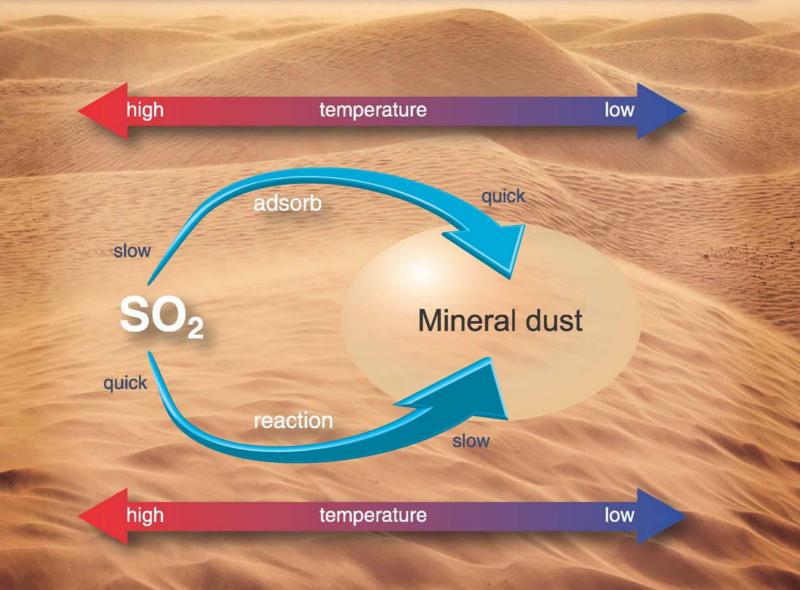


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Enhanced removal of ethylbenzene from gas streams in biotrickling filters by Tween-20 and Zn(II)

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ABSTRACT

The effects of Tween-20 and Zn(II) on ethylbenzene removal were evaluated using two biotrickling filters (BTFs), BTF1 and BTF2. Only BTF1 was fed with Tween-20 and Zn(II). Results show that ethylbenzene removal decreased from 94% to 69% for BTF1 and from 74% to 54% for BTF2 with increased organic loading from 64.8 to 189.0 g ethylbenzene/(m³·hr) at EBRT of 40 sec. The effect of EBRT (60-15 sec) at a constant ethylbenzene inlet concentration was more significant than that of EBRT (30-10 sec) at a constant organic loading. Biomass accumulation rate within packing media was reduced significantly.

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Introduction

Ethylbenzene, the monocyclic, volatile organic compound (VOC) which was listed as a priority pollutant by the US Environmental Protection Agency (USEPA), was typically found in petroleum products, like diesel fuel and gasoline (Es'haghi et al., 2011). It is commonly used as an intermediate or solvent in the manufacture of such organic synthesis, and during these manufacturing processes, exposure to ethylbenzene may occur. This pollutant has major influences on central nervous systems and it has been found to cause many serious side-effects to human health (e.g., respiratory problems, skin and sensory irritation, cancer, leukemia, and some disturbance of the liver, kidney, and blood systems) (Aivalioti et al., 2010).

Considerable efforts regarding liquid ethylbenzene removal from wastewater and soil have been devoted in the past years, and several methods have been proposed and successfully applied (Yuan and Weng, 2004; Mohamed and Ouki, 2011; Santos et al., 2012), while few reports were available on gas-phase ethylbenzene removal from waste gas streams (Álvarez-Hornos et al., 2008). In some areas where industries are highly developed, air pollution by ethylbenzene is a real problem, so it would be a benefit if an effective technology could be implemented in such regions. Conventional chemical and physical treatment techniques, however, suffer from great technical limitations for their hazardous byproducts, so, biologically-based technique, which offers lots of advantages such as low capital costs and innocuous byproducts, is turning into an extremely attractive alternative for gas pollutant removal (Cox and Deshusses, 2002; Sercu et al., 2005; Cheng et al., 2011). Biotrickling filter (BTF) is one of these biologically-based techniques.

Although biotrickling filtration of ethylbenzene provides a promising alternative to other conventional technologies, the poor performance for hydrophobic volatile pollutants removal,

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especially under a higher concentration, has intrinsically limited its large scale applications (Sempere et al., 2008). This can be explained that the hydrophobic contaminants are very recalcitrant to undergo biodegradation within the BTF reactor because it can penetrate only a small way into the filter bed (Kraakman et al., 2011). That is to say, transportation of ethylbenzene from the gas phase to the liquid and biofilm phase might be the main rate limiting factor (Hassan and Sorial, 2010; Yang et al., 2010a). Hence, some hydrotropic agents should be added into the reactor to lower the mass transfer limitations.

