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Research Article

Operation of Moving Bed Biofilm Reactor in Terms of Organic Matter and Triethylene Glycol from Simulated Petrochemical Wastewater

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Abstract

Background: Triethylene glycol (TEG) is an organic compound of the two-factor or di-alcohol alcohols and is used as a vinyl plasticizer. TEG has high toxicity and is classified in the chemical and polymer production group of petrochemical industry.
Methods: The current experimental study was conducted on a pilot scale. The total volume of the pilot study was 35.1 liters and its useful volume considering freeboard was 30 liters. The range of variables in the current study was input COD (chemical oxygen demand) (1000 - 3000 mg/L), pH (6, 7, and 8), C6H14O4 (600, 800, 1200, and 1800 mg/L), and hydraulic retention time (6, 8, 10, and 10 hours).
Results: The results of the study showed that by increasing the compatibility time within 30 days, the COD input to the system also increased, as the input organic loading of the system in the 10 days was 769 mg/L, and then this amount after 20 days, the time spent for 30 days was 941 mg/L, during which high concentrations of sewage could be significant. On the other hand, output organic loading also increased with the overtime and increase of the input organic loading. By increasing the moving bed biofilm reactor (MBBR) hydraulic retention time after 5 hours, residual COD level of input to the amount of 1165.2 mg/L reached 40.5 mg/L.
Conclusion: The obtained results showed that the MBBR system had the highest efficiency after 5 hours and optimized pH 8 for concentrations of TEG entering the system about 600 and 800 mg/L were 96.5% and 92.87%, respectively; and in the hydraulic time of 1 hour reached the efficiency of about 70% at 600 mg/L concentration, and no removal was observed in 800 mg/L, which can be concluded that in 1 hour or less and at concentrations of 800 mg/L and above, it can be used as pretreatment.

Keywords: Triethylene Glycol, Moving Bed Biofilm Reactor, Petrochemical, Wastewater

1. Background

Along with the development of the petrochemical industry in Iran that increases the capacity of the existing units by adding new units to the available complexes, it is necessary to consider relevant environmental issues (1, 2). In the petrochemical industry, similar to other industries, various wastewaters are produced that need to be refined before being discharged into the environment. Triethylene glycol (TG) is an organic two-factor or di-alcohol compound used as a vinyl plasticizer. TG has high toxicity and in the petrochemical industry is classified in the chemical and polymer production group (3). Although ethylene glycol (EG) is produced directly with chlorine hydrolysis by alkaline hydrolysis, the ethylene oxide hydrolysis method is currently a common method to prepare EG. Feeding stream of reactor to synthesize EG contains water and EG (from direct oxidation of ethylene).

Regularly, diethylene glycol (DEG) and TEG are utilized from the reaction of EG along with excess ethylene oxide. The crude glycol solution is utilized under the impact of various dehydrators and the last product is obtained by purification (4).

