of Figure 8 shows that as flotation time and air flow rate increased from low to high, the removal of TSS increased to a peak (77.83%) and gradually fell indicating the interaction between these two factors. Longer contact time between wastewater particles leads to high value in TSS. Hidayah *et al.* (2022) recorded with a contact time of 22 minutes and under 100% recirculation wastewater, flotation process performed better at removing TSS by about 79.71%. Increasing the air input resulted in larger bubbles with smaller specific surface areas, which resulted in poorer gas transfer. The larger bubbles, instead of dissolving in solution, were rapidly ejected from the water. column and exited with the dissolved air flow.

3.2. Performance of modified MBBR1 and MBBR2

3.2.1. COD removal

There are several biological processes that can be used to remove organic matter. COD one of the important organic matters that should be removed in wastewater. From the Figure 9, it is obvious that performance of both MBBRs is good in removing COD. Maximum removal efficiency of 83.19% and 79.10% were obtained for MBBR1 and MBBR2 respectively. Same result was obtained by Lu *et al.* (2013), the removal of COD was higher than 83% for HRT 36 and 72 hrs using sequential aerobic-anaerobic MBBR. Dias *et al.* (2012) recorded that the MBBR was able to remove 90% of COD when combined with slow sand filter for treating oil refinery wastewater. In a study by Falletti, et al. (2014), combined flotation and MBBR resulted in 97% COD removal. According to Zafarzadeh *et al.* (2010), using MBBR with nitrification and denitrification processes, they were able to remove up to 99% of COD with a 20-hour HRT and polyethene biocarrier. It is clear from the figure that increasing mixing time and HRT resulting in increasing in COD removal for both MBBRs (Sosamony and soloman 2018). This is supported by Dargahi *et al.* (2021) by increasing HRT to 24 hrs the COD recorded the highest removal efficiency of 88.95% used MBBR combined to 3D electrochemical. In addition, A balanced and appropriate mixing time can ensure effective mass transfer of organic matter from the wastewater to the biofilm, leading to better microbial growth and COD removal. The longer the HRT, the better the treatment efficiency, but the larger the reactor and the more energy it consumes. Furthermore, very long HRTs may result in reduced removal efficiency due to the accumulation of inert or refractory organic matter (Zafarzadeh *et al.* 2010, Lu *et al.* 2013).

3.2.2. Oil and grease removal

From the Figure 10, it is noted increasing mixing time from 5 min to 25 min and HRT from 0.5 hr to 23.5 hr resulting in increasing in oil and grease removal from 12.5 to 98%. For MBBR1 and 30 to 97 % for MBBR2. A study by Falletti *et al.* (2014) for treating food wastewater based on flotation and MBBR. In this study the whole plant removed 99% of oil and grease. Longer HRT allows more time for biological processes to occur including the degradation of oil and grease by microorganisms present in the biofilm. However, excessively long HRTs may lead to overgrowth of biomass, potential washout of biofilm, and increased energy and operational costs (Santos *et al.* 2020).

3.2.3. Ammonia removal

Figure 11 illustrated the effect of mixing time and HRT on ammonia removal for MBBR1 and MBBR2. From the figure, it is obvious by increasing mixing time and HRT, the removal of ammonia increased. Ashkanani *et al.* (2019) assessed a study using MBBR with three different biocarriers. The research demonstrated that biocarriers with larger surface areas were more susceptible to clogging, affecting ammonia removal efficiency and system sensitivity to temperature changes. Lu et al. (2013) found that using a suspended ceramsite bio-carrier arrangement in MBBR effectively removed ammonia from wastewater. The reactor achieved over 85% removal efficiencies 36 hrs of HRT. Maximum removal efficiency of 97.74% and 97.98% were obtained at 12hr and 0.5 hr for both MBBR1 and MBBR2 respectively. The removal efficiencies obtained were good compared to other studies in the literature (Magdum, and Kalyanraman 2019; Makisha 2021). Nitrification took place in the reactors due to the aerobic conditions generated by mixers, resulting in the infusion of air into the reactors. This assertion finds support in the findings of Wang *et al.* (2020).

