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REMOVAL OF TRIETHYLAMINE VAPOR FROM WASTE GASES BY BIOTRICKLING FILTER

N. Mehrdadi, H. Keshavarzi Shirazi, A. A. Azimi, *M. Mirmohammadi

Department of Environmental Engineering, Faculty of Environment, University of Tehran, Tehran, Iran

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ABSTRACT

Sampling of triethylamine in the cold-box unit in an auto-manufacturing company in Iran has indicated the average concentration of 430 mg/m^3 in the emission duct. In this study a biotrickling filter was used for treatment of triethylamine in air stream. Triethylamine removal efficiency (K/L) pattern was evaluated by changing volumetric loading (L), superficial gas velocity (U_o), empty bed gas retention time (EBRT) and recirculation liquid flow rate (V_L), while operating at constant temperature of 25 ± 1ºC. For finding the effect of EBRT on the triethylamine removal efficiency, tests were performed at EBRT of 156s, 52s and 31 s and a constant liquid recirculation velocity of 3.466 m^3/m^2/h. Results showded that for a test period of 65 days, triethylamine removal efficiencies of more than 98% were obtained for EBRT of 156 s and loading rates of less than 48 g/m^3/h. With an EBRT of 52s removal efficiencies of > 90% were obtained for loadings of < 57 g/m^3/h and maximum removal capacity was 53.4 g/m^3/h at volumetric loading of 64 g/m^3/h. Also with an EBRT of 31 s the maximum removal capacity was 53.6 g/m^3/h at volumetric loading of 68 g/m^3/h. Thus in the range of implemented EBRTs the proper absorption of triethylamine from gas to liquid phase took place and the elimination efficiency was shown to be dependent on microorganisms activity rate. The effect of liquid flow rate on the triethylamine removal efficiency was investigated by changing V_L in the range of 3.46 to 10.40 m^3/m^2/h at EBRT=31 s and influent triethylamine concentration of 600 mg/m^3. Results showed that the triethylamine removal efficiency was nearly independent of the liquid recirculation rate.

Key words: Biotrickling filter; Triethylamine; Biodegradation; Air pollution

INTRODUCTION

Biological treatment of contaminated air in biofilter and biotrickling filter is an established and cost-effective technology. The principle of biofilter and biotrickling filter is relatively similar. Polluted air is passed through a porous packed bed on which pollutant-degrading mixed cultures form a biofilm. The pollutants are transferred from the waste gas to the biofilm where they are subsequently biodegraded (Devinny *et al*., 1999).

A biofilter system consists primarily of a reactor packed with solid material on which a biofilm with a proper microbial population is formed (Ottengraf and Van den Oever, 1983; Ergas *et al*., 1993; Chou and Hung, 1993; Tang et al.,1996). In a biofilter, the packed solid media provide the nutrient source, pH buffer, and matrix for the attachment of microorganisms. Once the buffering capacity or nutrient source is exhausted, the packing material can be restored by spraying an aqueous solution of alkaline material or nutrient salts while reblending. Natural organic media such as compost and peat must be replaced every two to three years because, in time, they can be biodegraded and compacted (Chou and Wu, 1999).

A Biotrickling filter system contains packing materials such as wood, ceramic, lava rock or plastic and is operated with the recirculation of liquid through the packing (Hartmans and Tramper, 1991; Chou and Huang, 1999).

*Corresponding author: E-mail: mohsen1692@yahoo.com)
Tel: +98 22 32 18 16, Fax: +98 22 32 18 15

The recycled liquid enables a better control of the conditions, hence biotrickling filters are usually more effective than biofilters (Huub and Deshusses, 2001). Nutrients and pH buffering agents can be easily added to the recirculated liquid. Acidic or alkaline products formed during the bioreaction can also be easily removed by replacing the recirculated liquid (Togna and Singh, 1994). For the biodegradation of contaminants such as halogenated hydrocarbons, hydrogen sulfide, and ammonia, which produce acidic or alkaline end products, the biofilter media needs to be replaced frequently, but there is not such need for biotrickling filter media (Hartmans and Tramper, 1991). Therefore, in treating triethylamine (TEA) which is alkaline itself and its byproducts are acidic, biotrickling filters are more effective than biofilters.

