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Research article

Simultaneous biofiltration of BTEX and Hg° from a petrochemical waste stream

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ABSTRACT

A biofiltration system was developed to treat benzene, toluene, ethylbenzene, and xylene (BTEX) and Hg° vapour from a petrochemical waste stream during overhaul maintenance. The biofilter compost bed was inoculated with a microbial consortium provided by a petrochemical wastewater treatment plant. The effect of the a BTEX concentration (192.6–973.8 g/m^{3}h) and empty bed residence time (EBRT) of 20–100 s were studied under the conditions of steady state, transient, shock BTEX-loading, and off-restart. The findings revealed that during a biofilter start-up, an increase in the influent BTEX concentration to around 334.3 g/m^{3}h did not notably affect the biofiltration function at an EBRT of 100 s, and the removal efficiency was higher than 98%. Further, the low EBRT of 60 s did not have adverse effects on the BTEX and Hg° biofiltration (the removal efficiency in both was >93%). For the biofiltration system, the BTEX and Hg° critical attenuation capacity were obtained as 663 g_{BTEX}/m^3h and 12.6 $g_{Hg°}/m^3h$ respectively. A maximum attenuation capacity of 774.5 g_{BTEX}/m^3h was achieved in the biofilter when the BTEX loading rate was 973.8 g_{BTEX}/m^3h. The parameters of k_m and r_{max} of the Michaelis–Menten kinetic model were obtained as 0.099 g/m^3 and 0.578 g/m^{3}min respectively. Both BTEX and mercury vapours were completely mass balanced during a continuous biofiltration test. In general, the developed treatment system exhibited a good performance in the treatment of the BTEX stream containing Hg° vapour in the off-gas of a petrochemical company.

1. Introduction

Oil, gas, and petrochemical activities lead to the release of various carcinogenic volatile organic compounds (VOCs) into the environment (Wang et al., 2015). The most hazardous of the VOCs in gas and petrochemical products are compounds represented by BTEX, comprising benzene, toluene, ethylbenzene, and xylenes (Šoštarić et al., 2016). According to the International Agency for Research on Cancer (IARC), BTEX exposure is a human health concern. Benzene is classified as a Group I carcinogen, ethylbenzene as a suspected IIB carcinogen, and both toluene and xylenes are classified as Group III neurotoxins (Liu et al., 2015). The industries producing plastics, paints, resins, rubber, adhesives, lubricants, coatings, drugs, detergents etc., are known sources of BTEX pollutants (Šoštarić et al., 2016). As reported by Aleghafouri et al. (2015), petrochemical plants are a major BTEX producer in the world; hence, petrochemical plants are the main sources of emitted BTEX into the environment, especially during overhaul and maintenance periods. In this context, according to Rene et al. (2010), high concentrations of benzene (around 450–2000 mg/m^3) were found in petrochemical industries; these high levels of benzene doubles the chances of leukaemia among those exposed to them than people in general. Thus, it is extremely important to eliminate BTEX compounds before being released into the atmosphere.

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During the overhaul and maintenance of the petrochemical industry, high levels of some other pollutants such as mercury vapour (Hg°), in addition to BTEX, are released into the environment. Mercury emissions are also considered a global environmental problem because of its toxicity to human health and long-distance transmission (Zhang et al., 2016). Therefore, abatement techniques for treating the BTEX and mercury vapour are essential.

The biological treatment, which relies on degrading microorganisms, is a well-known and eco-friendly technique to treat and oxidize off-gas vapours to inert or less toxic compounds (Blázquez et al., 2017; Rahul et al., 2013b; Skerman et al., 2017). Among the biological treatment systems, biofiltration serves as the most reliable technology (Zamir et al., 2011). Furthermore, this process has been confirmed to be a cost-effective technology to control many pollutants like odours and volatile organic compounds, hence, is most widely used as a biological off-gas treatment technique (Sorial et al., 1998). Although many studies have revealed promising findings and the biofiltration system's high efficiency in BTEX removal under experimental conditions (Cheng et al., 2016; Firmino et al., 2015; Lu et al., 2002; Rahul et al., 2013a; Torretta et al., 2015), based on authors' best knowledge, there is no reported study for BTEX removal from waste streams that also contains mercury vapour (Hg°).

This paper focused on exploring the efficacy of biofilter and evaluating the influent BTEX and Hg° concentration, and empty bed residence time (EBRT) effects on the capability of a biofiltration system. The capability of the biofilter under transient, shutdown, and shock conditions was also evaluated for a better insight into bioreactor behaviour under real conditions. In another attempt, the kinetic study, carbon and Hg° mass balance, and the evaluation of the fate of mercury vapours were also assessed.

2. Materials and methods

2.1. Chemicals and source of BTEX

All chemicals and reagents used in this study were of analytical grade (purity > 99%) and purchased from Merck Company. Wastewater containing BTEX from a petrochemical company located in Asaluyeh, Iran, was selected as a source of BTEX. The Asaluyeh area, located next to the northern part of the Persian Gulf, has one of the largest reserves of natural gas. There are 18 active petrochemical companies in this area. A required volume of the wastewater was provided from a manhole during the overhauling of the petrochemical company. The characteristics of the wastewater are presented in Table 1. As can be seen from Table 1 and Fig. S1, the wastewater contains high concentrations of benzene, toluene, ethylbenzene, and xylene (BTEX) as well mercury vapour. The wastewater sample was collected in three 40-L containers, which were shut with about 35% of the containers empty.

Table 1
The characteristics of the petrochemical wastewater and the atmospheric level of pollutants in a drop manhole.