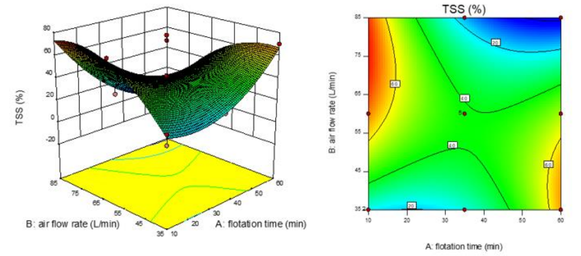


Figure 8. a) 3D surface plot b) contour plot of TSS removal efficiency

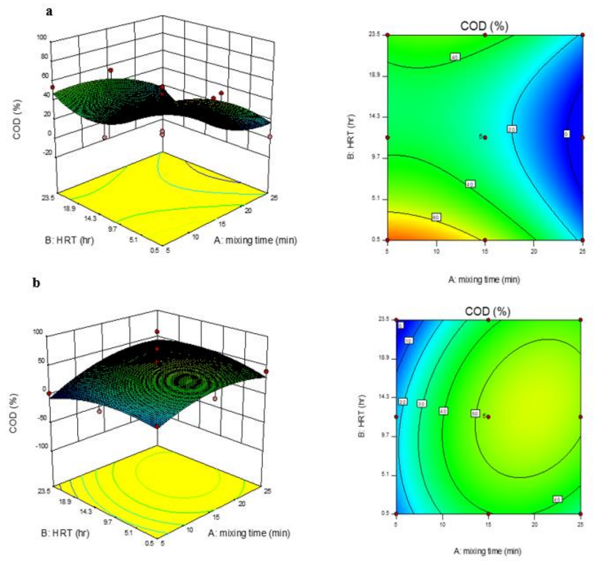


Figure 9. a) 3D surface plot & contour plot of MBBR1 COD removal efficiency b) 3D surface plot & contour plot of MBBR2 COD removal

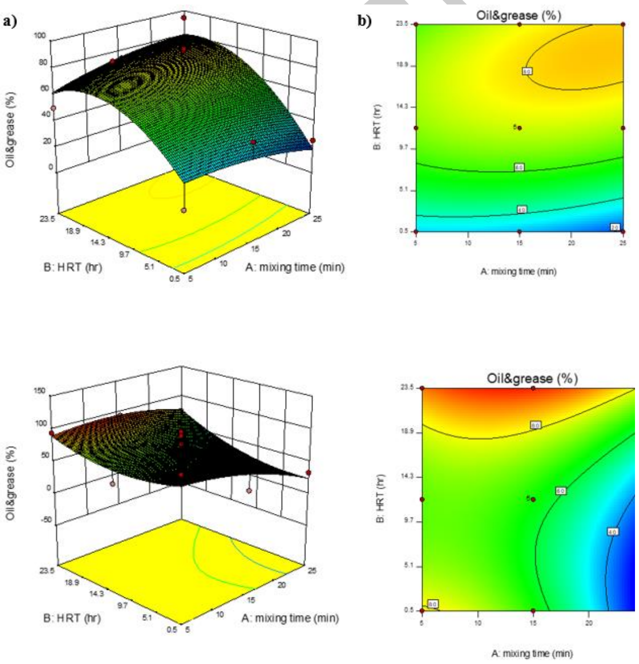


Figure 10. a) 3D surface plot & contour plot of MBBR1 O&G removal efficiency b) 3D surface plot & contour plot of MBBR2 O&G removal

3.2.4. TSS removal

As an indicator of system stability, TSS were measured. Figure 12 represented TSS removal efficiency as a function of mixing time and HRT. Maximum removal efficiencies for MBBR1 were 98.27% at 25 min mixing time and for MBBR2 98.95% at 5 min mixing time. Both MBBR's maximum removal efficiencies were observed at 23.5 hr HRT. The same result obtained by Kawan *et al.* (2022). A high TSS removal efficiency was observed in the MBBR at 24hr HRT with effluent concentrations less than 3 mg/L. This is because as the HRT increased, TSS concentrations gradually decreased, since the particles had more time to settle and attach to the surfaces of the media. In another research a TSS removal efficiency of 88% was observed at 12 hr HRT (Zinatizadeh and Ghaytooli 2015). In another study using multistage flexible fiber biofilm reactor (MS-MBBR), a maximum predicted TSS removal efficiency of 98.4% was obtained when HRT was 16hr. In contrast, at shorter HRT of 8 hours, a minimum predicted TSS removal of 52.48 % was observed. On the other hand, the mixing process effectively distributes nutrients, organic matter, and oxygen throughout the reactor, promoting healthy biofilm growth. Thus, in a well-developed biofilm, suspended solids are better captured and retained (di Biase *et al.* 2019). For MBBR1 increasing mixing time led to decrease in TSS removal. This is because excessive mixing time resulted in detachment of biofilm bonded to the surface of the biocarrier due to shear force (Kawan *et al.* 2022). In contrast, mixing time affects slightly increase in TSS removal. The same consequence obtained by Ghayebzadeh *et al.* (2019). It concluded that highest removal efficiencies were achieved when MBBR reactor mixed for a period of 90 min.