The ratio of the products by the United States environmental protection agency (EPA) (5) is as follows: EG, 87.1% - 88.6%; DEG, 9.4% - 10.4%; and TEG, 2.25% - 2.52%; and by ICI Chemicals and Polymers Ltd. as 90.3%, 9.1%, and 1.2%, respectively. Several methods were used to treat EG containing waste waters. Zevra et al. (6) used wet oxidation to treat oily wastewater containing alcoholic and phenolic compounds with high concentration of organic matters (chemical oxygen demand (COD) ~ 11000 mg/L). They studied a high-pressure agitated autoclave reactor at 180 - 260°C and 1 MPa of oxygen pressure and increased COD removal rate was reported with increasing the temperature. They observed that EG showed great resistance to this process among the other compounds of the wastewater and temperatures up to 240°C were effective for its good degradation (6). Means and Anderson determined the biodegradation of EG under oxic biological situations in 5 dissimilar experiments using miscellaneous fluid aqueous media. Degradation was observed using O_2 uptake rate (OUR), dissolved organic carbon (DOC) elimination, or carbon dioxide (CO_2) production. EG was quickly biodegraded in all of experiments with a delay time of up to 3 days. Degradation to 10% or less of the offset concentration was stated in all experiments afterwards in 1 to 21 days (7). Evans and David investigated the biodegradation of EG in 4 samples of water solution in vitro. The samples were incubated with EG at 0, 2, or 10 mg/L at 20 or 8°C. At 20°C, elementary biodegradation was full along with 3 days in all 4 samples; in addition, at 8°C, it was complete on the day 14. Degradation rates additionally decreased at 4°C (8). The moving bed biofilm reactor (MBBR) is a powerful biological process advanced on the basis of the activated sludge and bio-filter process (9). The main feature of this reactor is the growth of biofilm on the surface of small acnes that pass through the reactor. The advantages of this system included continuous purification operation, no clogging, no need for reverse washing, no need for return sludge, less hydraulic loss, high specific surface of biofilm, efficiency to treat various types of wastewater, high efficiency of the system, simultaneous elimination of nutrients , non-channelization of flow and sludge accumulation, no sludge escape problem, short startup time, flexibility in the process design, easy control of the process, resistance against all kinds of shocks, and low investment and operating costs. A specific standard that is not considered by the State Environmental Protection Agency to discharge EG compounds into the environment (9-11). However, in 1991, the Japanese environmental agency provided a standard dose of 0.1 to 0.4 mg/L for the presence of this toxic substance in water. Since the current study aimed at investigating the moving bed biofilm reactor in the treatment of TG in vitro, related studies were conducted in this regard (12). The MBBR and sequencing batch reactor (SBR) integrated reactor was operational in the anaerobic/anoxic/oxic (AAO) process to eliminate nutrients, which achieved the best removal efficiency during a 3 hour hydraulic retention time (13). A study was conducted on the treatment of EG wastewater using the ozonation method (14). A study conducted on 3 MBBR reactors for the simultaneous removal of nutrients and organic matters showed a good stability of the optimized system and MBBR function for residual values against input values of organic matters and nutrients (9). Since the use of chemical methods usually lacks functionality and using biological methods has many advantages, including the cost effective operation, therefore, the current study aimed at determining the effect of treating a toxic compound that under normal conditions directly affects the responsible microorganisms in biological processes.

2. Methods

The current experimental study was conducted on a pilot scale. Pilot processing and all of the experiments were conducted at Batab Sanat Ojan Co. of water and wastewater laboratory. Sampling in the current study was manual. The experiments performed in this project were based on the instructions given in the standard methods manual. The method of each experiment, the sampling site and the type of sample in the study are shown in Table 1.

Table 1. Experiments During Study Time (15)

Sampling Site	Sampling Type	Method	Experiment
Feed tank	Input	Instruction of 5220B Standard methods 2012	Chemical oxygen demand
Reactor	Output		
Feed tank	Input	Instruction of ESI 2012	TEG ($C_6H_{14}O_4$)
Reactor	Output		
Reactor	Daily	Instruction of 2540D & 2540E Standard methods 2012	MLSS, MLVSS
Reactor	Daily	Istek Portable set	pH
Reactor	Daily	Portable setHACH	Temperature

Abbreviations: MLSS, mixed liquid suspended solid; MLVSS, mixed liquid volatile suspended solid; TEG, Triethylene glycol.

In the current study, a Plexiglas pilot was built and used with a diameter of 0.5 cm and dimensions of 25.5 × 25.5 × 54 cm with 5 probes, in order to be flexible in operation. The total volume of the pilot was 35.1 L and its useful volume had a freeboard of 30 L. The purpose of selecting the reactor with these dimensions was to achieve ease of use in process calculations, as well as the operation of a disc diffuser on the floor of the reactor. To ensure a pilot seal, it was filled with water for one day and ensured that it was sealed.

