

Assessing the Ability of Biofiltration to Remove and Treat Diethanolamine from Contaminated Air Streams Using Compost-Based Biofilter

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ABSTRACT: Biofiltration method is one of the most commonly used and most effective methods to remove pollutants from the exhaust gas flow from different industries. One of the most important categories of air pollutants is HAP (Hazardous Air Pollutants). This Study assesses the ability of biofiltration method to remove and treat HAP DEA (Diethanolamine) from a gas stream through a laboratory-scale biofilter column filled with granular compost, plastic hose pieces and municipal wastewater sludge. After start-up period with an average concentration of 6 ppm, the main period began with an average DEA inlet concentration of about 51.7 ppm corresponding to a loading rate of 0.97 g/m³.hr and empty bed residence time of 89s, the biofilter reached a removal efficiency of about 89% by two weeks. The maximum EC of 26.85 g/m³.hr was achieved at a loading rate of 42.62 g/m³.hr, corresponding to an inlet concentration of DEA of about 258 ppm. Also the loading rates less than 28 g/m³.hr are recommended to achieve the efficiency higher than 80%. The biofiltration method had an efficiency of more than 80% for concentrations <170 ppm at 40°C. Also the maximum pressure drop was recorded 13.8 mmH₂O. It is because of using a mixture of shredded plastic hose pieces as a bulking agent due to a high level of porosity in the bed.

Key words: Diethanolamine, Bulking Agent, Biofiltration, Compost-Based Biofilter, Two-Stage Biofilter, Hazardous Air Pollutants, Shredded Plastic Hose

INTRODUCTION

Any matter in the air which usually exists due to various human activities and natural events and causes disease and disorders in humans, animals and plants and could damage objects is called air pollutant (ACCCE, 2010). According to the definition of EPA's Clean Air Act, HAP (Hazardous Air Pollutants) are toxic chemicals and those pollutants which are known to cause or may reasonably be anticipated to cause adverse effects to human health or adverse environmental effects (EPA, 2012).

Diethanolamine is a secondary amine containing two ethanol molecules bind to each other from their beta carbons (TPMC, 2002). This is a clear, colorless, hygroscopic liquid with a mild ammoniacal odor at temperatures higher than room temperature. At room temperature, the substance is a white, crystalline solid (HATC, 2008). This substance is one of 189 hazardous air pollutants with CAS number of 111-42-2 (ACS, 2010). DEA is widely used as an intermediate in the production

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of fatty-acid condensates formulated into soaps and surfactants used in liquid laundry and dishwashing detergents, cosmetics, shampoos, and hair conditioners. DEA also is used as a surface-active agent and corrosion inhibitor in metalworking fluids and as a dispersant in agricultural chemical formulas. Other applications include use in adhesives; snit-static agents; cement and concrete work; coatings; electroplating; printing inks and many other industries (NTP, 1999; IARC, 2000; TPMC, 2002).

American Conference of Governmental Industrial Hygienists (AGGIH) cited that the threshold limit value (TLV) for airborne DEA is 0.46 ppm and for skin exposure is 2 mg/m³. NIOSH cited that the recommended limit value of DEA is 3 ppm but OSHA didn't cite any data (IARC, 2000). The United States Environmental Protection Agency has classified this pollutant in group "D" of carcinogenicity, which means that the substance isn't able to be classified as carcinogenic to humans in terms of the organization's

(IARC, 2011). This pollutant is dangerous in contact with skin or eyes, also swallowing and breathing can be very dangerous. It Causes eye burning running and itching and it is likely to lead to cancer (MSDS, 2010).

Biological filtration or biofiltration was applied for the first time to remove and control odorous gases at wastewater treatment plants and to produce compost and gradually was used for refining volatile organic compounds as an innovative method for the treatment of toxic air pollution from industrial processes (Bellis, 2012). Recently, biological processes have received much more attention as an alternative for treatment of polluted air (Kim *et al.*, 2000). The principle of Biofiltration is relatively simple; a contaminated air stream is passed through a porous packed media on which pollutant degrading cultures of microorganisms are immobilized (Deshusses *et al.*, 2003).