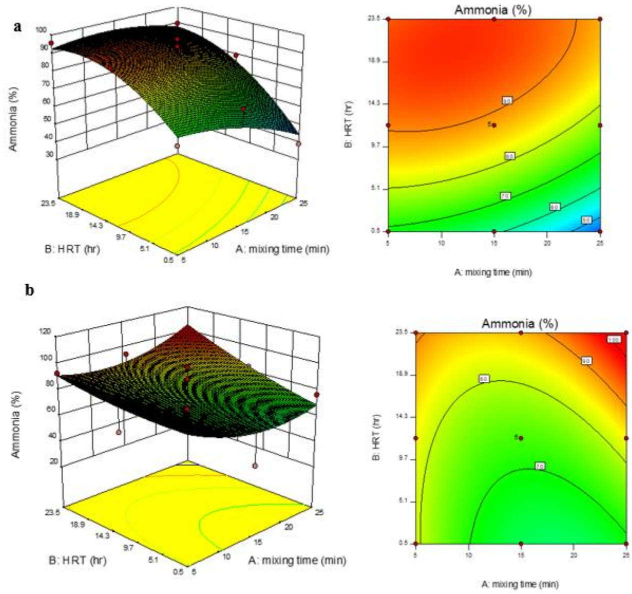


Figure 11. a) 3D surface plot & contour plot of MBBR1 Ammonia removal efficiency b) 3D surface plot & contour plot of MBBR2 Ammonia removal

3.3. Statistical Analysis

During this study, multiple responses were investigated, and it was found that significant model terms are essential to attain the optimal fit for a specific model. To quantify the curvature effects, the experimental data results were fitted to higher-degree polynomial equations, including two-factor interaction (2FI), quadratic, cubic, and other relevant models. Certain raw data may not conform to the fitting requirement, necessitating the application of mathematical transformations to the response data. These transformations are employed to fulfill the assumptions essential for the validating of the analysis of variance (ANOVA) (Zinatizadeh *et al.* 2010). Table 5 provides a comprehensive summery of the ANOVA results for all the responses. The chosen model terms are the results of eliminating insignificant variables and their interactions through a rigorous selection process. Through (CCD), a mathematical equation was developed to evaluate predicted results (Y) as a function of flotation time (A) and air flow rate (B) for DAF reactor. In the same manner, mixing time (A1 and A2) and (B1 and B2) refers to HRT for MBBR1 and MBBR2, respectively. This allowed for a comprehensive analysis of the relationship between the variables and the predicted outcomes. The computed result was derived from the sum of a constant, two first order effects (terms in A and B), one interaction effect (AB), and two second order effects (A2 and B2). The ANOVA results depicted the simplified quadratic models in relation to the actual factors, along with various other statistical parameters, Table 6 These findings provided valuable insights into the relationships between the factors and the overall model performance. Some models were not significant because probability values were more than 0.05. However, models for MBBR1 shows significance because probability values (p-value) were less than 0.05. Models are considered statistically significant if the p-value is less than 0.05 (Vasseghian 2015). Moreover, The F-value for lack of fit (LOF) clarifies the data's variability around the adapted model. The significance of LOF arises when the model poorly corresponds to the data. Frequently, a substantial probability value for LOF (>0.05) was observed. As detailed in Table 6, the insignificance of the F-statistic suggests a significant model relationship between variables and process responses. The R-square (R^2) value represents the fraction of the overall variability in the response that the model's predictions account for, illustrating the relationship between the sum of squares attributed to regression and the entire sum of squares. Desirable outcomes are achieved when R^2 values are close to 1, and a substantial R^2 coefficient guarantees a satisfactory adaptation of the quadratic model to the experimental data. Adequate precision refers to evaluating the extent of variation in the predicted response in relation to its corresponding error, essentially representing a signal to noise ratio. A value greater than 4 was found to be desirable for all models. Variance coefficient (CV) describes the relationship between standard error of estimation and average observed response. The model is considered reproducible if its CV is greater than 10%.