Parameters (unit)	Value
COD (mg O_2/L)	257–264
Grease (mg/L)	1.96–2.01
Turbidity (NTU)	37–40
pH	7.60–7.64
[a] Benzene (g/m^3)	0.30–2.10
[a] Toluene (g/m^3)	0.26–0.34
[a] Ethylbenzene (g/m^3)	0.20–0.29
[a] Xylenes (g/m^3)	0.15–0.21
[a] Mercury vapour (μg/m^3)	86–97
Mercury ion (μg/L)	0.03–0.04
[b] Methylmercury	0
[b] Ethylmercury	0

[a] The concentration was analyzed at the headspace of the wastewater manhole (the sampling point).
[b] The concentration was analyzed at the headspace of the wastewater manhole and in the wastewater (both concentrations were zero).

2.2. Biofilter system setup

A biofilter was designed as depicted in Fig. S2. The biofilter was a Plexiglas column with H = 50 cm and Φ = 4.5 cm. A punctured Plexiglas plate was set at 7 cm above the column bottom (see Fig. S2) to keep the bed and identical distribution of the influent polluted air through the media. The valve for the entry of the polluted air was set 2 cm below the punctured tray, thus giving the biofilter sump a volume about 0.11 L. Around 35 cm of the reactor was packed with compost with a diameter of 1.5–1.8 mm as the medium, to provide a bed volume of 0.52 L. The density, porosity, and specific surface area of the media were 640 kg/m^3, 0.69, and 340 m^2/m^3 respectively. The reactor had a 7-cm headspace for the solution injection nozzles. The purified air valve was set 3 cm above the column bed, which was also used as a sampling port. The influent gas stream, containing the target pollutants, was supplied at the bottom of the column at a height of 1 cm below the first section of the biofilter media to ensure even distribution of the gas. The filtrate solution of the column was repeatedly recycled and injected into the bed. The other details of the designation of the biofilter system are shown in Fig. S2.

The initial compost media was supplied by the Isfahan Compost Factory, Iran, and was immersed and cultured in an aeration tank of the petrochemical wastewater treatment plant for 48 h, and then packed into the biofilter bed.

2.3. Inoculum preparation and biofilter inoculation

To prepare the inoculums, about 17 L of a concentrated and activated sludge was provided from the Mobin wastewater treatment plant, where all the petrochemical companies in Asaluyeh, Iran released their wastewaters. The activated sludge was centrifuged for about 15 min at 5000 rpm and then washed several times with deionized water. This concentrated activated sludge was poured into 150 mL of nutrient solution to gain suspended solids (SS) concentration of around 3000 mg/L. Then it was entered to a 20 L closed tank with a 3 L head space and exposed to BTEX and Hg° vapour as a carbon and nutrient source for three consecutive days. We noted that all sections of the BTEX and Hg° were actually provided (from the petrochemical waste stream) at a flow rate of 0.5 g/m^3 and 0.02 g/m^3 respectively. The recirculation of off-gas to the tank was also done through a pump. This allowed for enriching the BTEX-degrading bacteria (BTEX-DB). The enriched suspension cell concentration of 12000 mg/L as mixed liquor suspended solids (MLSS) was gradually inoculated to the biofilter medium with a flow rate of 100 mL/min and the column filtrate was re-circulated using an injection pump (ALCBIO ALC-IP900) for about 3 days. The MLSS and mixed liquor volatile suspended solids (MLVSS) concentration of the biofilter bed were obtained 5900 and 4425 mg/L (about 75% of MLSS), respectively. The final amount of microbial cell attached to media was ca. 0.415 g-MLVSS/g-dry material. During the inoculation period, an air low of 0.7 L/min was regulated into the biofilter for a better biofilm development. The inoculation was supposed to be complete when the concentration of SS in the column filtrate was lowered to 250 mg/L. Then, the biofilter operation was initiated by interring the air containing BTEX and mercury vapour.

2.4. Biofilter operation

The biofilter was supplied with ≈67 mL/min (in a duration of 3 min) of nutrient solution/make-up water every 12 h for keeping the bed wet, preventing biofilter dehydration, and supplying the essential nutrients for microbial activities. The hydraulic retention time (HRT) of ≈31 h under normal operating conditions was calculated for make-up water according to flow rate of 0.4 L/d and bed volume (0.52 L). The HRT parameter is the time that make-up water remains in the biofilter and is calculated as the volume of the bed divided by the make-up water flow rate. The nutrient solution was renewed every three days by adding the following composition in double distilled water: 3.13 g/L $Na_2HPO_4 \cdot 12H_2O$, 0.9 g/L $NaHCO_3$, 1.21 g/L KH_2PO_4, 3.88 g/L KNO_3, 2.58 g/L $(NH_4)_2SO_4$, 0.35 g/L $MgSO_4 \cdot 7H_2O$, 0.37 g/L $MgCl_2 \cdot 6H_2O$, 2.03 mg/L $ZnSO_4 \cdot 7H_2O$, 0.28 g/L $FeSO_4$, 3 mg/L $CaCl_2$, 1.52 mg/L $MnSO_4$, and 1 mg/L Na_2MoO_4. The other basic operating conditions are listed in Table 2.

The off-gas containing BTEX and mercury was entered from the base of the biofilter in an upflow mode. Many valves, tubing, pumps, and flow meters were applied to regulate the influent BTEX and Hg° concentration to the reactor. Two air streams were separately compressed and, after passing the through flow meters and pollutant reservoir, were jointed together in a mixing chamber. After that, a predetermined concentration of the pollutants was put into the biofilter to provide a given EBRT by varying the air streams. All tests were performed at room temperature (24 ± 1 °C). The pressure drop across the biofilter packing media was periodically checked to monitor the clogging and compaction of packing materials and kept at around 10 mmH_2O/m bed by backwashing the reactor. Details of the experimental design are listed in Table 2.

The capability of biofiltration was calculated with the help of the following equations:

$$RE = \frac{C_i - C_o}{C_i} \times 100 \quad (1)$$

$$AC = \frac{Q}{V_f}(C_i - C_o) \quad (2)$$

where: *RE, AC,C_i, C_o, Q,* and V_f are the removal efficiency (%), attenuation capacity (g/m^3h), influent and effluent pollutant concentrations (mg/m^3), air flow rate (m^3/h), and bed volume of the biofilter (m^3) respectively.