As the odorous and contaminated air passes through the bed, the contaminants in the air stream are adsorbed by the biofilm which is a thin layer of moisture in which microorganisms are activating and then these contaminants are oxidized to produce biomass, CO₂, H₂O, NO₃⁻ and H₂SO₄. Biofiltration is an emerging technology that offers a number of advantages over traditional methods of air pollution control for the treatment of low-concentration polluted air streams. Besides its highly efficient removal of pollutants, low capital expenditure and operating costs, safe operating conditions and low energy consumption, it doesn't generate undesirable byproducts and it converts many organic and inorganic compounds into harmless oxidation products (Selvi *et al.*, 2007; Sheridan *et al.*,

2002; Deviny *et al.*, 1999). Also simplicity of design has been cited as a reason for the popularity of biofilters (Zilli *et al.*, 2001).

Biofiltration shows an appropriate efficiency for the removal and control of many gaseous pollutants. For example, in a study in 2010 on the removal of toluene vapors using biofiltration method, Singh and colleagues achieved the efficiency between 68.2% and 99.9% (Singh *et al.*, 2010).

Compost has been used widely for biofilter media because of its low cost, high nutrient content and ease of availability. Negative aspects include the development of back-pressure due to gradual compaction with time, and aging effects due to microbial mineralization (MacNevin *et al.*, 2000; Dehghanzadeh *et al.*, 2005). On the other hand, compost is commonly used as organic packing material because of its diverse microbial population and inherent nutrients (Galera *et al.*, 2008).

MATERIALS & METHODS

Two two-stage (biofilter A at 40°C and biofilter B at 30°C) lab-scale upward biofilters, each one constructed from two concentric cylindrical Plexiglas tubes with an effective overall height of 100 cm and internal diameters of 14 and 20 cm were used in this research (Fig. 1). The columns' stages were separated by perforated plates also acted as a support for the packing material. In each stage the columns were filled by packing material with a height of 30 cm. there were some spaces before the first stage, between the two stages and after the second stage in order to gas

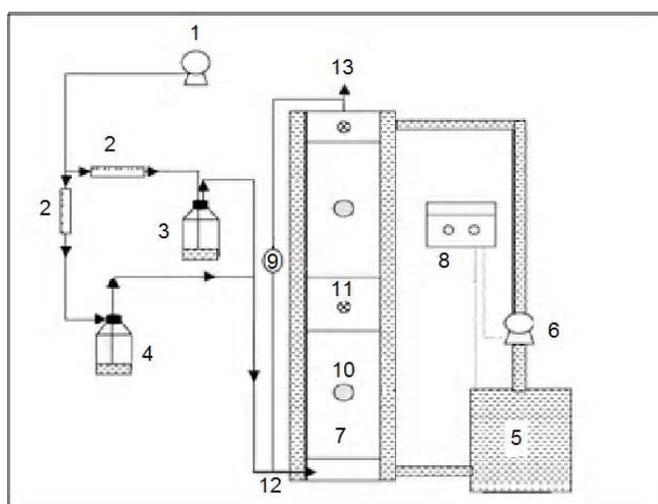


Fig.1. Schematics of the biofilter system: (1) Compressor; (2) Flow meter; (3) Contaminant Container; (4) Humidifier; (5) Water Tank; (6) Water Pump; (7) Biofilter Bed Media; (8) Electronic Switches; (9) Manometer; (10) Bed Sampling Port; (11) Air Sampling Port; (12) Inlet; (13) Outlet.

Table 1. General Characteristics of Bed Packing Material

Weight of Mixed Sludge (g)	636
Weight of Compost (g)	4428
Weight of Bed (g)	5364
Volume of Bed (lit)	4.62
Density of Bed (g/lit)	1161
Moisture (wt %)	59.2
Temperature of Bed (°C)	39.9-40.1
pH	6.85

redistribution. Provision of sampling ports at the stages and the spaces between the stages allowed access to the bed medium and air stream respectively.

In order to fix the bed temperature, the space between two concentric tubes was filled by water. This water was circulating through a heater and a water pump. A temperature sensor was used to control the temperature with a tolerance of $\pm 0.1^\circ\text{C}$. Compressed air was produced by an oil-free compressor. In order to control the effluents of humidifier and DEA container, two flowmeters were placed for the main stream and contaminant stream with ranges of 5-45 lit/min and 0.7-7 lit/min respectively. Humidifier was container which humidified the main air streams in by passing them through itself in order to stabilize the bed material's moisture content in desired range of 50%-60%. Air streams' relative humidity was higher than 95% in whole research. Contaminant container was a 125ml-volume glass container which contained 50-60 ml diethanolamine in order to generate contamination and pollution to the air stream. Passing a very low flow rate through this contaminant container, the inlet concentration pollution of 4-8 ppm was generated. At further levels, in order to generate higher concentrations of pollution, higher flow rates were passed through the contaminant container and the container was heated up to 80°C using a belt heater. The moisture content of the bed material was maintained at 50-60% during the research period.