In Figure 13 to 15, the predicted and experimental values are shown in good correlation, with the data points evenly distributed around the straight line. Hence, the response models effectively mirrored the experimental outcomes within the defined design space. It also indicated the majority of the points were distributed along a straight line, demonstrating the significance of the quadratic models created for response removals. The same result was obtained by Tetteh and Rathilal (2018).

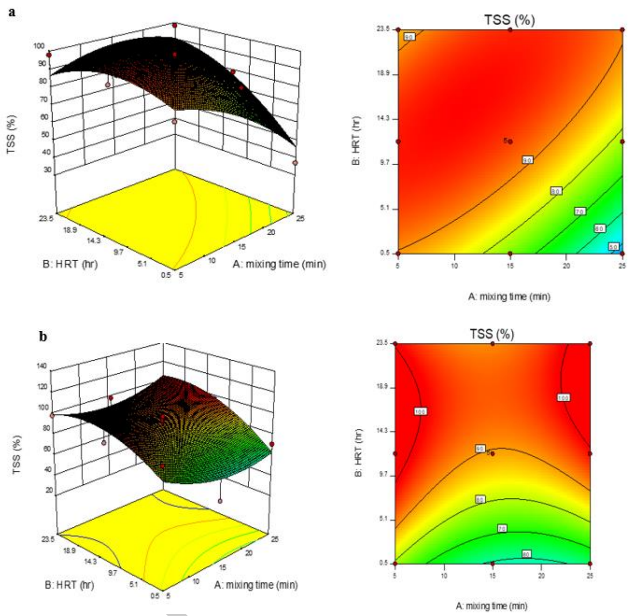


Figure 12. a) 3D surface plot & contour plot of MBBR1 TSS removal efficiency b) 3D surface plot & contour plot of MBBR2 TSS removal

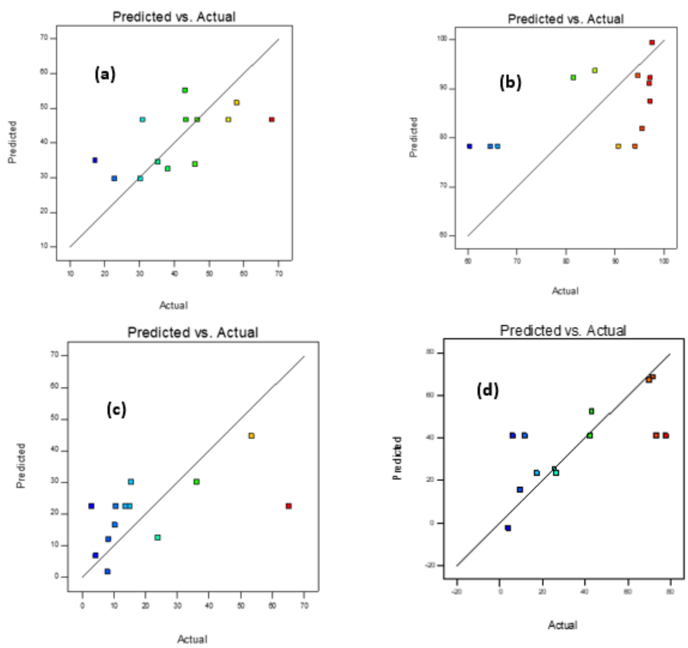


Figure 13. Predicted versus actual plots for DAF (a) COD% (b) oil& grease% (c) Ammonia% and (d) TSS%

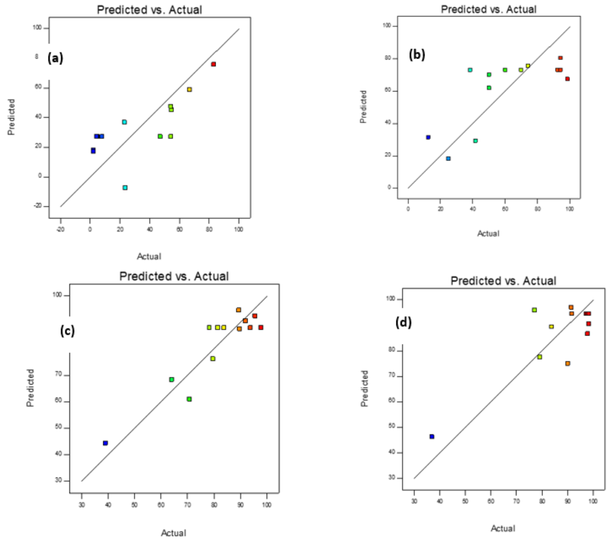


Figure 14. Predicted versus actual plots for MBBR1 (a) COD% (b) oil& grease% (c) Ammonia% and (d) TSS%

