original article

Biodegradation of benzene–toluene–xylene in petrochemical industries wastewater through anaerobic sequencing biofilm batch reactor in bench scale

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ABSTRACT

Aims: This study aims to evaluate the performance of the anaerobic sequencing batch biofilm reactor (ASBBR) for biodegradation of Benzene–Toluene–Xylene (BTX) that is present in petrochemical synthetic wastewater.

Materials and Methods: A laboratory-scale ASBBR was used to treat a synthetic substrate mixture representing petrochemical wastewater that contained BTX. The operation schedule was: Fill time: 10 minutes, reaction time: 22.8 hours, settling time: 60 minutes, and decant time: 10 minutes, at 35°C. The BTX samples were analyzed by gas chromatography-flame ionization detector (GC-FID) equipped with head space.

Results: After reaching to stable operation, the reactor was exposed to influent BTX concentrations of 5, 20, and 50 mg/l, with overall organic loading rate of 3 g COD/l.d resulting in 61, 79, and 50% removal efficiencies for the BTX, respectively. At this time, the removal efficiencies for COD were 75, 90, and 70%.

Conclusions: The optimum BTX removal of 79% was achieved in 3 g COD/l.d and HRT of 3.8 days, at influent BTX concentration of 20 mg/l. Thus, it could be concluded that ASBBR was a feasible, efficient, and consistent technology for treatment of petrochemical wastewaters containing BTX. The ASBBR might be an alternative to intermittent systems as well as batch systems due to its superior operational flexibility.

Key words: ASBBR, BTX, Petrochemical wastewater

INTRODUCTION

Monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene could be symbols of environmental pollutants due to their identified toxicity. Their high solubility in water is a considerable risk for ground water contamination. Benzene, Toluene, and Xylene (BTX) are natural constituents of crude oil and gasoline. These compounds are often found in surface and ground water as a result of leakage from storage tanks or pipelines, improper disposal practices, inadvertent spills, and leaching from landfills area.[1-4] On the other hand, effluents from petrochemical industries are increasing significantly. The main effect that is presented by BTX in gasoline is co-solvency, which increases the

Access this article online	
Quick Response Code:	**Website:** www.ijehe.org
	DOI: 10.4103/2277-9183.96145

This article may be cited as:
Estebar M, Amin MM, Poursafa P, Ghasemian M, Jaafarzadeh N, Hashemi H, Fatehizadeh A. Biodegradation of benzene-toluene-xylene in petrochemical industries wastewater through anaerobic sequencing biofilm batch reactor in bench scale. Int J Env Health Eng 2012;1:22.

solubilityof aromatic hydrocarbons in water sources. Therefore, contamination of water supplies bygasoline-amended BTX and other petroleum-derived hydrocarbons is a serious and widespread environmental problem.[5]

Benzene, Toluene, and Xylene compounds are dangerous carcinogens for humans, and exposeenvironmental problemsin water, soil, and indoor and outdoor air, as well as, create health risks for humans and animals.[6]

The application of pre-selected bacteria in the biodegradation processes can represent a reliable and effective tool in the treatment of water contaminated witha mixtureof benzene, toluene, ethylbenzene, and xylene(BTEX). Therefore, the rawpetroleum refinery effluent canbe a source ofhydrocarbonbiodegrading microorganisms.Some natural microorganisms havethe capability of degrading BTX.They are extensively present in the activated sludge of wastewater treatment plants as well as contaminated soil.[4]

It was revealed that the optimal temperature for microbial activity was 35°C, due to the maximization of cell growth and toluene degradation. A consortium augmented at 35°C showed increased degradation rates of benzene, toluene, ethylbenzene, and xylene in single-substrate experiments.[7]

Anaerobic batch processes planned for wastewater treatment provide more advantages than common anaerobic techniques, for example, the absence of hydraulic short-circuit, superior effluent quality control, no need for primary and secondary settlers, nonexistence of biomass transmission, and simple operation.[8]

In anaerobic systems, where multiple biodegradation pathways can be present, short-term inhibition of certain microbial populations may not result in anoticeable decrease in biogas production. However, long-term exposure to antimicrobials may result in the accumulationof intermediate products, which can negatively affect the anaerobic treatment performance.[9]

Agitation power and feeding strategies are effective factors for ASBBR performance and they can be manipulated for optimizing the process.[10]

The lag period prior to the start of anaerobic BTEX biodegradation varies in different compounds and various sites. To predict the required time for field biodegradation of individual compounds, by using laboratory microcosms or *in-situ* columns accurately, the source of this variability mustbe better understood.