Amines are widely used as catalysts in casting operations. They are also the major pollutants in the gaseous emissions of chemical manufacturing factories. During the production of casting cores with the so called "cold-box process", polyurethane is used as a binder in the sand core. Considerable amount of amine vapor is used in this process and is partly emitted to the ambient air.

Tertiary amines, such as TEA are the main gaseous catalysts comprising the majority of nitrogenous emissions (Borger *et al*., 1997). Previous studies have suggested suitable biodegradation potential of amines (Borger *et al*., 1997; Chou and Shiu, 1997; Keshavarzi, 2005). Three studies have previously used biofilter to treat waste gases containing TEA. In this study biotrickling filter was used to treat waste gases containing TEA.

MATERIALS AND METHODS

Experimental setup

The experimental setup consisted of a laboratory-scale biotrickling filter and an influent gas supply system, as illustrated in Fig. 1. The biotrickling filter was made of stainlees steel with an internal diameter of 21 cm. The head space and bottom space were both 30 cm. Biotrickling column with a height of 150 cm was packed with lava rocks (size range of 2-4 cm with average of 3 cm, initial bed porosity of 60% and a 52L packing volume). The biotrickling filter was equipped with a liquid recirculation system holding a total liquid volume of 40 L and volume of liquid was 15 L during the whole experiments. The main air stream was provided by a compressor. A side stream of air was sent through a 1L bottle containing pure liquid TEA. The rest was mixed with the exiting side stream containing pollutant vapor. Air flow rates were appropriately controlled using pressure regulators and flow meters to generate feed air with required concentration.

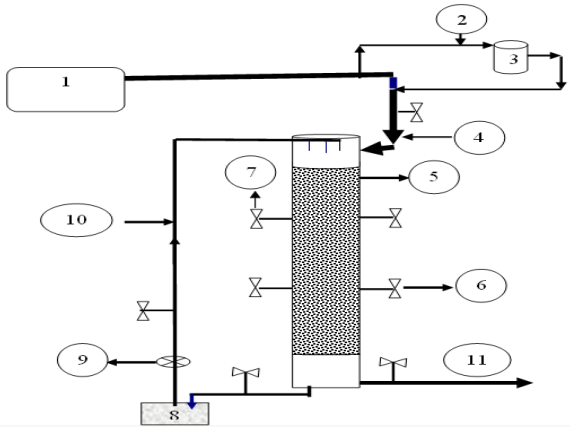


Fig. 1: Schematic diagram of the experimental system

1. Air pump, 2. Needle valve, 3. Aqueous solution of TEA, 4. Rotameter 5. Biotricking filter, 6. Gas sampling port, 7. Liquid sampling port, 8. Recycled water chamber, 9. Liquid pump, 10. Recycled water line, 11. pured air

Temperature control of the bed was achieved by placing the return liquid container in a water tank; the temperature was maintained constant at 25 ± 1 ºC. Heated element was used for temperature control in the water tank.

Materials

The lava rocks packed in the biotrickling filter were taken from mountains near Tehran. They are relatively inexpensive and easily obtainable in most parts of the country. Activated sludge for the seeding was obtained from a municipal wastewater treatment plant in Tehran.

Analytical methods

Gas samples were collected at the inlet, outlet, and in the 50 cm and 100 cm height of biotrickling

filter bed by passing the gas through the impinger containing 20 mL methanol as TEA solvent. The flow rate of gas was 340 mL/min for 15 min of sampling time. The amount of TEA in methanol was measured by UV spectrophotometer (UV/VIS) at a wavelength of 215 nm.