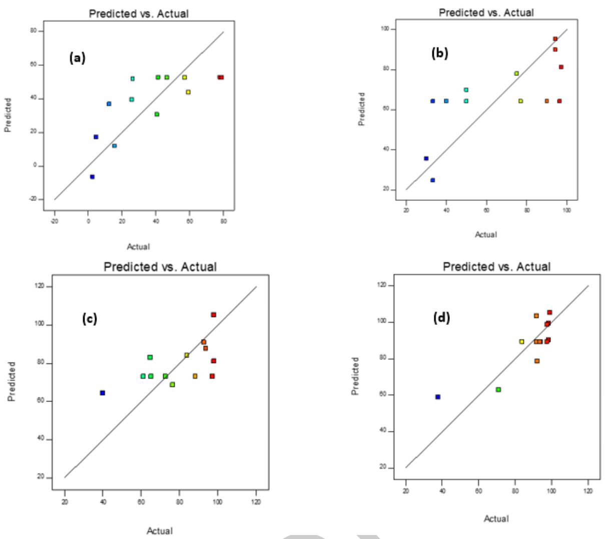


Figure 15. Predicted versus actual plots for MBBR2 (a) COD% (b) oil& grease% (c) Ammonia% and (d) TSS%

Table 6. Analysis of variance (ANOVA) results for response parameters

Reactor type	Removal of Responses (%)	Final equation in terms of actual factors	Prob.	R^2	Adj. R^2	Adeq. P	SD	CV %	Press	LOF
DAF	COD	$-16.33105+0.97835A+1.30945B-0.015464AB-5.43586E-003A^2-2.95586E-003B^2$	0.5557	0.3778	-0.0666	2.537	14.79	35.89	11827.59	2.28
	Oil&grease	$+133.12677-1.06587A-1.38032B-4.05003E-003AB+0.017664A^2+0.014488B^2$	0.6862	0.3092	-0.1841	2.077	15.00	17.37	7047.02	0.98
	Ammonia	$-8.77252-0.87366A+1.85084B-7.28999E-003AB+9.44264E-003A^2-0.012629B^2$	0.7379	0.3280	-0.1520	3.038	20.81	0.59	8658.31	0.32
	TSS	$-114.51901+0.33598A+5.36920B-0.047616AB+0.031451A^2-0.032493B^2$	0.8950	0.4991	0.1414	4.015	26.01	70.63	9750.23	0.11
MBBR1	COD	$+78.12228+0.73577A_1-6.06617B_1+0.063652A_1B_1-0.12349A_1^2+0.18840B_1^2$	0.4622	0.5389	0.2096	4.877	25.09	76.09	21919.99	1.05
	Oil&grease	$+27.00076+0.61424A_1+4.74812B_1++0.068717A_1B_1-0.043467A_1^2+-0.15684B_1^2$	0.3663	0.5359	0.2044	3.622	25.25	40.98	25854.28	1.40
	Ammonia	$+67.38796+0.14614A_1+2.68140B_1+0.041609A_1B_1-0.045498A_1^2-0.076861B_1^2$	0.0096	0.8440	0.7325	8.887	8.30	10.23	2377.08	0.98
	TSS	$+90.68110-0.037223A_1+1.00621B_1+0.10254A_1B_1-0.072416A_1^2-0.068292B_1^2$	0.0040	0.7121	0.5065	6.386	11.71	13.46	9312.13	27.17
MBBR2	COD	$-16.15462+6.35214A_2+1.50645B_2+0.068758A_2B_2-0.18176A_2^2-0.11041B_2^2$	0.2414	0.5558	0.2385	3.865	22.55	59.88	18387.37	2.53
	Oil&grease	$+82.65509+0.53810A_2-2.95325B_2+0.096974A_2B_2-0.11386A_2^2+0.11851B_2^2$	0.5666	0.5046	0.1508	4.152	25.04	37.84	16344.12	0.70
	Ammonia	$+97.56851-3.79159A_2-0.39995B_2+0.058249A_2B_2+0.10464A_2^2+0.022434B_2^2$	0.2495	0.3784	-0.0656	3.262	18.46	23.27	14400.44	2.05
	TSS	$+95.95400-4.38530A_2+3.31199B+0.047495A_2B_2+0.11902A^2-0.11041B_2^2$	0.0863	0.6888	0.4664	5.533	12.38	14.05	9150.68	12.66