Mechanisms of inhibition during short-term test conditions may be different from long-term operation.Moreover,the biomass in the ASBR can adjust by changing the populations or by developing adaptation through production of enzymes in response to the presence of recalcitrant compounds.[9]

The ecologically acceptable treatment method for wastes of benzene and other hydrocarbonsis amain challenge confronting the petrochemical industries as well as other chemical industries,[10-11] and the frequency of groundwater pollution with hydrocarbons, including BTX has been increasing. Therefore, development of more capable methods to remove or minimize the damages is necessary.[4]

The purpose of this study was to evaluate the efficacy of anaerobic sequencing batch biofilm reactor for BTX biodegradation in petrochemical synthetic wastewater.

MATERIALS AND METHODS

Reactor setup and operation

An ASBBR with a total volume of 7 l, a diameter of 25 cm, and a height of 32 cm, was used in this study. Five liters was considered for liquid (water) volume and two liters of reactor upside as a free board for biogas collection. The reactor was operated with a24-hour cycle including:Feed time (10 minutes), reaction time (22.8hours), settling time (1 hour), and decant time (10 minutes).[9]

The experiments were performed at 35 ± 0.5°C by circulating warm water around the reactors. Agitation of the rector contents was done by using a magnetic stirrer installed under the bottom of the reactor. The media were a plastic material basket including 6-cm long corrugated plastic pipe pieces arranged in parallel, in vertical rule, inside the reactor. The system was inoculated with sludge obtained from a full-scale anaerobic reactor treating wastewater. About 40% of the reactor(volume) was filled with this sludge (VSS, 68 g/l), [Figure 1].

Synthetic substrate

The inlet synthetic wastewater that was provided daily included: the main substrate (BTX), substrate-aid (Acetic acid), nutrients, and microelements, with a total chemical oxygen demand (COD) of 5000 mg/l. A substrate mixture model representing the petrochemical industry wastewater is described in Table 1.

The pH of the wastewater was adjusted to 7–8, through addition of NaOH and KOH (1:1 molar ratio). However, the pH of the reactor was not adjusted manually, and varied from 7.2 to 8.5 through good operation of the anaerobic process.

Organic and benzene–toluene–xylene loading rate and protocol

The reactor was operated with an organic loading rate(OLR) of 0.5 g COD/l.d for the initial 50 days of operation. In the next operation periods, OLRs of 1, 2, and 3 g COD/l.d for days 51–70, 71–90, and 91 – 130, respectively, were introduced to the reactor. When the BTX concentration was equal to 0 mg/L, acetic acid was used as a substrate aid. The influent substrate concentrations increased and the OLRs were

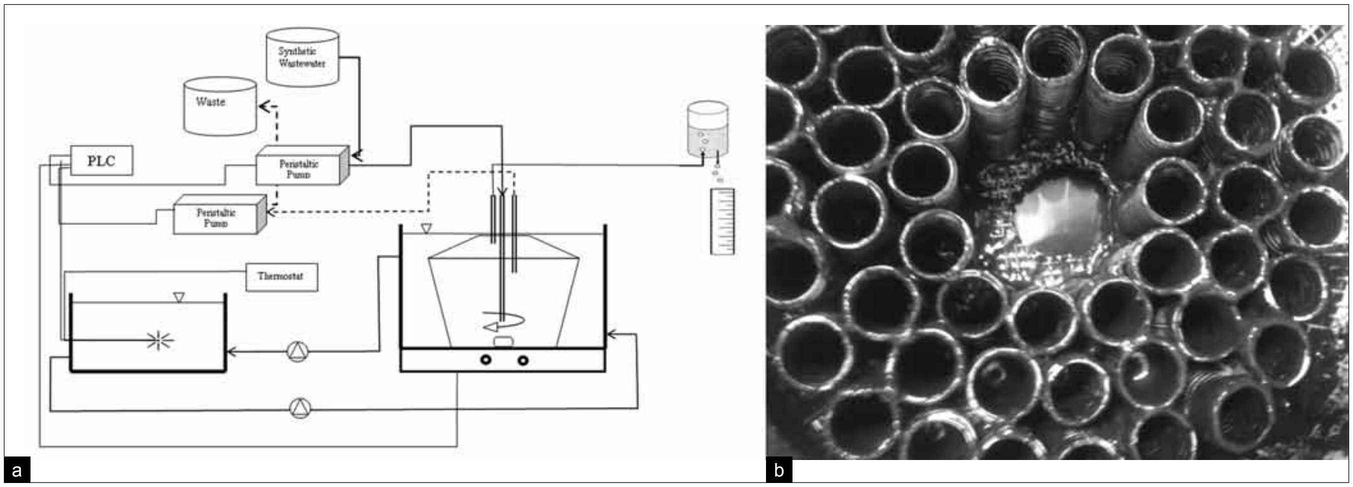

Figure 1: Experimental set-up of ASBBR reactor (a) and parallel 6 cm long pieces of corrugated plastic pipe as media (b)

Table 1: Substrate mixture model representing petrochemical industry waste water

Components	Concentration (mg/L)	COD (mg/L)
Acetic acid	7163	7500
Benzene	1000	2000
Toluene	1000	3750
Xylene	1000	2892
BTX	1000	2820

achieved by decreasing the hydraulic retention times from 10 to 2.5 days for the sequencingperiods.