Monitoring the pressure drop along the column bed was conducted using a plastic U-type water manometer. In this lab-scale research, municipal activated sludge was used as a mix-culture to cultivate compost medium without an enrichment process to enhance the microbial density and improve the homogeneity of the packing material. The reactor was packed with compost-based medium mixed with shredded plastic hose pieces as the bulking agent to reduce the pressure drop.

The bed medium was prepared by mixing municipal solid waste compost (Kahrizak Landfill Co.), shredded plastic hoses (0.5cm) as a bulking agent to increase the porosity of the bed material, and activated sludge at a volumetric ratio of 3:1:1. The activated sludge was obtained from Shahid Beheshti University's wastewater treatment plant as the mix-culture in order to add microbial population. To acclimatize the microorganisms to Diethanolamine, five ppm of contaminant was added to the activated sludge daily for a 20-day period of time. Finally the beds were aerated using a flow rate of 15 lit/min for 10 days. Bed's general characteristics are shown in Table.1. DEA inlet concentrations in biofilters A and B were 5-261 ppm and 6-273 ppm respectively. Also loading rates in biofilters A and B were 1.25-42.62 $\text{g}/\text{m}^3\cdot\text{hr}$ and 1.32-46.56 $\text{g}/\text{m}^3\cdot\text{hr}$, respectively. The moisture contents of both columns were between 50-60% and also pH in both of them was in neutral range.

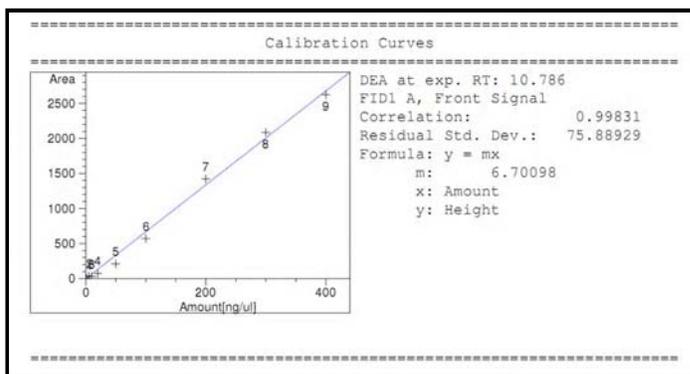


Fig. 2. Samples' Calibration Curve

Analytical Methods

Concentration of Diethanolamine in the air sample was determined using Gas Chromatography with Flame Ionization Detector (FID). Air sampling ports were connected to an impinger containing 100ml methanol (as a solvent) to trap DEA. The moisture content of the bed material was measured by drying a given amount of the bed material at 60°C (due to the organic content of compost) until the difference between two consecutive measurements doesn't exceed 0.1% of sample's primary weight (IRISI, 1998). To determine the pH of the medium, 50 ml of distilled water was added to a 5 g sample of medium and blended to be used for measurement (APHA, 1992). To make an exact calibration curve for GC, samples of 1, 5, 10, 25, 50, 100, 150, 200 and 300 ppm were prepared with high precision. After drawing calibration curve, the linear regression was measured and finally the most accurate regression number was $R^2=0.998$ as shown in Fig. 2.

RESULTS & DISCUSSION

After inoculation of the biofilter with activated sludge, the system was operated with an airflow rate (Q) of 0.342 m³/h corresponding to an empty bed residence time (EBRT) of 89s with an average loading rate (LR) of 0.97 g DEA/m³h. During the acclimation period (about two weeks), the removal efficiency was almost 100% which indicates that system still worked with its physical removal capacity not the biological removal. Complete removal of DEA couldn't be the sign of microbial degradation because if it was, the system should keep working with the same 100% efficiency. After the first two weeks of the main period, the efficiency declined from 98% to 66%. Passing the time, with accumulation of microbial population to the biofilter conditions, biological degradations have been raised and efficiency increased to 89%. The removal efficiency (RE) of biofilter A, as a function of time is shown in Fig.3 and the relationship between elimination capacity (EC) and DEA loading rate is presented in Fig. 4.