Standards were prepared by introducing known volumes of TEA into 5 L Tedlar bag. Appropriate volumes were selected based on vapor pressure calculations at room temperature and pressure. The equilibrium vapor pressures were calculated as 7.7 kPa (3142 mg/m^3) at 25 ºC and 101.325 kPa for TEA. Considering the volume of Tedlar bag and maximum concentrations possible at equilibrium, known liquid volumes were injected. For example, for a 5 L Tedlar bag, 5.67 µL TEA was injected to achieve 828 mg/m^3 concentration. Concentrations of the actual experiments were determined from the calibration curve prepared using absorption observed for known concentration of TEA. Temperature was maintained at 25°C and measured using alcohol in a glass thermometer.

Operation

The operation sequence shown in Table 1 was followed to investigate the effects of empty bed retention time, volumetric loading, superficial gas velocity, and liquid recirculation rate on the TEA elimination capacity and removal efficiency of the biotrickling filter.

In phase 1, in order to expedite the commencement phase, the returned sludge from municipal waste treatment plant was kept and aerated in a separate tank for 55 days. For the first 10 days, only powder milk (containing Fe-P-Na-Mn-Cu-Zn-Ca and K) was added to this tank. Afterwards, gradual injection of TEA was started with a daily increase in its dosage. After microorganisms were adapted, 15 L of this liquid was filtered and used as return liquid in recirculation liquid tank of biotrickling filter pilot.

In phase 2 during 65 days, the influent TEA concentrations were changed from 40 to 2000 mg/m^3. A constant EBRT of 312 s and a recirculation liquid velocity of 3.46 m^3/m^2/h (2 L/min) were maintained for the full test period. Gas samples at inlet and outlet column and liquid samples at liquid sampling port after liquid pump were taken every day and analyzed for TEA and by- products concentrations.

Afterward, the removal efficiencies of TEA were evaluated by varying the influent TEA concentrations and the superficial gas velocity through the column in the phase 3 of the experiment. EBRT was set to 156s, 52s and 31s(air inflow to the filter was adjusted at 20, 60 and 100 L/min), and a liquid recirculation velocity of 3.46 m^3/m^2/h was maintained for this phase. The effect of liquid flow rate on the TEA removal efficiency was investigated by varying V_L in the range of 3.46 to 10.40 m^3/m^2/h at EBRT= 31 s and influent TEA concentration of 600 mg/m^3.

Table 1: Operation sequence and conditions

Phase	Purpose	Duration (day)	C_{in} (mg/m^3)	*EBRT (s)	U_O (m/h)	V_L (m^3/m^2/h)
1	Adaptation	55	-	-	-	-
2	Biofilm cultivation	65	0-828	312	17.33	3.466
3	Effect of empty bed retention time	60	500-2600	156	34.5	3.466
		25	235-930	52	104	3.466
		15	140-620	31	173	3.466
4	Effect of liquid recirculation rate	14	600	31	173	3.466-10.4

* Empty Bed Retention Time = EBRT = V/Q (s or min) where V is the volume of the packed bed (m^3) and Q is the air flow rate (m^3/h)

RESULTS

Adaptation and start up

Fig. 2 shows the total concentrations of TEA injected and measured in liquid during the first 55 days. Fig. 3 shows the concentration of TEA in the influent and effluent of the system in the first 65 days of operation. The effluent TEA was undetectable and no TEA concentration was reported in all situations.

Effects of empty bed gas retention time

Time variations of TEA concentrations in the influent and effluent gas streams are shown in Figs. 4a , 5a and 6a, respectively, for fixed EBRTs of 156, 52 and 31 s. Variation of volumetric TEA loading, elimination capacity and residual TEA concentration in the recirculation liquid at different inlet TEA concentrations and EBRTs of 156, 52 and 31 s are shown, respectively in Figs. 4b, 5b and 6b.