It should be noted that in the current study, 60% of the reactor volume was filled with K3 media and the remaining 40% was considered as work volume. An aerobic system was supplied using a diffusor installed on the pilot floor, and the air was supplied by an aqua pump with a nominal air capacity of 80 L per minute, also feeding the reactor was performed using a peristaltic pump. Finally, in the pilot, the moving media K3 of HDPE (high-density polyethylene) type was used with a total specific area of 584 m^2/m^3. The pilot controller system consisted of a digital control circuit, all of which were programmed for pilot operation, and the tanks were guided by selecting the program and the desired cycle that was previously embedded on the controller system.

The MBBR reactor used in the current study was a fully interrupted biofilm reactor, which was run in 5 phases of filling, reaction, deposition, discharge, and resting in each cycle. In fact, with this modification, the system was changed from active sludge to biofilm mode. The system's operation schedule was designed to achieve optimal points in Table 2.

It should be noted that in the first phase, the amount of hydraulic retention time (HRT) and optimal discharges were recorded. Then, considering these points optimization, the TEG values of the output, SRT (solids retention time), MLVSS (mixed liquor volatile suspended solids), and the food-to-microorganism (F/M) ratio were investigated. Then, the organic load and TEG were measured and the results were analyzed and recorded. Figure 1 shows the reactor in use. The statistical test used in the current study included the SDM and RSM calculations performed by EXCEL software.

Figure 1. The MBBR Reactor in Operation

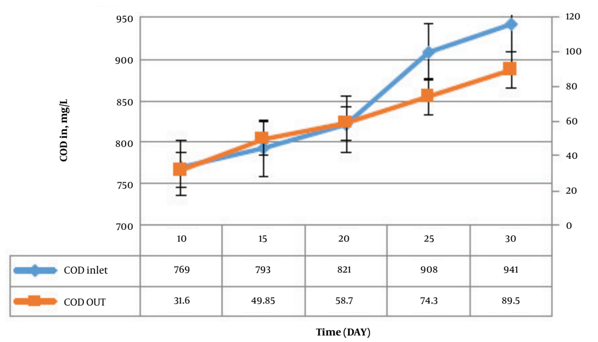

Figure 2. CODin, CODout Values During Steady States

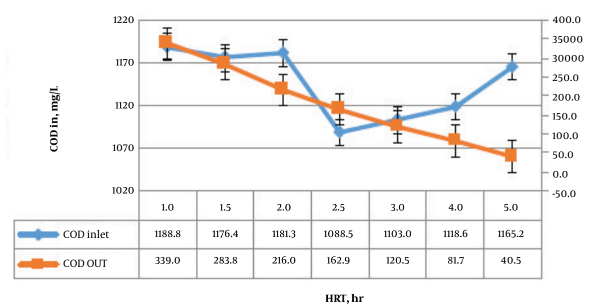

Figure 3. CODin and CODout Values at 600 mg/L Concentration in Different HRTs

graph. By increasing the HRT to 5 hours, the removal efficiency reached 96.5%.

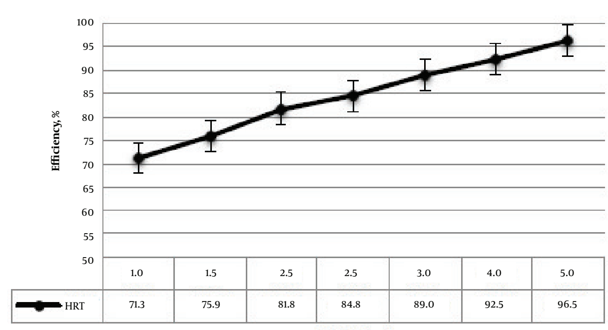

Figure 4. Efficiency in Different HRTs at 600 mg/L Concentration of TEG

3. Results

The relationship between the input and output COD during the adaptation of microorganisms in a time period of 30 days is shown. The results showed that by increasing the adjustment time during 30 days input COD also increased; therefore, organic inputs to the system reached a value of 769 mg/L within 10 days, and then this amount increased after 20 days, i e, HRT, after 30 days, reached 941 mg/L, when the high concentrations of wastewater were responsive. On the other hand, with the passage of time and the increased organic input, output organic also increased (Figure 2).