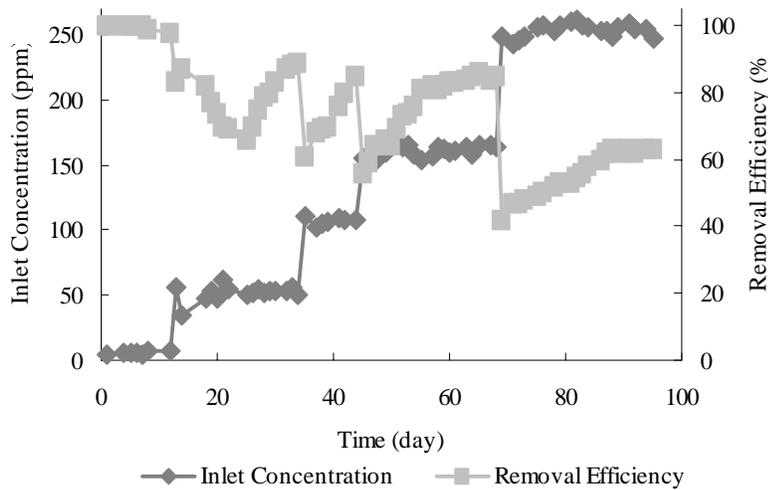


Fig. 3. Overall performance of biofilter A in removal of DEA

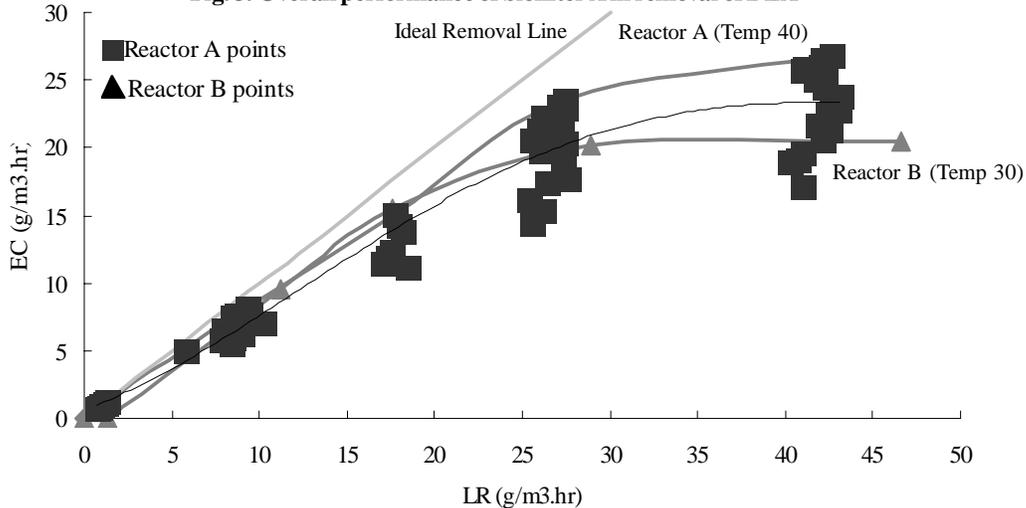


Fig. 4. Relationship between elimination capacity and loading rate of DEA

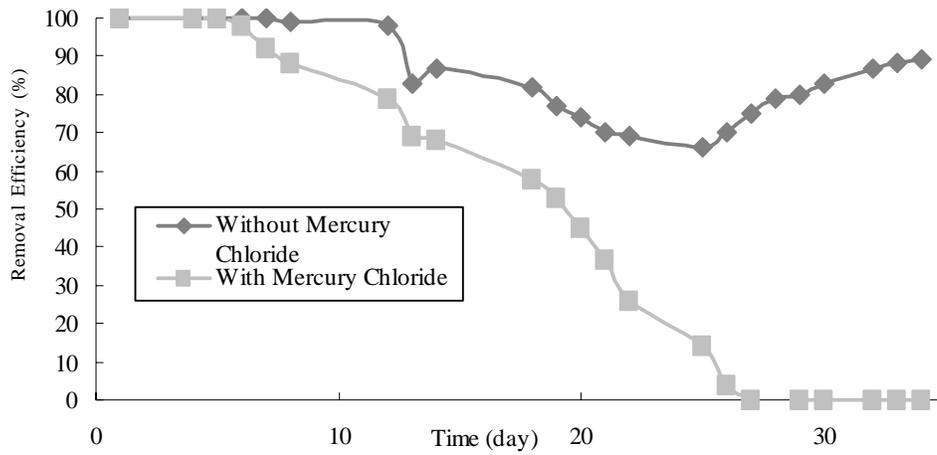


Fig. 5. The pure effects of microbial population on DEA removal

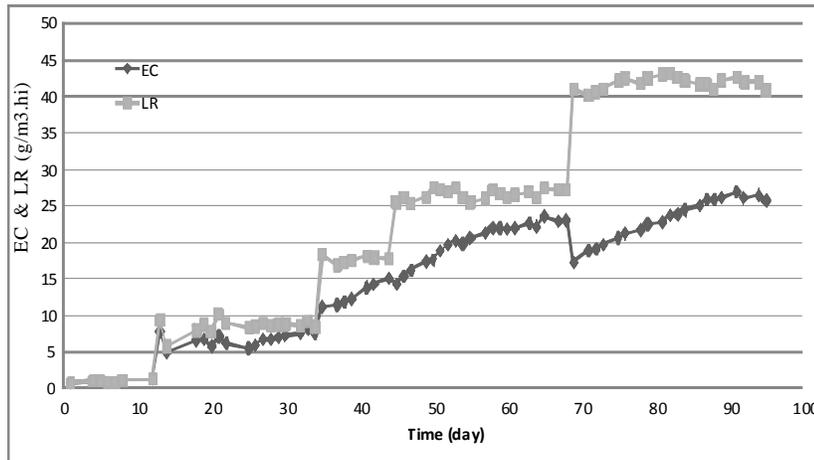


Fig. 6. Elimination capacity vs. loading rate by time (biofilter A)

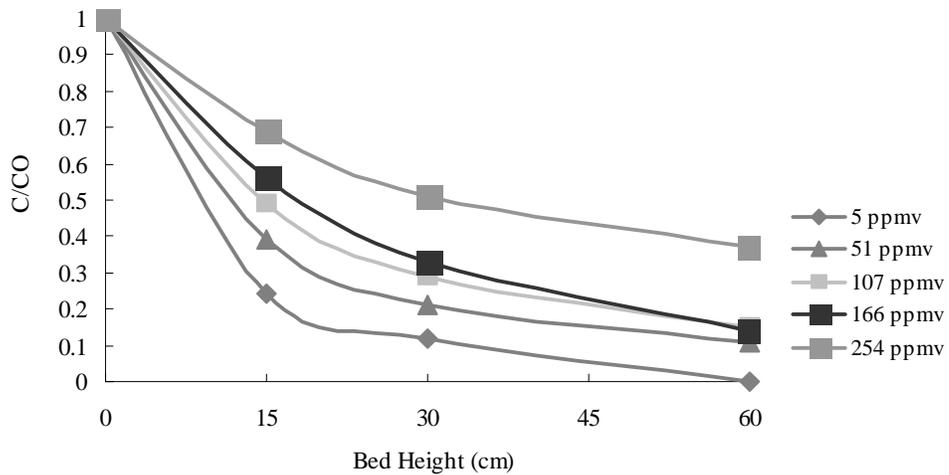


Fig. 7. The concentration gradient at biofilter A

Resistance to air flow is the major factor that determines the amount of energy required by compressor to force the contaminated air stream through the filter (Abumaizar *et al.*, 1998). In this study, the pressure drop was monitored continuously with a water manometer. The system had some pressure drops that might be related to the microbial population growth of the bed medium. The maximum and average pressure drops of the system were 13.8 and 4.3 mm H₂O, respectively. As mentioned, the system had a low average drop of pressure which is the sign of appropriate performance of the bed material. Also these results imply that using a mixture of compost and shredded plastic hose pieces was suitable for removal of DEA from air streams.

The results indicated that other mechanisms such as physical adsorption could be effective in removal of the contaminant in start-up period. In order to study

the operation of biofilter during setup phase and to study the amount of media's physical adsorption, the other column was prepared with the same media whose microbial population has been zeroed using Mercury Chloride as a germicide agent. Passing the contaminated air stream through the bed media, the outlet contaminant concentration was monitored. The results indicated that the efficiency was 0% after 27 days. With the same operational conditions, the biofilter A with microbial population had results shown in Fig.5. Both of the biofilters had the same conditions such as temperature.

