Performance And Behavior Under Transient Conditions For Membrane Bioreactor Treating Toluene Vapors

B.Sundar, V.Saravanan, M.Rajasimman

Abstract: Many petrochemical, polymer and paper industries uses the toluene as solvent for the processing it was used as the main compound in this study. The bench scale membrane bioreactor used for controlling the toluene as a main single pollutant. Toluene was treated effectively, with toluene influent concentrations maintained at less than 0.4 g m^{-3} and a total removal efficiency of over 96% achieved when the faced fluctuating loads. The maximum elimination capacity of the membrane biofilter system was 93.8 g m^{-3} h^{-1}. The membrane bioreactor showed a quick response to the transient condition (shutdown, restart, and shock load) and the stability of the membrane bioreactor was maintained. Further, the Bacillus sphaericus and Pseudomonas alcaligenes bacterial isolate was identified as the predominant strain involved in the toluene biodegradation in membrane bioreactor

Keywords: Elimination Capacity: Membrane Bioreactor: Removal Efficiency: Toluene

1. INTRODUCTION

Many industries produce Volatile organic compounds (VOCs) like wastewater treatment plants, dry cleaning, printing, coating and surface treatment activities. [1-2]. There are several control technique for the treatment of VOCs from the air. Among these techniques including biofilters, biotrickling filters and bioscrubbers, have successfully treated waste gas streams with relatively low VOC concentrations. Biofilters proven the most conventional processes among the biotechnology process, such as less energy requirement, working at the low substrate concentration, and the absence of waste products that require further treatment or disposal [2]. During recent years biofilters have been broadly useful in the treatment of streams contaminated with a large variety of pollutants, including oxygenated compounds [1] [3], aromatics or its mixtures [4]. However, these biotechnologies have existing restrictions such as clogging of the media, control of the moisture content and treatment of hydrophobic compounds [5], as well as large size requirements, especially for biofilters [6]. The new technology was developed to overcome these problems and limitations described above for waste air treatment was Membrane bioreactor (MBR). The conventional MBR technology is advancing rapidly for waste air treatment, two phases, gas and liquid, exist in the system and are separated by the membrane.Vapor pollutants diffuse through the membrane and are subsequently degraded by microorganism present in the biofilm. The liquid provides nutrients to the biofilm and is continuously recirculated, so pH and nutrients can be easily controlled. This paper describes the explanation on the performance of the gas membrane module under different conditions. Characteristics of microbes in the membrane bioreactor and membrane fouling were also investigated.

2. METHODS

2.1 Chemical

Toluene was selected as model pollutant in this study, the Environmental Protection Agency in the USA computed the toluene is listed in the 129 priority chemical, it is mainly present in the petrochemical, polymer and paper processing industries, mainly to natural resource pollution via the release of toluene-contaminated effluents and off-gases.

2.2 Membrane Materials

A commercially available composite membrane was provided by technic membrane system, Chennai, India. The polydimethylsiloxane (PDMS) membrane is hydrophobic dense top layer material with an average thickness of 0.3 m. Performance of the dense composite PDMS membranes manufactured by technic membrane system, Chennai, India. A schematic of the membrane bioreactor set-up is shown in Figure. 1. The flat configuration is preferred for its ability to clean the reactor and to incorporate different membranes. The reactor was made of acrylic sheet. Membrane sheets were kept between two identical compartments with each a volume of 8 cm^3. The effective membrane area was 40 cm^2. The packing density, defined as the membrane surface area per unit reactor volume, was 250 m^2/m^3. The specific gas-liquid contact surface area was 500 m^2/m^3. The design of the identical acyrilic halves with their dimensions is drawn in Figure 1. There were four channels with width w = 5 mm, height h = 2 mm and length l = 200 mm. The hydraulic diameter, dh = 2.w.h/(w+h), of the channels was 2.86 mm. The circulation of nutrient was continuously introduced opposite to the gas flow through the one membrane side. The nutrient flow rate was adjusted to 25 cm^3 min^{-1} by a peristaltic pump (Miclins, India). The essential nutrients were incorporated using a pH buffered nutrient solution [7]