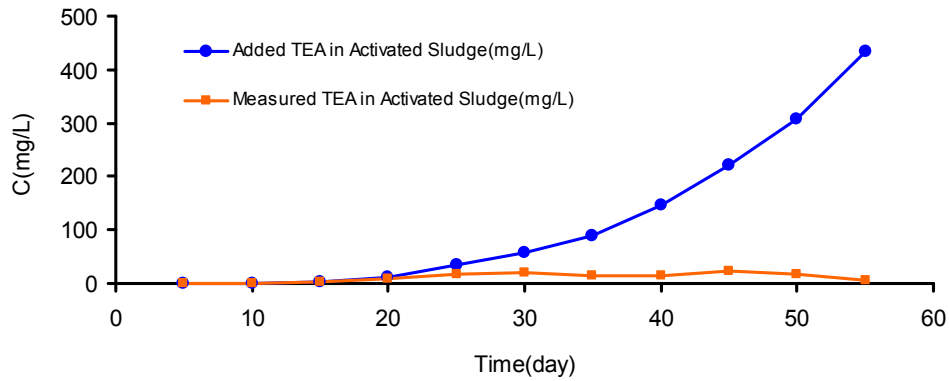


Fig. 2: Time variation of TEA concentrations in the activated sludge tank during the adaptation period (phase 1)

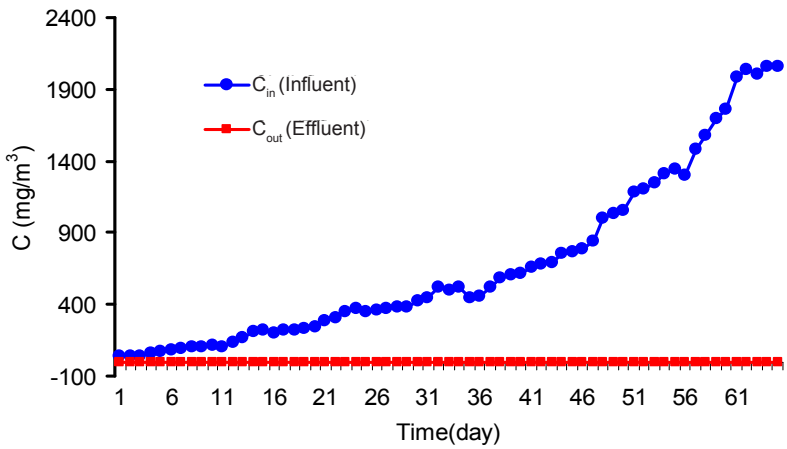
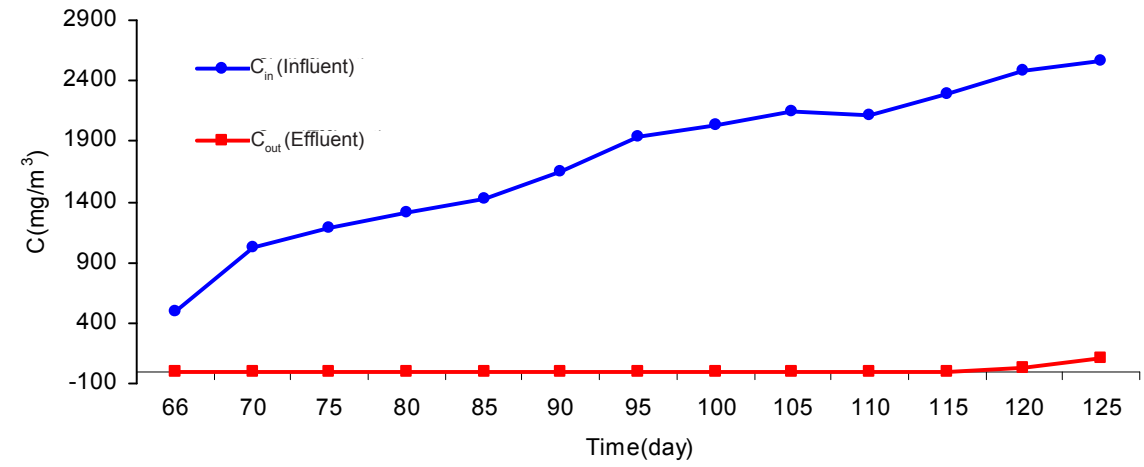
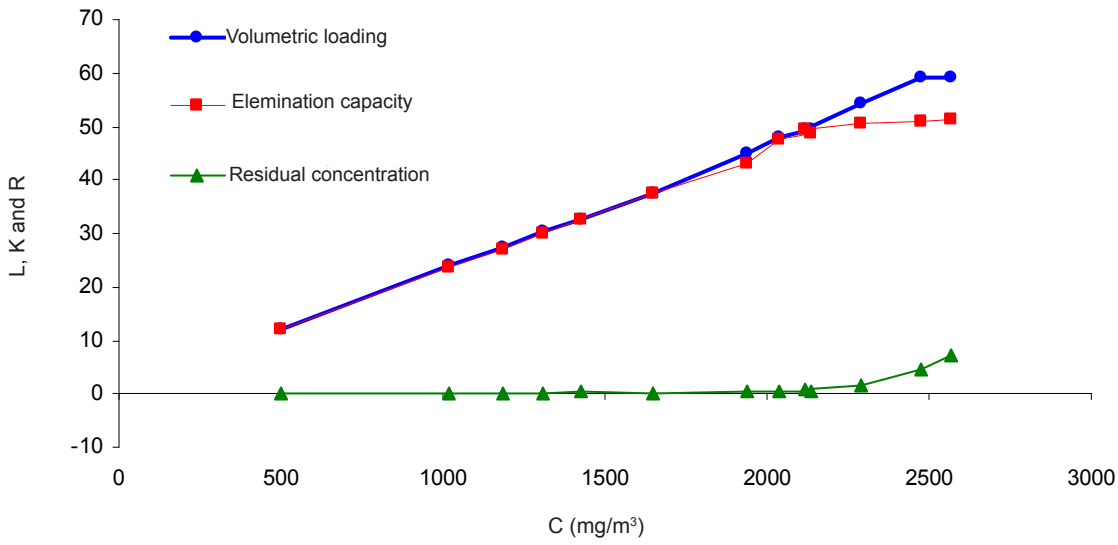