The non-ionic surfactant Tween-20 and the metal ion Zn(II) were selected as the suitable addition materials in this work. Volkering et al. (1998), Park et al. (2008) and Bilé et al. (2011) have indicated that surfactants can lower the surface tension as well as the interfacial tension for their amphiphilic property, thereby improving the wettability of the gas-phase VOC, making them more bio-available in the BTF reactor. And this solubilization process may be enhanced when the metal ion exists (Wu et al., 2008; Yang et al., 2010a). Ramirez et al. (2012) have devoted some efforts to discuss the possibility of applying hydrotropic agents in bioreactors for a better abatement of VOC. However, studies on combining two materials, such as surfactant and metal ion, for improved VOC removal are very insufficient.

In the previous study, the remarkable enhancement of BTF performance for ethylbenzene removal has been proposed and discussed, which was performed by providing the reactor with different concentrations of Tween-20 and Zn(II) (Wang et al., 2013). Results indicated that the reactor performed with 11.76 mg/L Tween-20 and 1 mg/L Zn(II) could show the maximum removal efficiency, and these hydrotropic agents could also significantly reduce the biomass accumulation in packing media and promote the recovery of microbial activity (Wang et al., 2013).

Therefore, the objective of this study was to make an improvement of the previous research. In this study, processes for continuous degradation of ethylbenzene gas under different organic loading rates and empty-bed residence times (EBRTs) (EBRT at a constant organic loading rate and EBRT at a constant ethylbenzene inlet concentration) have been conducted with BTF1 fed with Tween-20 and Zn(II) while BTF2 without them. The effects of the two additives on promoting the recovery of microbial activity and inhibiting excessive biomass accumulation were also studied in this article.

1. Materials and methods

1.1. Biofilters

Experiments were carried out using two identical BTFs named BTF1 and BTF2. Fig. 1 illustrates one of these experimental units. The main part of BTF was a closed plexiglas column (Guangda Machinery Manufacturing Co., Ltd., Changsha, China) with an inner diameter of 10 cm and a total height of 78 cm in which four sections were equally divided. A perforate plexiglas plate (Guangda Machinery Manufacturing Co., Ltd., Changsha, China) with a diameter of 10 cm was fixed at the end of each section with a layer of packing medium putting on it. There was a 4 cm plenum located between two sections to allow for sampling and re-distribution of the waste gas streams. Simulative waste gas was generated by mixing two separate air streams, with one stream bubbling directly into the flask containing ethylbenzene reagent, and the other delivered into a humidifier to be water saturated (Bailón et al., 2009). Nutrient solution supplied periodically (spray 3 sec every 3 min, 4.5 L/day) into the reactor in a downward mode without recirculation. Both BTF1 and BTF2 were operated in a

temperature controlled chamber with a constant operating temperature of (25 \pm 1)°C.

1.2. Chemicals

1.2.1. Model VOC

Analytical reagent grade ethylbenzene (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) (C_8H_{10} , 99%) was used as the test substance in this work. The ethylbenzene-contained waste gas streams were introduced into the bioreactor by using a vortex air pump (Wuxi Guangming Pump industry Co., Ltd., Wuxi, China) in a downward flow mode.

1.2.2. Tween-20 and Zn(II)

Reagent grade Tween-20 (Bo Mei Biotechnology Co., Ltd., Hefei, China) (purity of more than 99%) was used as one of the additives in this study and Zn(II) (obtained by dissolving solid zinc chloride into distilled water) was used as another additive.

1.2.3. Nutrient

Nutrients fed into the BTFs should consist of macronutrients (nitrate and phosphate), vitamins, and buffers (Chen et al., 2012). Table 1 gives the chemical composition of the nutrient solution.

1.3. Packing media

Open-pore reticulated polyurethane sponges (Shenzhen Jiechun Filter Material Corporation, Guangdong, China) have good permeability and higher mechanical strength, making them suitable bioreactor packing media for long-running removal processes (Moe and Qi, 2004; Ramírez et al., 2009). The polyurethane sponge with a pore size of 10 pores per cm has a porosity of 95.3% and an apparent density of 28 kg/m³. Before being inserted into the reactor column, the sponges were cut into cylinders with a diameter of 10 cm and a height of 10 cm.