As shown in Figure 3, increasing the hydraulic retention time of the MBBR system after 5 h was 1165 mg/L of the input organic loading into the system and the remaining COD level was 40.5 mg/L.

As shown in Figure 4, the efficiency of removal of TEG in the HRT in the MBBR system is shown in a significant graph. By increasing the HRT to 5 hours, the removal efficiency reached 96.5%.

As shown in Figure 5, by increasing the HRT in the MBBR system, the remaining organic loading in the effluent reached 116.9 mg/L. Meanwhile, cod input was 800 mg. It should be noted that the input COD varied depending on the different conditions, including fixing the TEG values.

Table 2. The Operation Schedule of the System for the Whole MBSBR Disregarding Shock

			FR, %	pH	COD, mg/L	$C_6H_{14}O_4$	HRT, h
60	6, 7, 8	3000 - 1000	600	6	8	10	12
			800	6	8	10	12
			1200	6	8	10	12
			1800	6	8	10	12

Abbreviation: FR, filling rate.

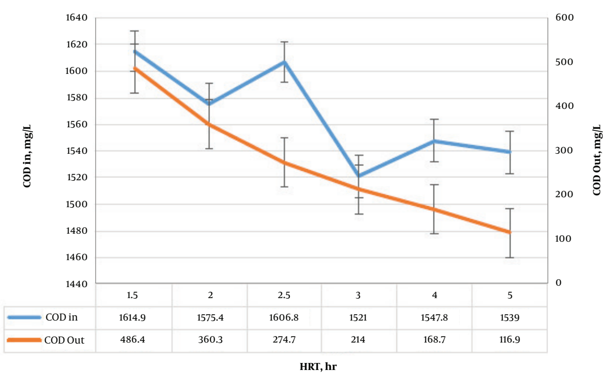

Figure 5. CODin and CODout Values in 800 mg/L Concentration at Different HRTs

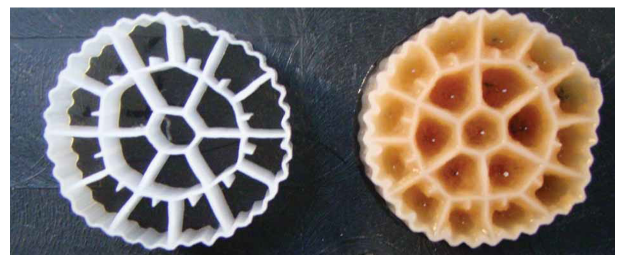

Figure 6. Biofilm Layer Formation of Light Brown Color on Media

4. Discussion

4.1. Reactor Working Phase

In the primary stage, the reactor with an initial dose of 600 mg/L TEG was started, which after the formation of biofilms, was step-by-step adapted to microorganisms with glucose. Afterwards, TEG was gradually replaced by glucose until glucose was not used as a food supplement for microorganisms. Hereon the system was adapted to the TEG. The system in a steady state was adjusted to 6, 8, 10, and 12 HRT, and investigated the effective elimination of COD and TEG, respectively. Also, TEG values at 600, 800, 1200, and 1800 mg/L were added to the system at the mentioned HRTs, respectively. Almost, each HRT was operated for 3 weeks. After 5 days, samples were taken daily (2 samples daily and nearly 20 samples per HRT).

The light brown biofilm layer formed on the media surface is shown in Figure 6.