2.5. Sample collection and analytical methods

Both the air and liquid samples were collected and analyzed to monitor biofilter performances during the study period. Gas samples were taken every half day. To analyze BTEX concentration of the influent and effluent of the biofilter column, only the gas sampling ports were left open and the air sample was drawn from the bottle by 5 mL-Hamilton gas-tight syringe (Series No. 1005, Sigma-Aldrich) and measured by a gas chromatograph instrument (Beifen 3430, China) equipped with a flame ionization detector (FID) and a capillary column type HP-5 (30 m × 0.249 mm × 0.25 μm film thickness). The temperature of the injector, detector and oven were kept at 210, 230, and 60 °C, respectively. The nitrogen gas (N_2) and hydrogen gas (H_2) were respectively used as the carrier gas and fuel. According to the standard procedure (Rahul et al., 2013b), predetermined amounts of BTEX was provided to plot the calibration curve.

The CO_2 concentration was immediately measured using a digital CO_2 analyser (AZ-7752, China), and TOC in the biofilter filtrate was determined by a TOC analyser (TOC-VCPH, Shimadzu, Japan). The biofilm inside the biofilter was determined using the weighing method (Okkerse et al., 1999). Briefly, in this method the gained weight of the biofilter media showed the amount of biofilm.

Table 2
Basic experimental conditions for BTEX removal by the biofilter.

Parameter		Value
Steady state		
Influent concentration (g/m^3)	[a] B	0.25–0.44
	[a] T	0.12–0.23
	[a] E	0.16–0.23
	[a] X	0.09–0.17
	BTEX	0.62–1.07
	Hg°	0.02–0.2
Air flow rate (L/min)		0.7
[b] EBRT (s)		100
Liquid recirculation velocity (m^3/m^2 h)		4.8
Operation		
Influent concentration (g/m^3)	B	0.44–2.2
	T	0.23–1.18
	E	0.23–1.18
	X	0.17–0.85
	BTEX	1.07–5.41
	Hg°	0.2–0.6
Air flow rate (L/min)		0.7–2.5
Loading rate (g/m^3h)	B	79.2–396
	T	41.4–212.4
	E	41.4–212.4
	X	30.6–153
	BTEX	192.6–973.8
	Hg°	7.2–21.6
EBRT (s)		20–100
Liquid recirculation velocity (m^3/m^2 h)		3
Superficial air velocity (m^3/m^2 h)		5.4–29.5

[a] B: benzene, T: toluene, E: ethylbenzene, X: xylenes.
[b] EBRT: empty bed residence time.

The Hg° concentration in the influent and effluent of the biofilter was measured by using the Hg analyser (MONITOR, 2000; Seefelder Messtechnik, Germany). The mercury adsorbed by the compost media was analyzed by leaching the solids with 3HCl + HNO_3 (aqua regia) and then measuring the mercury ion content of the solution by using a Cold Vapour Atomic Absorption (UNICAM, model 929, UK) and a reducing agent of $NaBH_4$. For the analysis of methyl mercury (CH_3Hg) and ethyl mercury (CH_3CH_2Hg), a given amount of the biofilter media was immersed in 100 mL of deionized distilled water: HCl (1:1) and sonicated for 0.5 h. After that, the mixture was centrifuged at 1000 *g* for about 0.5 h and then the extraction of the supernatant was performed twice with 5 mL of toluene. The product was passed through an anhydrous sodium sulphate filter to remove its moisture content. Finally, an analysis of the CH_3Hg and CH_3CH_2Hg in the filtrate was done by using a Gas Chromatography-Mass Spectrometry (GC-MS) (Philip and Deshusses, 2008). We noted that the acidification of liquid samples was applied for extraction. Using a scanning electron microscopy analyser (SEM, Sirion from FEI), the surface morphologies of the acclimated compost bed sample were examined.

Moisture content of the filter bed was determined through weighting method. The samples from different depths of biofilter were collected and oven-dried at 105 °C for 24 h. The percentage of moisture was determined from the difference between primary and secondary weights. Where there is needed, the moisture of the biofilter bed were set by regulating the make-up water flow. The compost pH were analyzed by adding 10 mL deionized distilled water to the 10 g dried bed samples and after 1 h measure the solution pH using a pH meter (Mettler Toledo, UK) (García-Carmona et al., 2017). The pH of re-circulated make-up water that collected from the bottom of biofilter was also monitored regularly to control the biofilter performance. For the electrical conductivity

(EC) measurement of compost bed sample a ratio of 1: 5 dried compost and deionized distilled water was prepared and after 1 h the EC of the solution was analyzed with an EC meter (AZ 86503, Taiwan) (Pen-Mouratov et al., 2008). The pH and EC parameters for compost bed samples were obtained 6.9–7.5 and 280–390 μs/cm, respectively at steady state conditions. Ambient and inlet flows temperatures were measured by a digital temperature meter (Model No. DT-615). The temperature of reactor off-gas was also regularly monitored. It was fall within the range of 30–35 °C, indicating the BTEX-DB in the biofilter was mesophilic. Other analyses such as TSS, MLSS, and MLVSS were done according to Standard Methods for Examination of Water Wastewater (Federation and Association, 2005).