1.4. Seeding microorganisms

The activated sludge used to inoculate the bioreactors was originated from Changsha Jinxia Wastewater Treatment Plant, Hunan, China. No enrichment procedures were applied before its utilization.

1.5. Analytical methods

The performance of BTFs was analyzed in terms of daily determination of removal efficiency (RE), elimination capacity (EC), and pressure drop for the whole bed (it is an indicator of biomass accumulation within the packing media).

Ethylbenzene concentration was analyzed by gas chromatograph (GC) using an Agilent GC 6890 apparatus equipped with a capillary column type HP-VOC (60 m × 320 μ m i.d. × 1.8 μ m film thickness) and a flame ionization detector (FID), according to Yang et al. (2010a). It was operated with a split ratio of 1:20 (V/V) and a split flow of 60 mL/min. Nitrogen (purity ≥ 99.99%) was used as the carrier gas at a constant flow rate of 30 mL/min and hydrogen gas (purity ≥ 99.999%) together with purified air was used as the feed gas. The temperatures of the injector, oven and detector were set at 120, 120 and 250°C, respectively.

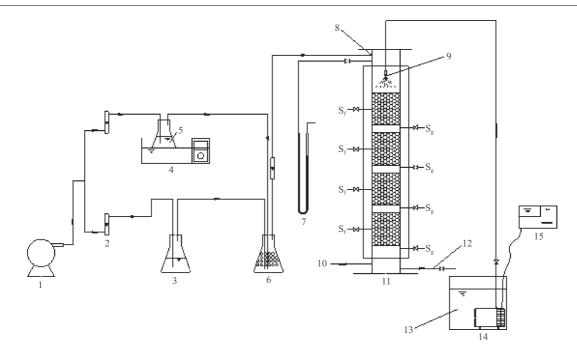


Fig. 1 – Schematic diagram of the biotrickling filter (BTF). (1) Air pump; (2) glass rotameter; (3) glass humidifier; (4) water-bath device; (5) ethylbenzene; (6) gas mixed bottle; (7) glass-U-tube manometer; (8) air inlet port; (9) liquid spraying device; (10) air outlet port; (11) biotrickling filter; (12) raffinate discharge tube; (13) nutrient solution; (14) suction pump; (15) time controller. S_{f} : biofim sampling ports; S_{g} : gas sampling ports.

1.6. Experimental plan

Both BTF1 and BTF2 were operated in parallel for about 170 days under pseudo-steady-state conditions. Experiments were carried out in two subsequent stages.

The packing media were immersed into the activated sludge for about 24 hr to seed with microbial cultures, then taken out of the sludge and transferred into the column to inoculate the two reactors. Subsequently, the simulated gas streams as well as the nutrient solutions were introduced into the reactor and this moment was counted as day 1 of the BTF start-up stage (the first stage). In this stage, both BTFs were operated under a reference condition with a low inlet ethylbenzene concentration of 350 mg/m³ and an EBRT of 40 sec to strongly encourage growth of suitable microorganisms.

After the BTFs were successfully started up, the second stage was subsequently carried out with BTF1 (the strengthened BTF) fed with optimum concentrations of Tween-20 and Zn(II) while BTF2 (the control BTF) without them (Song et al., 2012). All of the other operation conditions including nutrient solution feed rate and temperature remained the same. This stage lasted from day 26 to 168. Throughout day 26 to 70, day 71 to 115 and day 116 to 168, the effects of ethylbenzene organic loading rates, gas EBRTs at a constant organic loading rate, and gas EBRTs at a constant inlet concentration were respectively evaluated.

Gas flow rate can be adjusted by means of flowmeters (Kaide Flow Instruments Corporation, Hubei, China). Different inlet ethylbenzene concentrations were obtained by varying the flow rates of both the gas stream bubbling directly into the ethylbenzene reagent and the gas stream delivered into the humidifier, while the gas EBRT can be altered just by regulating the flow rate of the humidified air (Chen et al., 2012). When the inlet ethylbenzene concentration and the EBRT were finally set, the final organic loading rate could be obtained accordingly.