A: flotation time (min); B: air flow rate (L/min); A_1&A_2: mixing time (min); B_1&B_2: HRT (hr); Prob.: probability of error; R^2: coefficient of determination; Adj.R^2: adjusted R^2; Adeq. P.: adequate precision; SD: standard deviation; CV: coefficient of variance; Press: predicted residual error sum of squares; and LOF: lack of Fit

4. Experimental condition optimization

Optimal conditions were selected based on the combination of factor levels that resulted in the maximum amount of response. In order to identify the specific points that maximize the response desirability function, the numerical and graphical optimization of the RSM software were used. The independent variables were (flotation time and air flow rate for DAF, moreover mixing time and HRT for MBBRs) that produce optimum responses (oil and grease, COD, ammonia and TSS). In terms of optimization goal, the criteria chosen were 'maximize' for responses and 'in range' for input factor. Table 7 to 9 shows the solutions of the predicted model at different operating conditions for the DAF-MBBRs. The first option was recommended as the best condition, since it shows high removal efficiency and high desirability.

In addition, for MBBR1, the RSM was given one solution optimization and for MBBR2 two solutions are found as optimum results. The best removal efficiencies were selected as best conditions (Tables 8 and 9).

Table 7. Results of optimized DAF treatment by RSM

No.	Flotation time min.	Air flow rate (L/min)	COD%	Oil&grease %	Ammonia %	TSS %	Desirability
1	10	72.78	61.30	97.57	45.93	75.98	0.87
2	10	71.89	60.65	96.97	45.98	75.81	0.86
3	10	64.87	55.38	93.03	45.62	72.66	0.80
4	60	50.83	34.56	87.68	12.01	62.60	0.41
5	60	54.31	34.81	87.33	12.31	59.46	0.40

Table 8. Results of optimized MBBR1 treatment by RSM

No.	Mixing time (min.)	HRT (hr)	COD%	Oil&grease %	Ammonia %	TSS %	Desirability
1	13.33	23.50	47.41	73.96	94.85	95.37	0.77
2	13.44	23.50	47.29	74.07	94.84	95.42	0.77

Table 9. Results of optimized MBBR2 treatment by RSM

No.	Mixing time (min.)	HRT (hr)	COD%	Oil&grease %	Ammonia %	TSS %	Desirability
1	22.03	23.50	45.59	85.48	97.98	98.56	0.82

Thus, experimental runs were used to evaluate the predictability of the optimized model. The results of Figure 16 to 18 indicate good agreement between the predicted and measured values.

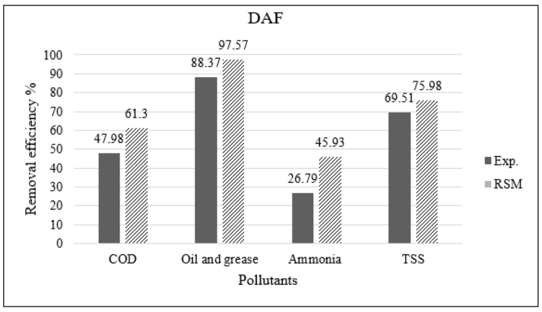


Figure 16. Experimental results compared to predicted values at 10 minutes of flotation and 72.78 L/min. of air flow

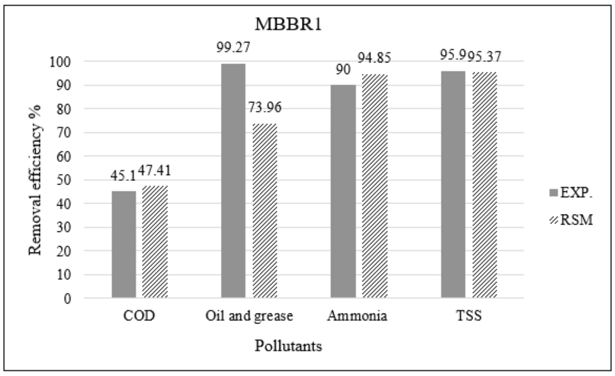


Figure 17. Experimental results compared to predicted values at 13 min. of mixing and 23.5 hrs. HRT