3. Results and discussion

3.1. BTEX-DB growth, start-up, and steady state of the biofilter

The concentrated mixture was injected into the biofilter with a desired flow rate and the mixture was then recycled several times to ensure greater attachment the microorganisms to the bed. The obtained attached microbial biomass of 415 mg-MLVSS/mg-dry material is in the ranges that of reported for attached growth systems (Cohen, 2001). BTEX- and Hg°-laden stream, plus the required nutrients, were counter currently injected into the reactor sump as a source of energy and nutrients of BTEX-DB. The criterion for biomass growing was evaluated using the amount of total suspended solids (TSS) in the recycled solution. After 4 d of recirculation of the mixture, the TSS concentrations reached 250 mg/L; demonstrating a cell mass of 415 mg (as dry mass basis) attached to the biofilter media. Such results were reported by Moussavi and Mohseni (2008). The cell mass of the media may even have been more than 415 mg, as it was submerged in the BTEX-DB suspension. An achievement of BTEX removal >99% reflected a satisfactory attachment and activity of the BTEX-DB in the biofilter.

After we ensured a satisfactory bacteria growth, the biofilter operation was initiated by feeding 0.62 g/m^3 of BTEX (as BTEX-DB electron donor) and 0.02 g/m^3 of Hg° vapour. The influent concentration of BTEX and Hg° was gradually increased to 1.07 and 0.2 g/m^3 respectively, at the flow rate of 0.7 L/min and the EBRT of 100 s. In the start-up time, the recycle flow rate was adjusted to 110 mL/min (corresponding to the velocity of 4.8 m^3/m^2 h). The solution pH and the fresh nutrient flow rate were regulated at 7 ± 0.3 (which is in the range of the optimum value for bacterial growth) and 66.67 mL/min respectively.

The biofilter capability during both the start-up and a steady state are depicted in Fig. 1. As seen from this figure, the removal of all BTEX components by the biofilter was fast and attained an efficiency >46% a day after reactor start-up. It is notable that the capability of the bioreactor rose to greater than 73% when the operation time reached the 8th day, with an influent BTEX concentration of 0.75 g/m^3. The removal efficiency was not affected by an increase in the BETX concentration from 0.75 to 0.9 g/m^3, but the mercury vapour concentration was elevated to around 0.135 g/m^3. A similar removal pattern for a start-up and steady state was also observed for mercury vapour removal (Fig. 1b). It could be concluded from the above explanation that, on the 9th day of the operation, a steady state for BTEX and mercury removal by the biofilter had been achieved. Moreover, the removal trend shown in Fig. 1, indicates the microorganisms involved in the biofilter bed were well acclimated, as they had a high biodegradation activity. We conclusively reached the steady state period faster than many previous studies (Mathur et al., 2007; Rahul et al., 2013a, b; Rene et al., 2012).

3.2. Removal efficiency study

3.2.1. Influence of influent concentration of BTEX and Hg°

The lengthy performance of evaluation of the biofilter at different influent BTEX concentrations of 0.68–1.04 g/m^3, corresponding to loading rates of 24.48–37.44 g_{BTEX}/m^{3}h, and mercury concentrations of 0.02–0.2 g/m^3, corresponding to loading rates of 0.72–7.2 $g_{Hg°}$/m^{3}h at EBRT of 100 s are also seen in Fig. 1. Here, the average measurements of BTEX and mercury removal by the biofilter based on data collected under steady state conditions (see Fig. 1a and b; especially for operation times after the 9th day). The less change (<3%) in the BTEX and mercury vapour removal efficiency during one week's operation was adopted as the measure of the steady state. For all ranges of influent BTEX and mercury vapour concentrations, the average removal >98% was obtained. The obtained attenuation capacities and removal efficiencies were much greater than many reports for the removal of BTEX with biofilters. Rahul et al. (2013a,b) reported around 96.43% BTEX removal for acorn cobbed-biofilter inoculated with *Bacillus sphaericus* and operated with an EBRT of 1.15 min and influent BTEX concentration up to 1.23 g/m^3 (corresponding to the influent loading rate to around 60.89 g_{BTEX}/m^{3}h). Davidson and Daugulis (2003) also studied the impact of influent toluene concentration up to 84.5 g/m^3 on its biofiltration and attained 95% efficiency and an attenuation capacity of 233 g/m^{3}h. However, researches on mercury vapour biofiltration are very rare in order to be compared with the results of this study. In a study by Philip and Deshusses (2008), sulphur-oxidizing bacteria in a biotrickling filter removed 100% of Hg°, with an influent concentration of 300–650 μg/m^3 and a reaction time of 6 s.

The high capability of the biofilter in this study is due to several factors like a relatively high bed surface area and microbial density as well as the use of an activated sludge of a petrochemical wastewater treatment plant with pre-acclimated bacteria. Furthermore, the most important factor is the existence of BTEX-DB as active metabolizing microorganisms of BTEX.

Moreover, the developed biofilter was four times more efficient than another biological system such as the airlift bioreactor (Littlejohns and Daugulis, 2009), indicating the higher capability of the biofilter.

3.2.2. Influence of air flow rate and EBRT

Achieving a high removal percentage of off-gas pollutants at low EBRTs made the biofilter more cost-effective. Therefore, the attempt was focused on assessing the influence of the air flow rate on the biofiltration of BTEX containing a mercury vapour stream. The assessed EBRTs were 100, 80, 60, 40, and 20 s at a constant influent BTEX and mercury vapour concentrations of 3.25 and 0.35 g/m^3 respectively. The biofilter was operated 14–16 d for each EBRT run. With the above-mentioned EBRTs and influent concentration, the BTEX and Hg° mass loading rate to the column was in the range of 225 and 415 g_{BTEX}/m^{3}h and 8.8 and 17.11 $g_{Hg°}$/m^{3}h respectively. Fig. 2 depicts the average BTEX and mercury vapour removal efficiency of steady state at each EBRT. As shown in Fig. 2, the mean BTEX and mercury vapour removal efficiencies for EBRTs of 100, 80, 60 s were obtained >93.5%, while, at EBRT = 40 s, the removal efficiency of all pollutants dropped to around 84%.