To ensure pseudo-steady-state operation conditions of the two bioreactors so that the experimental results under

Component	Concentration (mg/L)	Component	Concentration (mg/L)
K_2HPO_4 (AR)	28.16	MnCl ₂ ·4H ₂ O (AR)	0.144
KH ₂ PO ₄ (AR)	9.25	CoCl ₂ ·6H ₂ O (AR)	0.866
MgSO ₄ (AR)	4.40	Folic acid (BR)	0.00089
NH ₄ Cl (AR)	4.90	4-Aminobenzoic acid (AR)	0.0023
NaHCO ₃ (AR)	24.00	D-Pantothenic acid (BR)	0.00345
FeCl ₃ (CP)	0.0926	Riboflavin (BR)	0.0023
CaCl ₂ (AR)	2.69	Nicotinic acid (AR)	0.0023
CuCl ₂ ·4H ₂ O (AR)	0.062	Biotin (CP)	0.0023

AR: analytical reagent; BR: biological reagent; CP: chemical pure

different operating parameters were comparable, the BTFs were resumed to the reference condition for 5-6 days to go through a recovery period before and after a change of the operating parameter (Chen et al., 2012).

2. Results and discussion

2.1. Start up

This stage lasted from day 1 to 25. Performances of BTF1 and BTF2 for ethylbenzene removal are revealed in Fig. 2 where the inlet and outlet ethylbenzene concentrations have been plotted along with operational time.

As can be seen, the RE was very low at the first two days of operation, which was less than 50% for both BTF1 and BTF2. Then the RE of each BTF was gradually increased and more than 90% was reached for BTF1 after day 13 and BTF2 after day 14, indicating that it would take a relatively long time for microorganisms to adapt to the ethylbenzene contained environment. On day 20 of the start-up phase, near complete removal (RE = 98.5%) of ethylbenzene was achieved for both BTFs and the fluctuation range of ethylbenzene RE was within 3% for the next five days, this was counted as the successfully start-up moment of the BTF and the corresponding EC was nearly 31 g ethylbenzene/(m³·hr).

2.2. Effect of organic loading rate

In this stage, the gas flow rate remained constant (0.28 m³/hr, corresponding to EBRT of 40 sec) but the organic loading rate of ethylbenzene multiplied when the inlet ethylbenzene concentration multiplied. The relationship between the organic loading rate and the ethylbenzene removal efficiency is presented in Fig. 3. As evident in Fig. 3, no detrimental effects on ethylbenzene degradation were observed in BTF1 which applied with both Tween-20 and Zn(II), as indicated by the higher RE of it compared to that of BTF2. When the inlet ethylbenzene concentration was increased from 720 to 1450 and 2100 mg/m³, corresponding to organic loading rates of 64.8, 130.5 and as high as 189.0 g ethylbenzene/(m³·hr), the average RE of BTF1 could reach 94%, 84% and 69% accordingly, while for BTF2, the final RE of it was just 74%, 63% and 54%. This phenomena may be attributed to the fact that, ethylbenzene possesses a higher aqueous solubility in the

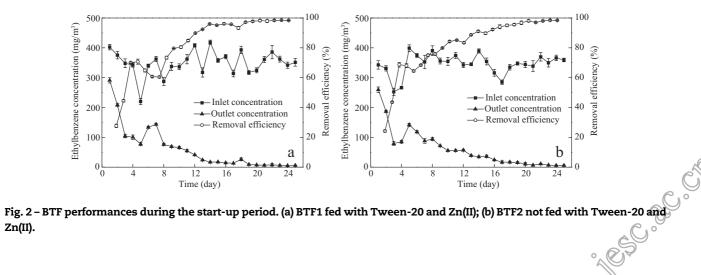
presence of Tween-20 and Zn(II), which lead to a lower mass transfer resistance between the gas phase and the biofilm phase, thus making this hydrophobic organic substance more bio-available in the strengthened BTF. Surfactant addition promoting waste gas biodegradation has already been confirmed in some other cases. Song et al. (2012) has previously reported that the RE and EC of the BTF applied with surfactant Triton-100 were higher than those of the control BTF for treatment of high-concentration styrene. Ramirez et al. (2012) has also demonstrated that the RE could increase from 35% without surfactant to 65% when the BF was operated under Tween-20 at 0.5% (W/W).