Fig. 5 shows that biological treatment of DEA begins as well as other removal mechanisms. Comparing two columns' results, it can be concluded that during the first 30 days, the amount of biological treatment was less than other mechanisms but after that, the biological treatment has been increased so

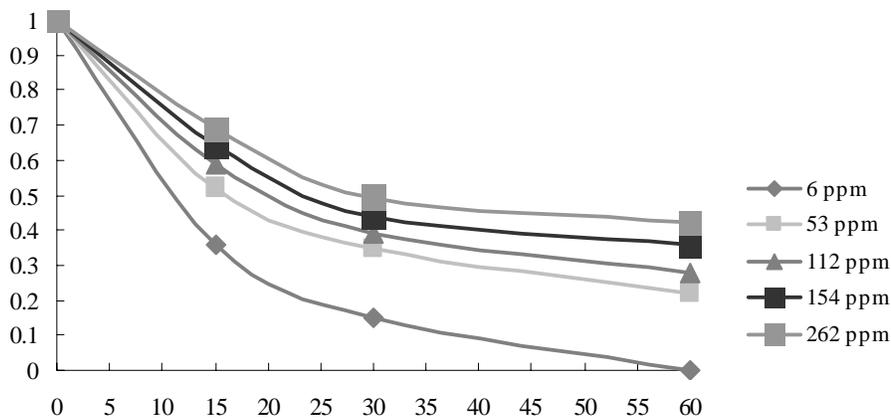


Fig. 8. The concentration gradient at biofilter B

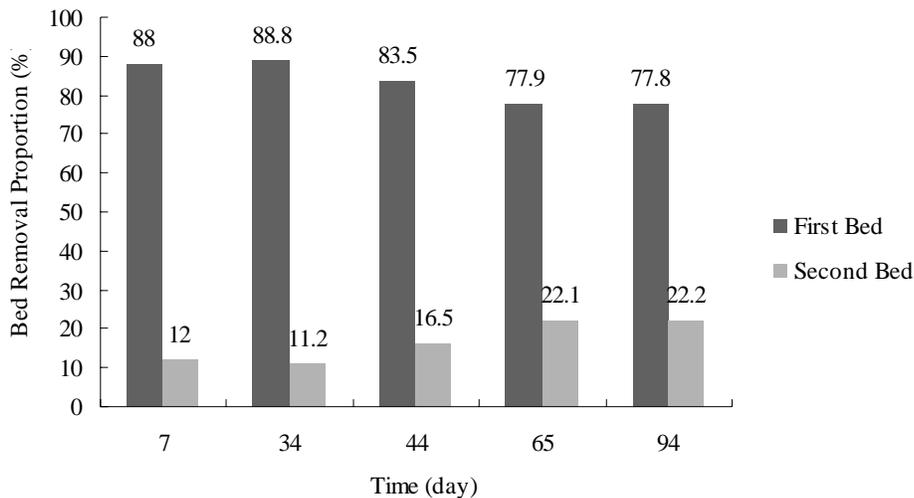


Fig. 9. The proportion of the beds in DEA's total removal

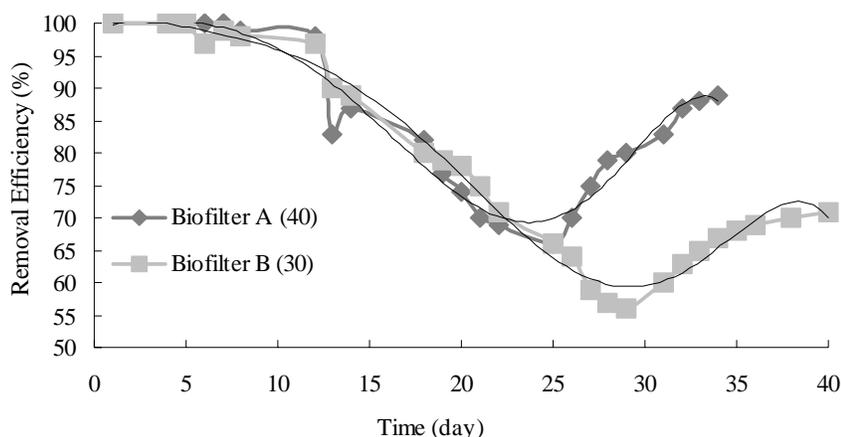


Fig. 10. The temperature effects on RE

that after 38 days, biological treatment was the only working mechanism.