A review of the published researches indicates a significant difference between the studied EBRTs for biofiltration of BTEX. However, some studies with lower EBRTs than this study were found, but the common EBRTs for the removal of many pollutants such as H_2S, pharmaceutical VOC, total hydrocarbon, and paint solvent mixture VOCs were in the range of around 1 min to over 5 min (Balasubramanian et al., 2012a, b; Fernández et al., 2014; Mathur and Majumder, 2008). A typical EBRT reported for

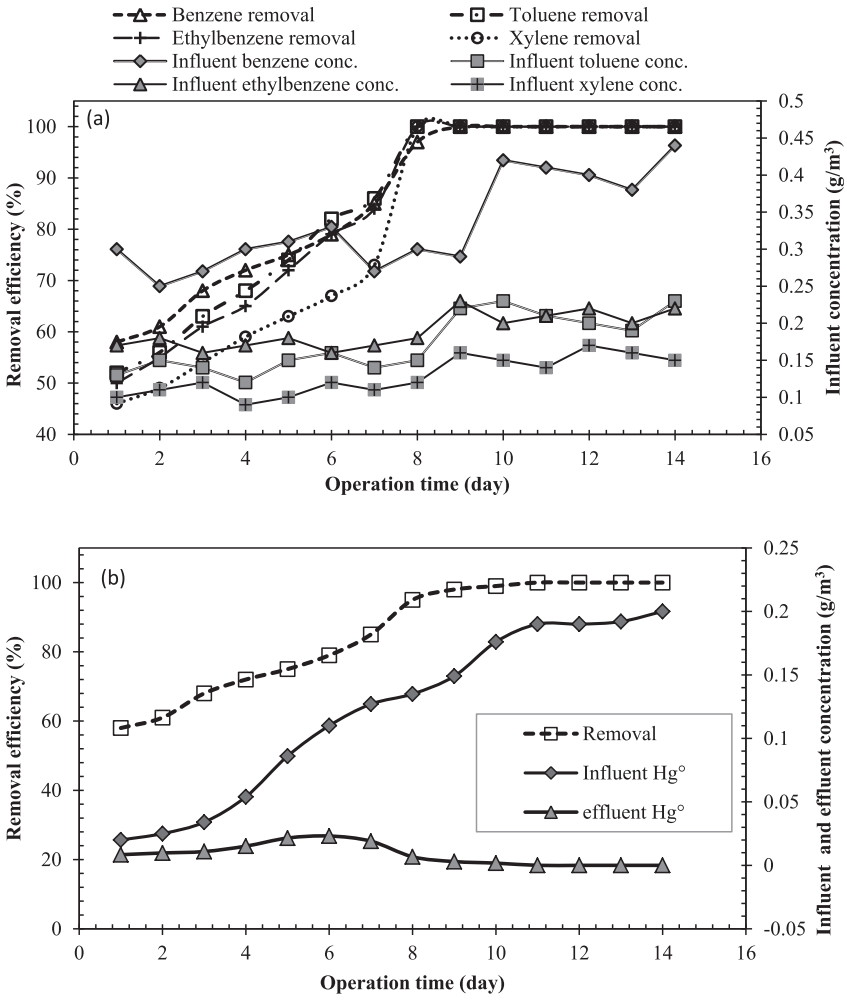

Fig. 1. Start up and steady state of the biofilter for treating of (a) BTEX mixture containing (b) Hg°.

treating concentrated VOCs by biofilters is over 1.5 min [e.g., Maliyekkal et al., 2004; Tsang et al., 2008; Tu et al., 2015]. An EBRT >1.5 min were reported for eliminating real VOCs concentrations (Lebrero et al., 2014; Lu et al., 2010). Thus, the studied system demonstrated efficient (98% removal) and affordable technique, as it could be degraded BTEX in the real off-gas with inorganic pollutant of mercury vapour at very low EBRT of 60 s.

Another plausible reason for the high capability of the studied biofilter is the high specific surface area (468 m^2/m^3) and spongy structure of the compost bed (see Fig. S3) that led to a uniform distribution of air streams in the column bed and, consequently, lowered channelling and short-circuiting of air streams and an elevated and even distribution of the nutrients and applied target pollutants. This sequentially promoted the mass transfer and attenuation of BTEX and mercury vapours.

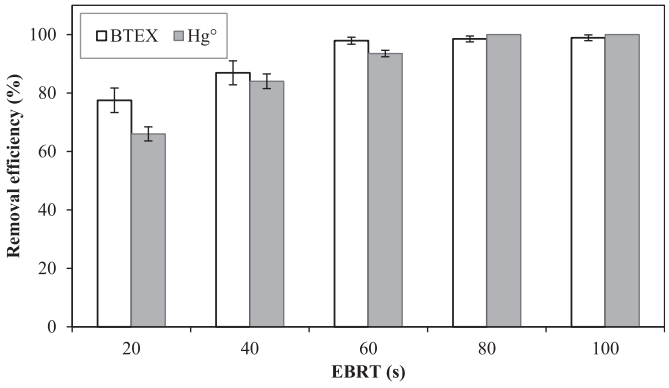

Fig. 2. Average BTEX and Hg° removal efficiency of the biofilter at different EBRTs (n = 15, BTEX = 3.25 g/m^3, Hg° = 0.35 g/m^3).

3.3. Attenuation capacity

The capability of the biofilter in terms of removal efficiency and attenuation capacity for different BTEX influents and mercury vapour loading rates are shown in Fig. 3. To estimate the maximum attenuation capacity, the amount of BTEX and mercury vapour in the influent air stream was expanded to 5.41 and 0.6 g/m^3 respectively at the EBRT of 60 s. It is clear from Fig. 3 that the BTEX loading rate, up to around 668 g_{BTEX}/m^3h, could be completely (>99%) degraded, as there is no deviation from the 100% conversion line. Thus, the critical attenuation capacity for BTEX removal was 663 g_{BTEX}/m^3h after a slow lowering of the removal efficiency. At the same time, the critical influent loading rate for biofiltration of Hg° gained 12.8 $g_{Hg°}/m^3h$ and the critical attenuation capacity was 12.6 $g_{Hg°}/m^3h$ (see inserted figures in Fig. 3).