Although the RE decreased with the increased organic loading rate, the EC increased. Under a constant EBRT of 40 sec, the calculated EC was 60.8, 109.4, and 130.5 g ethylbenzene/(m³·hr) for BTF1 with the surfactant and 47.9, 81.9, and 101.7 g ethylbenzene/(m³·hr) for BTF2 without the surfactant at organic loading rates of 64.8, 130.5 and 189.0 g ethylbenzene/(m³·hr).

Each organic loading rate test was followed by a recovery period (day 35-40, day 50-55, day 65-70) in which the reactor performance and the microbial activity could return to their initial status. An increase was observed in RE when switching from the experimental condition to the recovery condition. However, the increase degree differed for the two BTFs. From Fig. 3, it was clear that when resumed to the reference condition, BTF1 re-acclimated sooner as compared to BTF2. The average RE for BTF1 could reach more than 95% on the first day of recovery, while it was less than 90% for BTF2. Furthermore, it just took two days for RE of BTF1 increase to its normal level, however for BTF2 it took at least three days. This may be due to the renaturation role of Tween-20 in increasing the bioactivity of damaged microorganisms. In a review, Singh et al. (2007) indicated that microbial growth rate could be recovered by dilution of non-ionic surfactants, and in experiments of Lee et al. (2004) total viable bacterial counts increased more than four-fold when non-ionic surfactant was applied.

2.3. Effect of EBRT at a constant organic loading rate

Experiments were carried out by subjecting both the BTFs to constant organic loading rate of 248.4 g ethylbenzene/(m³·hr) and different EBRT values of 30, 20 and 10 sec. And the corresponding inlet ethylbenzene concentrations were about



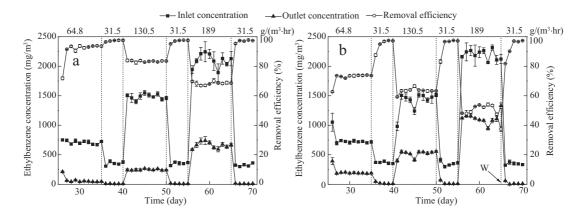
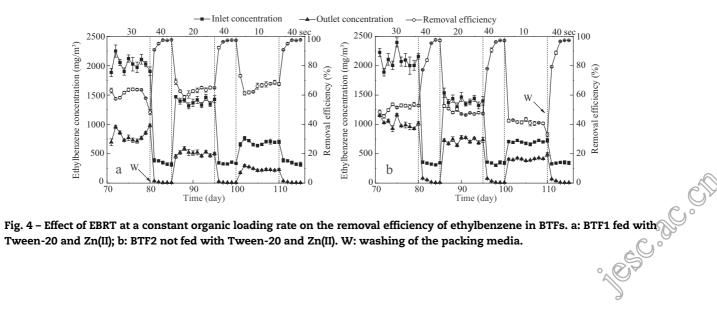


Fig. 3 - Effect of organic loading rate on the removal efficiency of ethylbenzene in BTFs. a: BTF1 fed with Tween-20 and Zn(II); b: BTF2 not fed with Tween-20 and Zn(II). W: washing of the packing media.

2070, 1380 and 690 mg/m³. Fig. 4 compares the RE during this process of the two BTFs. BTF1 and BTF2 presented differences in adaptation to ethylbenzene degradation during this process, as seen from the removal profiles presented in Fig. 4a and b. When the EBRT went lower, the RE and EC for BTF1 kept going up while the RE and EC for BTF2 gradually declined. The performance of BTF2 was quite similar with the previous research conducted by Yang et al. (2008b, 2011) and Álvarez-Hornos et al. (2008), both indicating that the decrease of gas EBRT can directly decrease the gaseous pollutants RE of biotrickling filters because the time for absorbing and transporting of gas-phase ethyl-benzene contained in the streams also decreased.

However, the removal performance of BTF1 was not in conformity with the previous results. Two mechanisms have been proposed to explain this difference: (1) The decrease of inlet ethylbenzene concentration accounted for this difference. When the EBRT decreased, the inlet organic loading rate remained constant but the inlet ethylbenzene concentration decreased accordingly. The adverse effect of subjecting reactors to low EBRT values might be mitigated by the beneficial effect of subjecting reactors to low inlet ethylbenzene concentrations. That is to say, BTF applied with the two hydrotropy materials might be more sensitive to the change of inlet ethyl-benzene concentrations than EBRTs in this stage. (2) Surfactant Tween-20 and Zn(II) leaded to a reduction in interfacial mass transfer resistance. Although the transport time of ethylbenzene from the gas phase to the liquid and biofilm phase decreased, the mass transfer resistance between the gas phase and the biofilm phase reduced and, therefore, more gaseous ethylbenzene could dissolve into the biofilm layer and been biodegraded by microorganisms within the packing media.