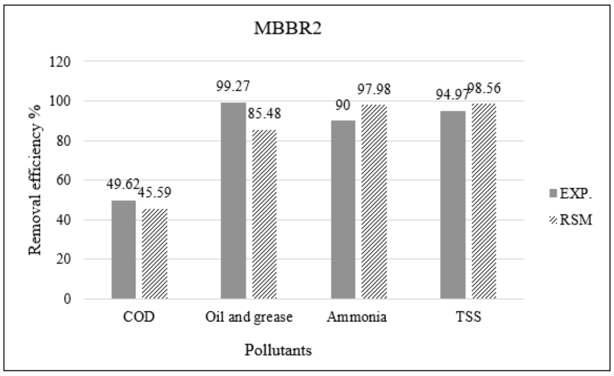


Figure 18. Experimental results compared to predicted values at 22 min. of mixing and 23.5 hrs. HRT

5. Conclusions

Synthetic oily wastewater using combined DAF-MBBRs were investigated. A number of input variables, including flotation time and airflow rate along with mixing time and HRT for DAF and MBBRs respectively were studied. The removal of COD, oil and grease, ammonia and TSS were also modeled using response surface methodology (RSM). The result showed for DAF system, increasing input variables had a significant impact on increasing removal of pollutants(responses). However, for MBBRs, excessive mixing time resulted in lower the removal efficiency of TSS and led to detach the biofilm from surface of biocarriers. In addition, the optimum results of RSM for DAF were 10 min for the flotation time and air flow rate of 72 L/min. in addition, HRT for both MBBRs was 23.5 hr and mixing time of 13 min and 23 min for MBBR1 and MBBR2 respectively.

References

Adlan M.N., Palaniandy P. and Aziz H.A. (2011). Optimization of coagulation and dissolved air flotation (DAF) treatment of semi-aerobic landfill leachate using response surface methodology (RSM). *Desalination journal*, **277**(1–3), 74–82.

Ahmadi S. and Kord Mostafapour F. (2017). Treatment of textile wastewater using a combined coagulation and DAF processes, Iran, *Archives of Hygiene Sciences journal*, **6**(3), 229–234.

Ashkanani A., Almomani F., Khraisheh M., Bhosale R., Tawalbeh M. and AlJaml K. (2019). Bio-carrier and operating temperature effect on ammonia removal from secondary wastewater effluents using moving bed biofilm reactor (MBBR). *Science of The Total Environment journal*, **693**, 133425

Dargahi A., Shokoohi R., Asgari G., Ansari A., Nematollahi D. and Samarghandi M.R. (2021). Moving-bed biofilm reactor combined with three-dimensional electrochemical pretreatment (MBBR–3DE) for 2, 4-D herbicide treatment: application for real wastewater, improvement of biodegradability. *Journal of RSC advances*, **11**(16), 9608–9620.

De Nardi I.R., Fuzi T.P. and Del Nery V. (2008). Performance evaluation and operating strategies of dissolved-air flotation system treating poultry slaughterhouse wastewater. *Resources, Conservation and Recycling journal*, **52**(3), 533–544.

di Biase A., Kowalski M.S., Devlin T.R. and Oleszkiewicz J.A. (2019). Moving bed biofilm reactor technology in municipal wastewater treatment: A review. *Journal of environmental management*, **247**, 849–866.

Dias I.N., Cerqueira A.C., Sant'Anna Jr G.L. and Dezotti M. (2012). Oil refinery wastewater treatment in biofilm reactor followed by sand filtration aiming water reuse. *Journal of Water Reuse and Desalination*, **2**(2), 84–91.

Dong Z., Lu M., Huang W. and Xu X. (2011). Treatment of oilfield wastewater in moving bed biofilm reactors using a novel suspended ceramic biocarrier. *Journal of hazardous materials*, **196**, 123–130.

Falletti L., Conte L., Zaggia A., Battistini T. and Garosi D. (2014). Food industry wastewater treatment plant based on flotation and MBBR. *Modern Environment Science and Engineering journal*, **1**, 562–566.

Fayed M., Shewitah M.A., Dupont R.R., Fayed M. and Badr M.M. (2023). Treatability Study of Car Wash Wastewater Using Upgraded Physical Technique with Sustainable Flocculant. *Sustainability journal*, **15**(11), 8581.

Ghayebzadeh M., Sharafi K., Azizi E., Rahmatabadi S. and Pirsaheb M. (2015). Removal of nitrogen and phosphorus from municipal wastewater using intermittent cycle moving bed biofilm reactor (ICMBBR). *Journal of Chemical and Pharmaceutical Research*, **7**(6), 979–987.