By further increasing of the influent BTEX and mercury vapour loading rate, the attenuation capacity deviated from the 100% conversion line and appeared flattened at the maximum of 774.5

g_{BTEX}/m^3h and 15.7 g_{Hg°/m^3h at the loading rate of 973.8 g_{BTEX}/m^3h and 21.6 g_{Hg°/m^3h. Accordingly, BTEX and mercury vapour removal ceased around 76 and 73% respectively. Results show that BTEX and mercury removal in this work was notably higher than those reported in other studies (Cheng et al., 2016; Lu et al., 2002; Rahul et al., 2013a, b). For instance, a 1.42 fold biofiltration rate more than the obtained (233 g/m^3h) in a research conducted by Davidson and Daugulis (2003) could be mentioned as another evidence of the effectiveness of the studied system.

In the presence of O_2 and all required nutrients, two probable mechanisms i.e., biodegradation and mass transfer correspond to the pollutant attenuation in a biofilter. A gradual increase in the of pollutant attenuation capacity by raising the influent loading up to the critical point indicated that the biodegradation mechanism might not correspond to the entire removal the BTEX and mercury vapour in the biofilter. Furthermore, the findings (BTEX and Hg° removal at the steady state) were assessed by the zero- and first-order kinetics which fitted well the first- order one. Based on this result, the mass transfer of BTEX and Hg° was bottle-necked of the kinetic. BTEX and Hg° monitoring in the recycled solution had shown no measurable levels of these pollutants in the solution, emphasizing that the BTEX and Hg° removal by the biofilter had occurred biologically.

The reaching of the flattened state in BTEX and mercury vapour attenuation at loading rates over the critical point indicates that the consortium of bacteria in the column obtained the maximum degradation capacity. Oxygen restriction could be accounted for as another avoidable parameter in efficient BTEX removal at very high loads. In other words, after a long-term working of the biofilter, the effluent concentration of BTEX and mercury vapour gradually increased, which could have been the signs of the exhaustion of the maximum removal capacity of biologically eliminating pollutants.

3.4. Influence of transient, shock BTEX-loading, and off-situation period-restart

BTEX are released from industrial processes in a wide range of concentrations (from zero to shocked or overdose concentration), depending on the variable operating conditions and purposes like overhaul maintenance, resulting in fluctuating off-gas emissions. The fluctuations in the influent pollutant(s) concentration will affect the efficiency of the biofilter. The biofilter should be reliable at every influent concentration; hence, a core component of this work was to determine the capability of the system and its handling assessment at transient and shock BTEX loading as well restarting the system after a long shutdown. For this purpose, the system EBRT was set to be 60 s and the influent BTEX concentration was changed in the range of 1.07–5.41 g/m^3. The air and nutrient solution were still provided during this section of the study.

Fig. 4 shows the BTEX biofiltration performance during the transient, shock loading, and off-restart. An average BETX removal of 99% was attained for the first period with an average loading rate of 327.5 g_{BTEX}/m^3h. After that the influent load was multiplied by a factor of 2.23, while the removal efficiency did not deviate from the average of 99%. The BTEX concentration was quickly levelled off to around 194.4 g_{BTEX}/m^3, resulting in a slight increase in the biofilter performance i.e., complete biofiltration. Then the biofilter was again posed to the shock situation by increasing the influent BTEX to 382 g_{BTEX}/m^3h. The biofilter kept its efficiency, demonstrating the appropriateness of the consortium microorganisms and their efficient reaction to the prompt handling of shock loads. Generally, it could be concluded that the consortium bacteria could successfully oxidize the BTEX and the biofilter could easily and consistently handle all the pollutant loading ranges while the loading rate was lower than the critical value (see Fig. 3). The mercury vapour loading for a mixture of BTEX and mercury stream were ranged from 0 to 21.5 g/m^3h; the removal efficiency trend was very similar to those reported for BTEX removal in Fig. 4. Thus, it is implied the developed biofilter with high efficient consortium bacteria is very reliable and flexible for field use.

In another attempt (as shown in Fig. 4), the BTEX removal efficiency was studied after two long (10 and 15 days) off-situation periods. The off-situation tests were done by cutting off the mixture of BTEX and mercury vapour feed and then re-entering the amount of 433 g_{BTEX}/m^3h after each off-situation period. We noted that the air and nutrient supplement were provided during this period. The findings of the biofilter capability during the operation days of 118–127 (first off-situation) and 143–157 (second off-situation) are also shown in Fig. 4. On the restarting of the biofilter after the first off-situation period, the BTEX removal reached 75.8%. The biofiltration efficiency rapidly rose to 98% within just four days of restarting and did not change or lessen until the end of

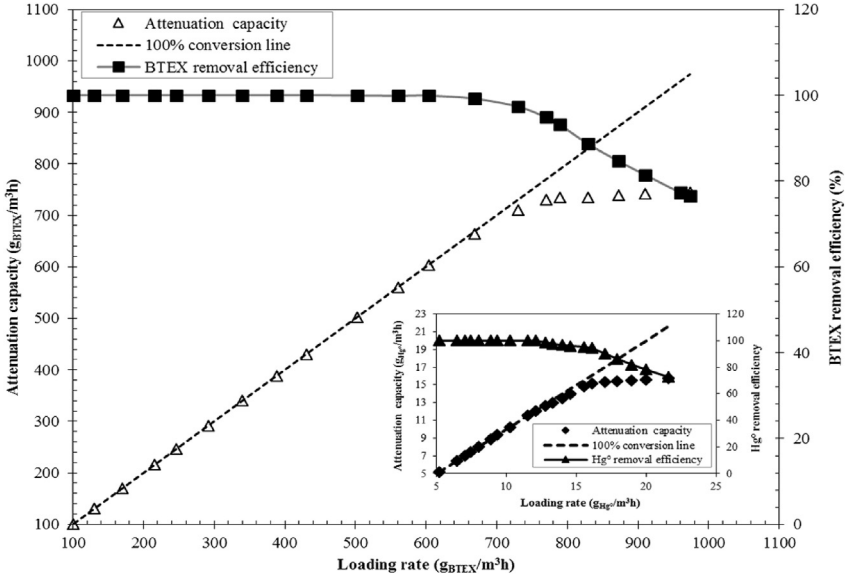

Fig. 3. BTEX attenuation capacity of the biofilter at different loading rates.