According to Fig. 4, although the removal rates of BTF1 were higher than that of BTF2, the performance of BTF1 was still not satisfying for these three EBRTs. When EBRT decreased from 30 to 20 and 10 sec, the RE of BTF1 was respectively 64%, 65%, and 68%, corresponding to the EC was 159.0, 161.5 and 168.8 g ethylbenzene/(m³·hr), which was a not significant enhancement compared to that of the control BTF who performed with a final RE of 53%, 48% and 41% and the corresponding EC of it was 131.8, 119.3 and 101.9 g ethylbenzene/(m³·hr). A probable explanation for this poor performance is that at high organic loading rate of 248.4 g ethylbenzene/(m³·hr), microbial activity can be inhibited, and hence negatively affected their pollutant-degrading ability, leading to a lower removal performance (Rene et al., 2010).



Recovery of deteriorated BTF was carried out during days 81-85, days 96-100 and days 111-115. Results showed that the strengthened BTF restarted in shorter period of time (1-2 days) than the control BTF (3-4 days).

2.4. Effect of EBRT at a constant inlet concentration

The effect of EBRT at a constant inlet concentration on ethylbenzene removal was examined in the following set of experiments at a fixed inlet concentration of 1650 mg/m³ and the results are presented in Fig. 5. As can be seen, addition of surfactant and Zn(II) had a positive effect on ethylbenzene biodegradation, the biodegradation rate was increased to 91%, 78%, 61% (BTF1) from 73%, 59%, 37% (BTF2) when EBRT was set at 60, 30 and 15 sec, respectively. Apparently, explanation to the better performance of BTF1 was the reduced mass transfer resistance of ethylbenzene to the layer/biofilm phase. It can be also found that the overall extent of ethylbenzene elimination decreased as the EBRT was decreased, either in BTF1 or in BTF2. When EBRT was decreased from 60 to 30 sec, the corresponding RE decreased relatively milder for both BTFs, however, when the minimum EBRT was applied (15 sec) at an organic loading rate of 396 g ethylbenzene/($m^3 \cdot hr$), the RE dropped suddenly. This phenomenon was consistent with the results achieved by Gabaldón et al. (2006) and Volckaert et al. (2013) that high organic loading rates could greatly diminish the ethylbenzene biodegradation extent. In a rotating drum biofilter for the removal of VOC gases, Yang et al. (2008a) indicated that a short exposure to high VOC organic loading rate could easily inhibit the activity of the microorganisms, which could be regarded as another explanation for the poor performance of both BTFs.

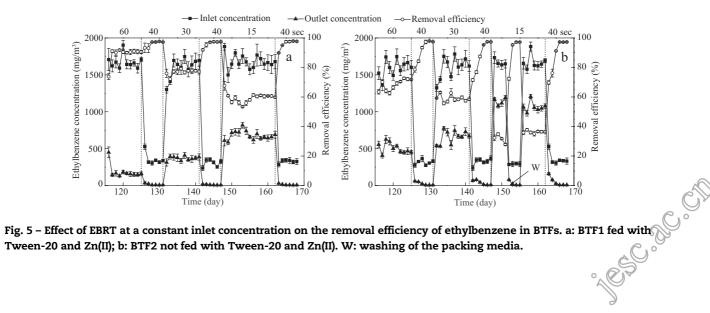
As the EBRT decreased, the EC of ethylbenzene increased. When EBRT was decreased from 60 to 30 and 15 sec, the strengthened reactor achieved a maximum EC of 67.5, 115.8 and 180.8 g ethylbenzene/(m³·hr), respectively. While in the absence of surfactant and Zn(II), the ethylbenzene removal performance of BTF2 was much poorer than that observed in BTF1, the EC of BTF2 was 54.3, 87.8 and 109.8 g ethylbenzene/(m³·hr), respectively.