On operation day 131, BTX was added to the influent wastewater at a concentration of 10 mg/l. On days 139–150, the influent concentration of BTX was decreased to 5 mg/l, with an efficiency removal of 60%, and on days 151 – 210, the influent concentration of BTX was increased to 20 mg/l, with an efficiency removal of 87.5%, and a concentration of 50 mg/L was the inhabitation step that decreased the efficiency removal to 40%.

Analytical methods

The reactor performance was evaluated through daily monitoring of the physicochemical characteristicsof the influent and effluent, including chemical oxygen demand (COD), pH,suspended solids(SS), volatile suspended solids(VSS), temperature, and gas chromatography (GC), for BTX.[12] Biodegradation of BTX by the ASBBR was monitored using a gas chromatographequipped with a head space. Gas chromatography was conducted using Varian 3800 that included a column with a length of 25 m and a diameter of 0.32 mm. The initial temperature was fixed at30°C for 3 minutes and then, the temperature was increased at rate of 15°C/min, upon reaching 300°C. The carrier gas was nitrogen, and flame ionization detector (FID).The injector temperatures were 325°C and 258°C, respectively. The amount of biogas production by the ASBBR was monitored through liquid displacement.

RESULTS

Anaerobic sequencing batch biofilm reactor performance

The ASBBR was operated for 290 days [Table 1]with OLR ranging 0.5 to 3 g COD/l.d. On days 1 – 162, the BTX concentration was zero. On days118 – 162, the COD removal reached to >90%. Therefore, the OLR was increased from 0.6 to 1, 2, and 3 g COD/l.d. The average biogas production ranged from 0.6 to 2 l/d during this period [Figure 2a]

Starting on day 164, 10 mg/l of BTX was added to the influent of the ASBBR, to evaluate the influence of the relatively low levels of BTX on the reactor performance.

After an initial adjustment period, with influent COD of 7500 mg/L, the COD removal efficiency reached approximately 50%, and the biogas production decreased to 0.5 l/d (days 164 – 171).

On operation days 172 – 210, the OLR was kept to 3 gCOD/l.d and the BTX concentration was decreased to 5 mg/l. On days 211 – 252, using influent COD of 7500 mg/l, OLR was reached to 3gCOD/l.d, through decreasing the co-substrate (acetic acid) concentration and increasing the concentration of the main substrate (BTX)to 20 mg/l. In this period, the biogas production was 1.5 l/d.

In the last step (days 253 – 298), with an influent flow rate of 3 l/d, an OLR of 3gCOD/l.d and BTX concentration of 50 mg/l, the removal efficiency of COD and BTX decreased from 90 and 87% to 67 and 20%, respectively.

The concentrations of acetic acid during the initial 162 days of operation were 5000 and 7500 mg/L. When the BTX influent concentration was increased from 5 to 20 mg/l on day 211, a further increase of the effluent-soluble COD was observed, up to 7500 mg/l, the COD removal efficiency had reached to >90%, and the biogas production had reached to1.5 l/d (days 164 – 252).

Table 2: ASBBR Performance

Operation (d)	COD			BTX		
	In (mg/l)	OLR g/l.d	Removal (%)	In(mg/l)	Out(mg/l)	loading mg/l.d
Start-up and stable operation, BTX concentration = 0						
7 – 62	5000	0.6	61.4 ± 4.7	0	0	0
63 – 96	5000	1	75.8 ± 4.7	0	0	0
97 – 117	7500	2	85.6 ± 1.7	0	0	0
118 – 162	7500	3	89.5 ± 4.3	0	0	0
BTX Concentration = 10 mg / l						
164 – 171	7500	3	69.5 ± 8.8	10	-	4
BTX Concentration = 5 mg / l						
172 – 210	7500	3	77.9 ± 7.1	5	2	2
BTX Concentration = 20 mg / l						
211 – 252	7500	3	89.7 ± 4.6	20	2.12	6.8
BTX Concentration = 50 mg / l						
253 – 298	7500	3	67.4 ± 10.3	50	26.4	12.5