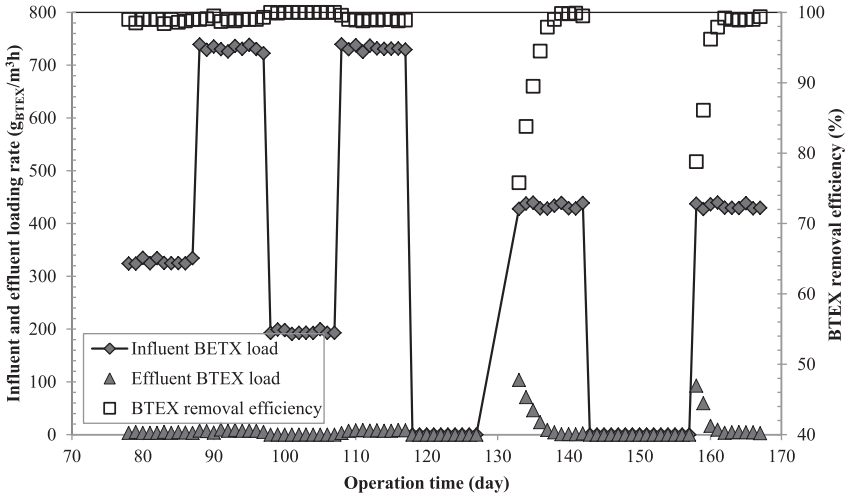

Fig. 4. BETX biofilteration during the transient, shock loading, and off-restart.

the period. During the operation on Day 118, the BTEX feeding to the reactor was again discontinued; the second off-situation period was started for15 d. The day after the second off-situation, the BTEX removal obtained was 78.8% and, about three days after restarting, the biofilter performance >96% recurred and the biofilter returned to usual conditions. The results support Moussavi and Mohseni (2008) findings, which treated a phenol-laden waste air by a biotrickling filter. They also stated that the biotrickling performance returned to the pre-off-situation condition. In another study (Sedighi et al., 2016), *Ralstonia eutropha* was used as a phenol oxidizing agent in a gas-recycling trickle-bed reactor, which could effectively recover their capability after an off-situation period. However, the off-situation periods (10 and 15 days) in this study are much longer than the selected off-situation period in the aforementioned studies.

The low removal efficiency upon the restarting of the biofilter may be due to these reasons: 1) as the sources of energy and carbon (here, BTEX) was discontinued during the off-situation period this could affect the activity of biofilm and, thus, lose some its pollutants treatment efficiency, 2) during the off-situation period, the consortium bacteria went into an endogenous phase, thus lowering the metabolic potential for the removal of BTEX, and 3) inactivation of some efficient inefficient use of some parts of the bed.

3.5. Kinetic analysis

The transport of pollutants to the biofilter biofilm is revealed by kinetic parameters. Thus, in this section, the kinetic behaviour of biofilters and the removal rate of BTEX as the main pollutants in the mixture of the polluted stream within the biofilm were assessed. The data of BTEX removal for 10 days after achieving a steady state condition was used for kinetic evaluation. The Michaelis-Menten model, the best-known model, was used for BTEX biofiltration kinetic. This model, based on the assumptions that there is no restriction to the aeration of the system, plug flow type of air stream through the biofilter bed, and the conversion of the substrate (here BTEX) is the reaction-controlled (i.e., the biofilm should be active). In a steady state condition, the rate of consortium bacteria growth is balanced by the rate of their decay, resulting in a biological equilibrium of the biofilter. Therefore, the kinetic constants should remain unchanged over a period of time. The constants for the BTEX biofiltration kinetic were determined from Eq. (3) by plotting $[(V_b/Q)/(C_i - C_o)]$ versus $(1/C_{lm})$ (see Fig. 5) (Mathur and Majumder, 2008).

$$\frac{V_b/Q}{(C_i - C_o)} = \frac{k_s}{r_{max}C_{lm}} + \frac{1}{r_{max}} \quad (3)$$

where C_i and C_o is the influent and effluent BTEX concentration. C_{lm} the log average concentration $[(C_i - C_o)/\ln (C_i/C_o)]$, V_b the bed volume of the biofilter (m^3), and Q is the off-gas flow rate (m^3/min). r_{max} is the maximum decomposition rate per unit of biofilter bed volume (g/m^3min) and k_s is the saturation (Michaelis-Menten) constant (g/m^3) in the gas phase. k_m, half saturation constant (g/m^3), is an important characteristic of a biological reaction and is significant for its biological function. The Michaelis-Menten kinetic constants for BTEX removal by the biofilter was derived from the regression equation in Fig. 5 as 'r_{max} = 1/intercept = 0.578 g/m^3minand $k_m = r_{max} \times$ slope = 0.099 g/m^3'. As observable from Fig. 5, the coefficient of determination ($R^2 = 0.982$) was satisfactory high. A relatively higher amount of k_m in this study compared to other studies (Krailas et al., 2004; Mathur and Majumder, 2008; Mathur et al., 2006; Rene et al., 2015) showed BTEX to be efficiently degraded by a consortium bacteria acclimated by the petrochemical wastewater treatment plant.