4.2. Role of Applied Organic Rate on COD Removal Efficiency in HRT

At first, the reactor was run at a dose of 600 mg/L TEG (COD = 1188 ± 33.2 mg/L) and a retention time of 1 hour. COD removal efficiency achieved at this HRT was 71.48% ± 3.5%. However, increased retention time gradually increased the efficiency to 75.87% ± 4.1%, 81.71% ± 3.9%, 85.03% ± 4.1%, 89.07% ± 3.2%, 92.69% ± 2.8%, and 96.52% ± 1.8% at HRTs of 1.5, 2, 2.5, 3, 4, and 5 hours, respectively. The highest removal percentage, that is, 96.52% ± 1.8%, at this organic load (COD = 1165.2 ± 29.3 mg/L) was achieved at a HRT of 5 hours. When sampling was completed at concentration of 800, 1200, and 1800 mg/L, the system was maintained at a retention time of 6, 8, 10, and 12 hours and TEG amount was increased step-by-step, hence, the concentration reached up to 800 mg/L. The inlet organic loading, at a TEG dose of 800 mg/L, was raised by about 426.1 mg/L (1614.9 ± 42.6 mg/L). The highest COD eliminate efficiency of the reactor achieved at the 12 hours was up to 92.4% ± 3.1%.

At the end of this phase, TEG amount increased up to 1200 mg/L and HRT was set to 12 hours to prohibit any possible shock due to a raise in the TEG amount. Then, the inlet TEG was gradually increased. The general raise of TEG amount to 1200 mg/L led to the raise of COD by 627.2 mg/L. The removal efficiency of the system at an HRT of 12 hand a COD input of 1816.3 ± 16.0 mg/L reached 92.49% ± 3.5%. After reducing the HRT and increasing OLR for example at an HRT of 4 hours, the COD removal in the moving bed bio-reactor significantly reduced; hence, the efficiency reached 26.31 ± 2.2. Needless to say, seeming specifications of the reactor were not attractive, which was usually determined by the existence of white foam on the system's surface area. It is recommended to use antifoam under such circumstances. The maximum and minimum organic loads achieved in this step were 32.16 ± 0.23 and 15.42 ± 0.11 kg COD/m^3/d, respectively.

In a similar study, Li et al. (16) reported that MBBR was capable of 73% COD removal efficiency, with an inlet COD dose of 1000 mg/L. The COD removal efficiency for MBBR was reported at a concentration of 1000 mg/L COD of 73% and for an inorganic load of 2000 mg/L, 79%. Delnavaz et al. (17) showed that in COD = 2000 mg/L, the maximum removal efficiency of COD in MBBR reached 90% to treat aniline from industrial wastewater. In another study, Aygun et al. (18) utilized an MBBR reactor at a laboratory scale to remove organic matters in 5 various OLRs: 1.5, 3, 6, 12, and 24 kgCOD/m^3/d, respectively. Their study showed that moving bed bio-reactor is able to remove 95.1%, 94.9%, 89.3%, 68.7%, and 45.2% of the organic loading rate (OLR) of the system, respectively (18). Results of these studies were similar to those of the current study.

5. Conclusions

The results of the current study in the laboratory scale showed that the MBBR has the high ability to remove TEG from industrial wastewater. After obtaining the results, it was observed that the MBBR system for 5 hours and optimized pH 8 for inputs of about 600 and 800 mg/L TEG to the system the highest efficiency was 96.5% and 92.87%, respectively; in the hydraulic retention time of 1 hour in concentration of 600 mg/L approximately 70% efficiency was achieved, and in 800 mg/L concentration no removal was observed. It can be concluded that at the time of less than 1 hour and in concentrations of 800 mg/L and above, this system can be used as a pre-treatment with regard to the nearly optimal conditions obtained in the current study; the range of pH 8 can be used to verify the claim that the proper pH range in the most previous studies for different microorganisms were in the same range (13). Rusten et al. also obtained similar results in their study on the moving bed biological reactor systems (19).

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Footnotes

Authors' Contributions: All authors contributed: concepts, design, manuscript editing, manuscript review, literature search, experimental studies, data analysis, manuscript preparation, statistical analysis, method analysis.

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