Fig. 3: TEA concentrations in the influent and effluent gas streams during the biofilm cultivation period (phase 2) (U_o=17.33 m/h and EBRT=352 s)



(a)



(b)

Fig. 4: (a) Time variation of TEA concentrations in the influent and effluent (b) volumetric TEA loading (L: g/m^{3}h), elimination capacity (K: g/m^{3}h), and residual TEA concentration in the recirculation liquid (R: g/L) at different inlet TEA concentrations at U_0 = 34.7 m/h and EBRT = 156 s

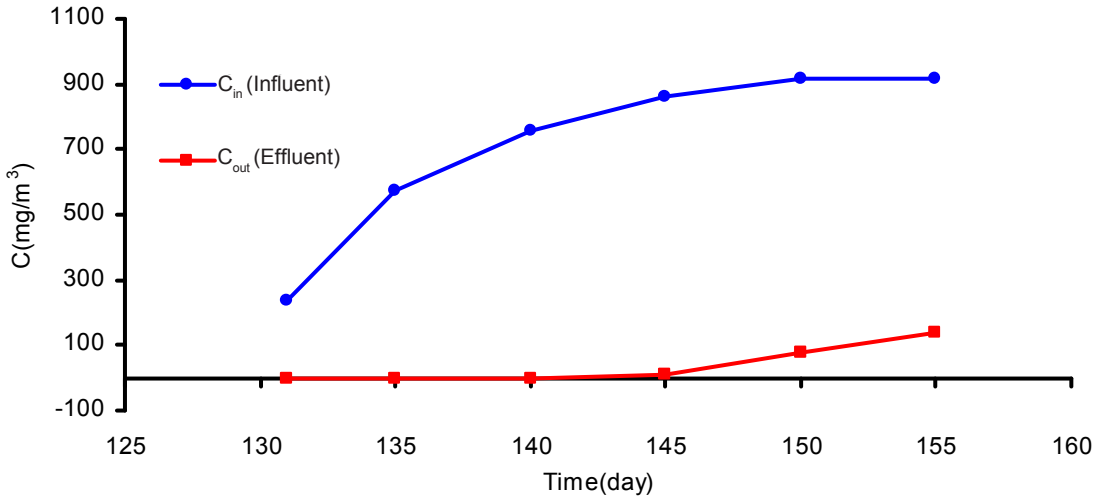
Effects of liquid recirculation velocity