3.6. Mass balancing of carbon and mercury

Carbon mass balance analysis is a suitable method for estimating the biomass production. As mentioned before, BTEX was

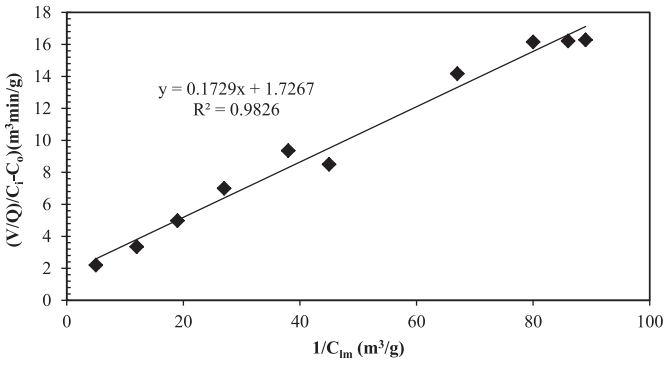

Fig. 5. Kinetic determination of Michaelis–Menten kinetic constants of BTEX.

Table 3
Mass balancing of carbon in the biofilter.

Pollutant	Influent carbon (g)-A	Carbon in CO_2 (g)- B	Carbon in leachate (g)-C	Carbon in biomass (g)- D	Carbon in untreated BTEX (g)- E	Total (B + C + D + E)
BTEX	21.81	11.39	1.03	8.93	0.41	21.76
Percentage (%)	100	52.35	4.73	41.04	1.88	≈100

Table 4
Mass balancing of mercury in the biofilter.

Pollutant	Influent Hg° (μg)-A	Effluent (untreated) Hg° (μg)-B	Mercury in leachate (μg)-C	Mercury in the bed (μg)-D	Methyl or ethyl mercury (μg)-E	Total (B + C + D + E)
Mercury vapour	13.65	0.09	1.52	11.98	0	13.59
Percentage (%)	100	0.66	11.18	88.15	0	≈100

the sole carbon source for the consortium bacteria in the biofilter. The influent carbon content into the biofilter (A) was inevitably converted into four portions (Hu et al., 2015): emission in the form of CO_2 (B), discharge by leachate (C), accumulation by the biomass in the biofilter (D), and discharge into the effluent in the form of untreated BTEX (E). According to the literature, $C_5H_7O_2N$ was assumed as the biomass composition (Hu et al., 2015; Xi et al., 2014). Based on the above explanation, the carbon balance was performed by a simple formula of 'A = B + C + D + E'.

Data of 10 days' operation (under a steady state condition) were used for the mass balancing of carbon and mercury of the biofilter. The findings are listed in Table 3. The total amount of influent carbon was 21.81 g and the total amount of the detected carbon in CO_2 form, leachate, biomass, and untreated BTEX was obtained to be 11.39, 1.03, 8.93, and 0.41 g respectively, which were approximately identical to the influent carbon in BTEX. More than 52% of the influent carbon was fixed carbon dioxide, and nearly 41% of carbon was catabolized to produce biomass. Slightly (less than 5%) of the influent carbon was leached to the biofilter leachate. The kinetic results showed that the BTEX degradation in the biofilter inoculated by efficient consortium bacteria was coincidental to other published studies (Hu et al., 2015; Wang et al., 2012).

The influent mercury vapours to the bioreactor could be retracked in effluent, leachate, and compost bed of the biofilter system as demonstrated in Table 4. The negligible amount (<1%) of Hg° was found in the effluent of the reactor. GC-MS analysis of organic mercury species in the biofilter leachate and compost bed, affirmed that no methyl or ethyl mercury, compounds that are hazardous and are a health concern, was found in the biofilter effluent. According to Table 4, most of the Hg° was captured in the biofilter bed. As noted by Philip and Deshusses (2008), elemental mercury is difficult to adsorb by current adsorbents and to scrub, and, hence, another mechanism may be involved in its attenuation. It has been reported that genetically modified bacteria and some species of microorganisms can absorb Hg° through their cell wall and oxidize it to mercury ionic form (Hg^{2+}) by using a cytosolic enzyme of catalase (Philip and Deshusses, 2008; Rezaee et al., 2006). If Hg^{2+} was formed in the system bed, it must be safely managed to avoid environmental pollution by mercury ions. Generally, the biofilter could effectively treat both BTEX and Hg° from a contaminated waste stream.

4. Conclusions

The capability of a laboratory scale biofilter, inoculated by efficient consortium bacteria, was examined to treat the BTEX stream containing mercury vapours from a real waste stream during the overhauling of a petrochemical plant. It was observed that the solid waste compost, which was initially acclimated by the petrochemical wastewater, is a suitable material and can be used as a media for the biofiltration of the mixture BTEX and Hg° vapour. Efficient BTEX biofiltration was done at different loading rates (192.6–973.8 g_{BTEX}/m^3h). Removal of both BTEX and Hg° from 66% to 100% was obtained, depending on the EBRT and the influent pollutant concentration. Further, the BTEX removal of >86% at EBRT of 60 s at a critical loading of 663 g_{BTEX}/m^3 hand 12.6 $g_{Hg°}/m^3h$ was attained by the biofilter. The biofilter offered a very suitable and reliable capability that was not distressed by fluctuations, overloading, and off-situation in influent loading. Based on the kinetic study, BTEX is susceptible to oxidation by microbial consortium acclimated by the petrochemical wastewater treatment plant. A carbon mass balance analysis showed that relatively high fractions of the biofiltered BTEX were converted to CO_2 and biofilm, whereas small amount of BTEX were transformed to the carbon fraction of the leachate. More than 88% of the influent mercury was also captured by the biofilter bed. The findings offer a greater insight and understanding to recognize the behaviour of a biofilter in simultaneously attenuating BTEX and mercury vapour in the wasted stream from the petrochemical industry.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2017.09.033.

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