To investigate the effect of inlet concentration on performance, each time after increasing the inlet concentration of DEA and increasing and then fixing of efficiency, inlet concentration was increased again. Each time of increasing the inlet concentrations, efficiency was decreased due to the low microbial population and making the inhibition condition because of DEA's toxic effects on microbial population. Also it'll be seen in next diagrams that inhibition effects of DEA has been seen between 240-260 ppm. When the inlet concentration reached the amount of 240-260 ppm, the amount of system's elimination capacity wasn't increased. Also it is concluded that the more inlet concentrations, the more time to reach to the maximum efficiency. Fig. 6 shows the variation of elimination capacity versus loading rates by time. Also the relative increasing and decreasing procedure of elimination capacity of Diethanolamine can be seen.

It's completely clear that the removal performance of the system wasn't weakened when DEA inlet concentrations increased because this process needed some time to acclimate to the new concentrations. There are similar procedures for variation of EC in both columns. The maximum EC recorded for elimination of DEA in columns A and B are 26.85 g/m³.hr and 20.43 g/m³.hr, respectively.

The trend of DEA's concentration variations in different heights of the bed was determined using sample ports placed in lateral parts of the columns in 15, 30 and 60 cm from the bottom. Calculating the outlet concentrations / primary concentration for each part, the C/C₀ diagram was plotted by time. Fig. 7 and Fig. 8 show the concentration gradients for biofilters A and B, respectively. As shown in both Fig. 7 and Fig. 8, the removal efficiency of the first sample port in different inlet concentrations was more than the other sample

ports. This is because of entrance of more DEA concentrations in first section and so the more microbial growth. The higher concentrations cause more amount of DEA enters the other sections, more microbial growth and less difference in concentration gradient in beds. During the study, the first section of biofilter "A" had a 31%-76% proportion of elimination. The similar procedure at biofilter B was observed.

As mentioned before, each bed had a different proportion in removal of the contaminant but these proportion has changed by time. Fig. 9 shows these proportion variation by time. As shown, it could be concluded that in the first days of biodegradation, the second bed had a little role on DEA removal but by the time its proportion has increased. In total, the proportion of first bed in both biofilters was more than about 78%. It is also concluded that the time can affect the proportion variation of beds. Fig. 10 shows the effect of different temperatures (30°C & 40°C) on removal efficiency of biofilters A and B. Overall comparison between the efficiencies of biofilters A and B at inlet concentration range of 50-60 ppm indicates that biofilter A has a higher performance comparing to biofilter B. In the mentioned concentration range, column A reached to maximum efficiency of 89% by 34 days from beginning but column B reached to maximum efficiency of 71% by 40 days. This results indicate that from both time and efficiency point of view, biofilter A has a higher performance than biofilter B. This is because of higher microbial population growth in column "A" which can lead to more biological treatments in fewer time.

It's known that every 10-degree increase in temperature often doubles the rate of microbial growth. On the other hand, Henry's constant in organic compounds rises when temperature increases and will cause lower solubility in the liquid phase (biofilm) and so the lower efficiency, but as shown in Fig. 10, the increase in microbial growth is the determining factor.

CONCLUSION

- Biofiltration method is useful for biological treatment of DEA. This method has an efficiency more than 80% for concentrations <170 ppm at 40°C.
- The biofilter A with 40°C had a higher efficiency than the biofilter B at 30°C.
- Concentration's gradient along bed height was not uniform. The first section at both biofilters played more role in DEA removal.
- The optimum conditions in DEA Biofiltration are moisture content of 50-60%, temperature of 40°C and neutral pH range. Also the loading rates less than 28 g/m³.hr are recommended to achieve the efficiency higher than 80%.
- An acclimation period of about 12 days for degradation of DEA in a biofilter achieved an average loading rate of 0.97 g/m³.hr, EBRT of 89s.
- A maximum EC of 26.85 g/m³.hr was achieved at a loading rate of 42.62 g/m³.hr, corresponding to an inlet concentration of DEA of about 258 ppm.
- The maximum and average pressure drops were 13.8 mmH₂O and 4.3 mmH₂O for each meter across the biofilter bed. Using a mixture of shredded plastic hose pieces as a bulking agent reduced the pressure drop, due to a high level of porosity in the bed.

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