The control BTF showed a poorer removal performance compared with the strengthened BTF, and with the run-time extended, their differences caused by biodegradation became more evident. Removal performance of BTF2 was gradually deteriorating with the operation, thus longer recovery time (6 days) was needed to re-establish the pseudo-steady-state. The recovery process was carried out during days 126-131, days 142-147 and days 163-168. From Fig. 5 it can be seen that an overall efficiency of more than 90% was achieved on the first day of recovery for BTF1, while for BTF2 it takes at least three days. The recovery time of the control BTF was much longer than that of the surfactant-strengthened BTF, which was in accord with the previous two set of experiments, further confirming that the application of the surfactant and Zn(II) can increase the bioactivity of damaged microorganisms and extend the feasibility of bioreactors.

2.5. Biomass accumulation dynamics throughout entire period

To achieve a stable performance during long-term operation of biofilters, the control of excess biomass accumulation within the medium bed was very important. Wang et al. (2012) have shown that the biomass accumulation and the increase in pressure drop occurred simultaneously during the whole operation period, indicating that pressure drop can be utilized to predict biomass accumulation in packing media. Therefore, pressure drop was observed daily and the results are shown in Fig. 6.

From Fig. 6 it can be seen that, at the beginning of the operation period, the pressure drop value increased slowly due to the low inlet ethylbenzene concentration and the in-adaptation of the microorganisms to the ethylbenzene environment. The maximum pressure drop value was only 20 Pa at the end of the start-up stage. Thin ivory white biofilms were observed on surface of the packing media for both BTFs. Then the pressure drop grew relatively quickly after day 25 and the growth rate increased as the inlet ethylbenzene concentration was raised. This may be because that more microorganisms were produced due to higher ethylbenzene feed, which may further minimize the external porosity of the polyurethane sponge and thus led to a higher growth rates of pressure drop across the bioreactor (Mathur and Majumder, 2008). From day 55 to 85, when both BTFs were operated under an inlet ethylbenzene concentration higher



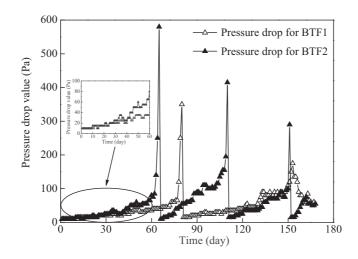


Fig. 6 - Pressure drop values during the whole period of operation of the BTFs.

than 2000 mg/m³, the pressure drop increased extremely quickly and excessive biomass accumulation occurred (dense, deep brown biofilm was attached to the packing media) at day 80 for BTF1 and day 65 for BTF2, respectively. Excessive biomass accumulation leaded to clogging across the bed and, concomitantly, to a poor removal performance of the bioreactor (Kim and Sorial, 2007; Yang et al., 2010b). So, the packing media were immediately carried out and washed with nutrient solution repeatedly to remove the excess biomass. After this washing process, pressure drop could decrease to its initial value (below 15 Pa) instantaneously, however, biomass re-growth followed when returning to the operating conditions. In BTF2, at day 109 and day 150 the biomass accumulation occurred again (pressure drop increased to 415 and 290 Pa, respectively) and the ethylbenzene removal efficiency decreased at the same time. In BTF1, there was only one mild re-growth in pressure drop (just reached to 175 Pa) at day 152, and interestingly, the pressure drop returned to its normal values in the following few days without any clean-up process, which was in accordance with the results obtained by Ramirez et al. (2012). A likely explanation to this result was that the non-ionic surfactants had a washing effect on packing media due to its detergent principle.

The results indicated that bioreactor operated with the application of Tween-20 and Zn(II) showed a slow biomass accumulation process and presented a better operational condition. Application of surfactant and metal ion could probably be considered as a strategy efficiently removing the excessive biomass without damaging the BTF performance.

3. Conclusions

Results showed that the RE and EC of the strengthened BTF (BTF1) were higher than that of the control BTF (BTF2) and the re-acclimation time was also much shorter. Ethylbenzene RE of both BTFs decreased with increased organic loading rate or decreased EBRT (60–15 sec) at a constant inlet concentration, while the EC increased. Although the effect of EBRT (30–10 sec) at a constant organic loading rate on ethylbenzene removal was not significant for both BTFs, BTF1 and BTF2 presented opposite performance trends. Throughout the

entire process, excessive biomass accumulation of BTF1 was relatively infrequent compared with that of BTF2.

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