Fig. 7 shows the TEA removal efficiency as a function of the liquid recirculation velocity in the range of 3.46 to 10.40 m^3/m^2/h at EBRT=31 s and influent TEA concentration of 600 mg/m^3 in the phase 4 of the experiment.

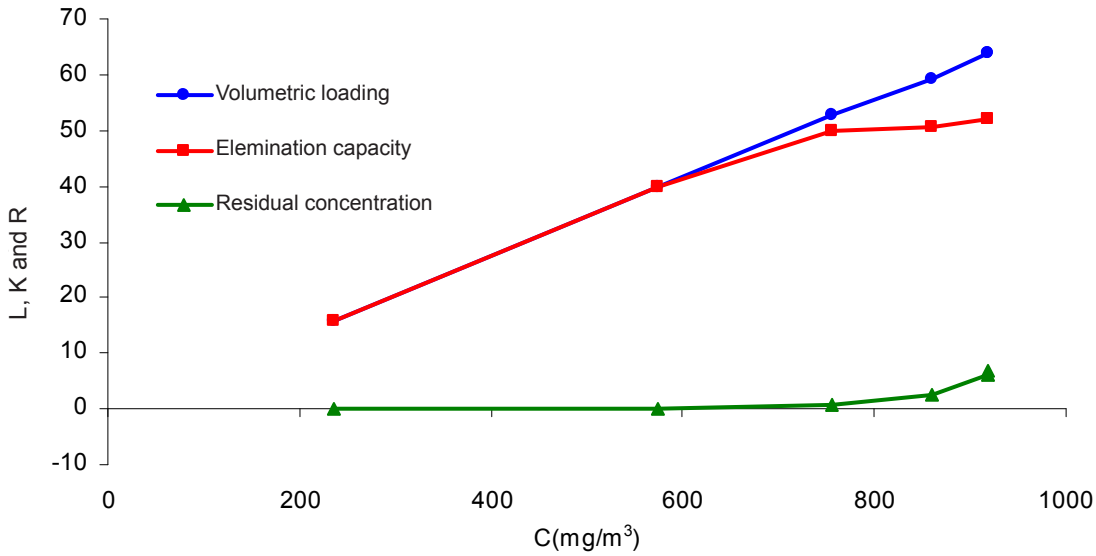
DISCUSSION

Adaptation and start up

According to Fig. 2, after TEA injection started, its degradation did not occur during the first 10 days; results show that organic matter content was high due to the increase of milk powder. Degradation



(a)