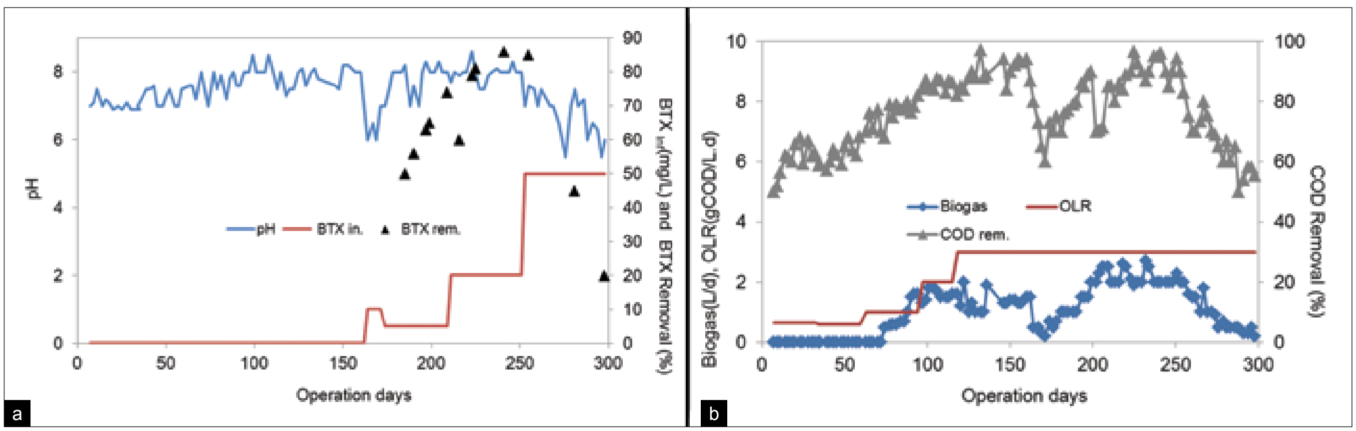

Figure 2: ASBBR performancefor COD (a) and BTX (b) removal during the experiment

DISCUSSION

In this study, after reaching stable operation, the reactor was exposed to BTX influent concentrations of 5, 20, and 50 mg/l [Table 2], with organic loading rate of 3 g COD/l.d, resulting in 61, 79, and 50% removal efficiencies for the BTX, respectively. The removal efficiencies for COD were75, 90, and 65%, respectively, at this organic loading rate. Gusmao *et al.*, achieved the BTEX removal efficiency of 99% at an initial concentration of benzene 26.5 mg/l, toluene 30.8 mg/l, m-xylene 32.1 mg/l, ethylbenzene 33.3 mg/l, and BTEX 26.5 mg/l.[5]

In this study, the BTX removal of 90% was achieved in 3 g COD/l.d, at an influent BTX concentration of 20 mg/l [Figure 2.b]. Siman *et al.*, concluded that ASBBR with an immobilized biomass could be efficient for organic removal at organic loading rate of up to 5.4gCOD/l.d, to be more constant to organic loading variations for 12-hour cycles.[13]

Formaldehyde is another material that is applied in chemical and petrochemical industries. A study in 2009, stated that in an ASBBR reactor, the formaldehyde degradation rate increased from 205 to 698 mg/l.h, as the initial concentration of formaldehyde was increased from about 100 to around 1100 mg/l.[14]

However, accumulation of organic matter was observed in the effluent (COD values above 500mg/l) due to the presence of non-degraded organic acids, especially acetic and propionic acids.[14] Another investigation showed that the removal efficiency for COD and formaldehyde were 94 and 99%, respectively, with an organic loading of 0.54 KgCOD/m^3.d. The lowest efficiencies were 48 and 63%, respectively, with an organic loading of 7.09 KgCOD/m^3.d.[15] Organic loading has a significant effect on the performance of the anaerobic sequencing biofilm batch reactor (ASBBR) by mechanically stirring. It depends on the influent concentration and cycle period.[13]

The experimental results indicated that BTX compounds could be effectively removed when the optimal concentrations of phosphates (650–1250 mg/l), ammonia chloride (10–50 mg/l), and sulfates (10–20 mg/l) were amended into the simulated aquifer. However, when the added concentrations were less than 250 mg/l, 10 mg/l, and 2.5 mg/l, respectively, the bacterial growth and BTX degradation became limited.[16]

Further investigations for cost-effective and environmentally friendly methods of benzene removal fromcontaminated sites need to be continued.[17]

CONCLUSIONS

In this study, thehighest BTX removal of 90% was achieved in 3 g COD/l.d and HRT of 3.8 days at BTX influent concentration of 20 mg/l. Thereafter, with increasing the BTX influent concentrations to 50 mg/l, the BTX removal decreased to 50%.

Based on the findings, it can be concluded that the ASBBR is a feasible, efficient, and consistent technology for treatment of petrochemical wastewaters containing BTX. The ASBBR might be an alternative to intermittent systems as well as batch systems due to its superior operational flexibility.

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Source of Support: Nil. **Conflict of Interest:** None declared.