Hidayah E.N., Rahmawati W., Hendriyanto O., Cahyonugroho F.R. And Wahyusi K.N. (2022). Effect of Flow Rate and Recirculation on The Flotation Process in Removing Fat, Oil, Grease, And Solid. *Journal of Engineering Science and Technology*, **17**(4), 2594–2601.

Kawan J.A., Suja F., Pramanik S.K., Yusof A., Abdul Rahman R. and Abu Hasan H. (2022). Effect of hydraulic retention time on the performance of a compact moving bed biofilm reactor for effluent polishing of treated sewage. *Journal of Water*, **14**(1), 81.

Lu M., Gu L.P. and Xu W.H. (2013). Treatment of petroleum refinery wastewater using a sequential anaerobic–aerobic moving-bed biofilm reactor system based on suspended ceramsite. *Water science and technology* journal, **67**(9), 1976–1983.

Magdum S. and Kalyanraman V. (2019). Evaluation of high rate MBBR to predict optimal design parameters for higher carbon and subsequent ammoniacal nitrogen removal. *Journal of Current Science*, **116**(12), 2083–2088.

Majid A. and Mahna M. (2019). Application of Lab-Scale MBBR to Treat Industrial Wastewater using K3 Carriers: Effects of HRT, High COD Influent, and Temperature. *International Journal of Environmental Sciences & Natural Resources,* **20**(2), 35–42.

Makisha N. (2021). Application of biofilm carrier in aerobic reactors as a method to improve quality of wastewater treatment. *Hydrology journal*, **8**(2), 77.

Palaniandy P., Adlan M.N., Aziz H.A., Murshed M.F. and Hung Y.T. (2017). Dissolved air flotation (DAF) for wastewater treatment. *In Handbook of advanced industrial and hazardous wastes management* (657–694). CRC Press.

Rattanapan C., Sawain A., Suksaroj T. and Suksaroj C. (2011). Enhanced efficiency of dissolved air flotation for biodiesel wastewater treatment by acidification and coagulation processes. *Journal of Desalination*, **280**(1–3), 370–377.

Santos A.D., Martins R.C., Quinta-Ferreira R.M. and Castro L.M. (2020). Moving bed biofilm reactor (MBBR) for dairy wastewater treatment. *Energy Reports journal*, **6**, 340–344.

Sinaga F.A., Lubis M.T. and Husin A. (2022). Reduction of TSS, COD, Oil and Fat in Palm Oil Mill Waste Using Dissolved Air Flotation Method. *Journal Serambi Engineering*, **7**(4).

Sosamony K.J. and Soloman P.A. (2018). Treatment of pretreated textile wastewater using modified Mbbr. *International Journal Engineering Technology*, **7**(3.8), 106.

Sperling M.V. (2007). Wastewater characteristics, treatment and disposal. Water Intelligence Online, *IWA publishing,* **6**.

Tetteh E.K. and Rathilal S. (2018). Evaluation of the coagulation floatation process for industrial mineral oil wastewater treatment using response surface methodology (RSM). *International Journal of Environmental Impacts*, **1**(4), 491–502.

Vasseghian Y. (2015). Modeling and optimization of oil refinery wastewater chemical oxygen demand removal in dissolved air flotation system by response surface methodology. *Advances in environmental technology* journal, **1**(3), 129–135.

Wang T., Wu T., Wang H., Dong W., Zhao Y., Chu Z., Yan G. and Chang Y. (2020). Comparative study of denitrifying-MBBRs with different polyethylene carriers for advanced nitrogen removal of real reverse osmosis concentrate. *International Journal of Environmental Research and Public Health*, **17**(8), 2667.

Yavari S., Malakahmad A. and Sapari N.B. (2015). A review on phytoremediation of crude oil spills. *Water, Air & Soil Pollution journal*. **226**, 279. https://doi.org/10.1007/s11270-015- 2550-z.

Zafarzadeh A., Bina B., Nikaeen M., Movahedian A.H. and Hajian N.M. (2010). Performance of moving bed biofilm reactors for biological nitrogen compounds removal from wastewater by partial nitrification-denitrification process. *Iran Journal of Environmental. Health Science Engineering,* **7**(4), 353–364.

Zinatizadeh A.A.L. and Ghaytooli E. (2015). Simultaneous nitrogen and carbon removal from wastewater at different operating conditions in a moving bed biofilm reactor (MBBR): process modeling and optimization. *Journal of the Taiwan Institute of Chemical Engineers*, **53**, 98–111.