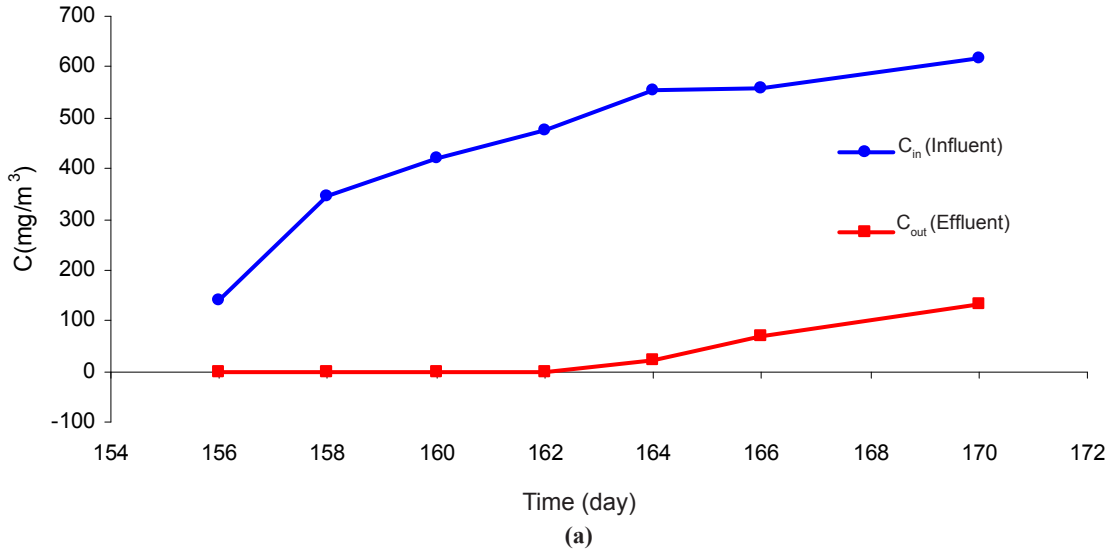


(b)

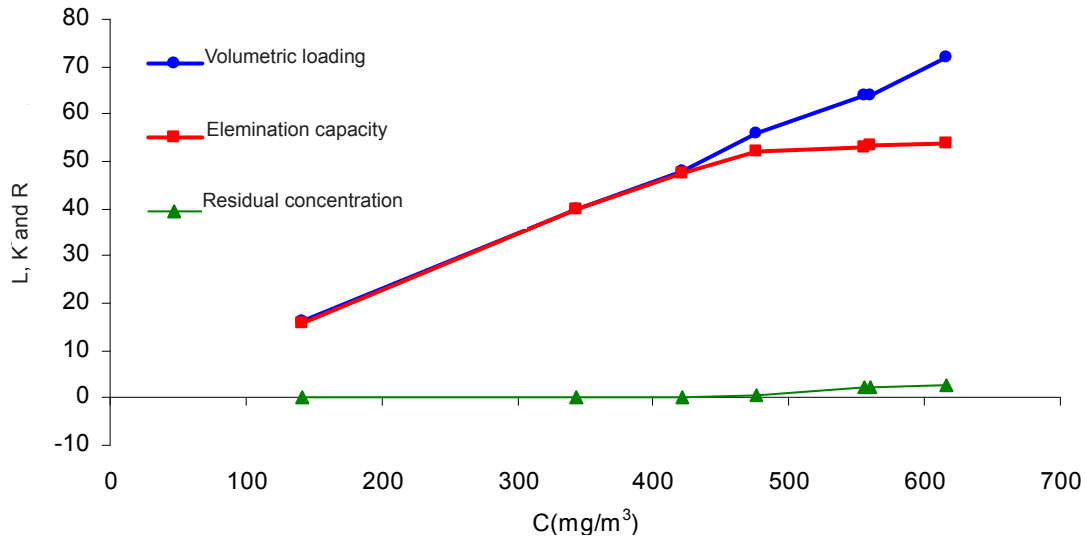
Fig. 5: (a) Time variation of TEA concentrations in the influent and effluent; (b) Volumetric TEA loading (L: g/m^{3}h), elimination capacity (K: g/m^{3}h), and residual TEA concentration in the recirculation liquid (R: g/L) at different inlet TEA concentrations at U_o=104 m/h and EBRT=52 s

slowly started from day 15 and increesed to 0.62 g/day in day 45. After microorganisms were adapted, 15 L of this liquid was filtered and used as return liquid in recirculation liquid tank. According to Fig. 3 the effluent TEA was undetectable and no TEA concentration was reported in the first 65 days of operation.

As microorganisms were adapted to use TEA in the previous step, in the following step, degradation started. Volumetric load on the system was 0.464 g/m^3/h in the first day and degradation was 0.40 g/m^3/h and reached to 23 g/m^3/h in day 65. A true steady state in biotrickling filters will never be obtained because the amount of biomass will change in time, and changes in the microbial population may occur even after 500 days of operation. However, when monitoring reactor performance at constant inlet concentration and constant nutrient feed, a pseudo-steady state can be defined when outlet concentrations are approximately constant, and a constant rate of biomass accumulation is observed (Huub *et al.*, 1998).



(a)



(b)

Fig. 6: (a) Time variation of TEA concentrations in the influent and effluent (b) Volumetric TEA loading (L: g/m^{3}h), elimination capacity (K: g/m^{3}h), and residual TEA concentration in the recirculation liquid (R: g/L) at different inlet TEA concentrations at U_0 = 173 m/h and EBRT = 31 s

Effect of empty bed gas retention time

According to Fig.4 and the experimental data for EBRT of 156 s and L<48 g/m^3/h or C_{in} <2000 mg/m^3, TEA elimination efficiencies of greater than 98% were achieved. For L < 56 g/m^3/h (C_{in} < 2430 mg/m^3), TEA elimination efficiencies of more than 90% were achieved and maximum elimination capacity was 51.2 g/m^3/h. For EBRT=52 s and loadings of < 57 g/m^3/h, as indicated in Fig. 5b, TEA removal efficiencies of > 90% were achieved. Influent TEA concentration was 235-930 mg/m^3 and maximum elimination capacity was 53.4 g/m^3/h at volumetric loading of 64 g/m^3/h.

Similar results were obtained at EBRT of 31 s and TEA concentration of 141-610 mg/m^3. By EBRT of 156, 52 and 31s when loading was greater than 51.2-53.4 g/m^3/h, microorganisms were not able to eliminate the loaded TEA effectively and dissolved TEA in the recirculation liquid increased. When TEA content in the liquid phase

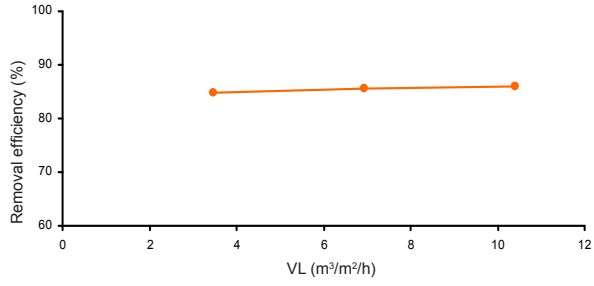


Fig. 7: Removal efficiency of TEA at different liquid recirculation rates (V_L); C=600mg/m3; Uo=173m/h; EBRT=31s

increased, some TEA in the gas phase was not able to transfer into the liquid phase and removal efficiencies were thus reduced. By comparing data shown in Figs.4a, 5a and 6a, it seems that with EBRT of 156, 52 and 31s, C_{out} is not dependent on C_{in}. Because of high TEA water solubility, as far as TEA concentration in liquid phase was low, it was completely transfered from liquid phase to gas phase. Moreover, as the operation time increased, the removal capacity increased as well. Removal capacity increased from 0.464 to 23 g/m^3/h during phase 2 in 65 days and from 23 to 53.4 g/m^3/h during 100 days.

Effects of liquid recirculation velocity

Nutrients and pH buffering agents can be easily added to the recirculated liquid in a biotrickling filter. Acidic or alkaline products formed during the bioreaction can also be easily removed by replacing the recirculated liquid. According to Fig. 7 at the operation conditions, the TEA removal efficiency was nearly independent of the liquid recirculation rate. Results of other studies (Chou and Hung, 1993; Chou and Hung, 1997). have also shown that for treating water-soluble contaminants, the liquid recirculation velocity is minor operation factor in the case of low loadings. However, a high liquid recirculation velocity should be avoided at high levels of contaminant loadings, because some contaminants remaining in the liquid would be stripped.

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