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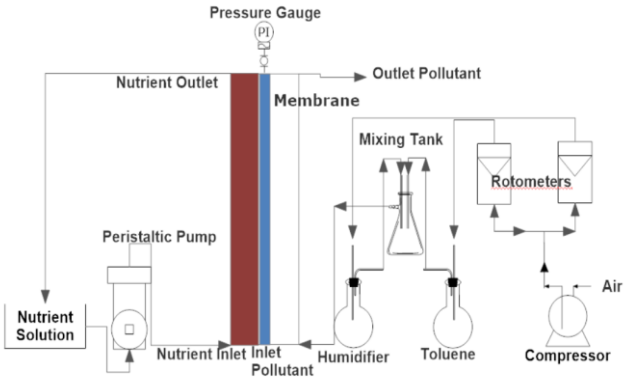


Fig 1. *Schematic of the membrane bioreactor set-up.*

2.3 Innoculum and experiments

The membrane bioreactor was inoculated with a mixed microbial culture obtained from paper industry waste water treatment plant, sivakasi, Tamilnadu, India. Inoculation of the membrane bioreactor was performed by recirculating 250 mL of the inoculum along the dense side of the membrane during 48–72 h. The performance of the membrane bioreactor for the 200 days of operation is shown in table 1. A air compressors supplied the airflow. A small stream of air was bubbled through the vessel containing pure toluene solvent, and was then combined with a larger air stream in the mixing chamber. This resulted in a synthetic gas with a concentration of toluene between 0.2 and 1.2 gm^{-3}. The desired concentration of toluene in the influent air stream was obtained by varying the two air flowrates. To determine the toluene concentrations in the untreated and treated stream, respectively. The experiment was performed in a laboratory, with temperature changes from 23 to 32˚C. The pH and relative humidity (RH) in the biofiltration column were measured regularly to ensure they stayed at optimal range. Pressure, and feed flow rates of permeate and residual streams were recorded. The performance was detected by measuring the concentrations of experimental compounds in the inlet and outlet gases, in addition to the pH and RH in the biofiltration column. Toluene and carbondioxide concentrations in the air stream were measured using a VOC and IR detector respectively.

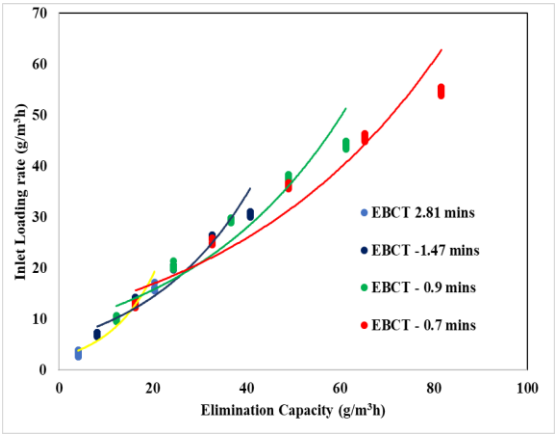
TABLE 1.
SHOWS THE EXPERIMENTAL PLAN

Stages	Days of operation	Gas flow rate	Inlet Toluene Concentration
I	1- 10	0.03	0.2
	11-20		0.2
	21-30		04
	31-40		0.6
	41-50		0.8
	51-60		1.0
II	61-70	0.06	0.2
	71-80		04
	81-90		0.6
	91-100		0.8
	101-110		1.0
III	111- 120	0.09	0.2
	121-130		04
	131- 140		0.6
	141-150		0.8
	151-160		1.0
	161-170		0.2
	171-180		04
IV	181-190	0.12	0.6
	191-200		0.8
	201-210		1.0

3. RESULT AND DISCUSSION

3.1 Startup performance of the membrane bioreactor

Membrane bioreactor was operated for 10 days as startup period to increase the cell holdup in to the reactor. Figure. 2 a shows the variations of the inlet concentration, outlet concentration and removal efficiency of the membrane bioreactor during the startup period at a low gas flow rate of 0.03 $m^{-3}h^{-1}$ corresponds to EBRT of 2.81 min with a inlet toluene concentration range from 0.2 to 1.2 g m^{-3}. Initially removal efficiency reached to 18% on the first day, and then considerably increased to stabilize between 78-83%. After 10 days of startup stable operation was attained with high removal efficiency of 80% and surface of the membrane are found filled with microorganisms which are confirmed from the light colored biomass observed on the surface of the membrane. This makes the microbial growth on porous surface of the membrane and also enhances toluene removal. The result of start up indicated that the membrane bioreactor could be quickly acclimatized by inoculating mixed culture and it could well utilize the toluene as its sole carbon and energy sour ce.



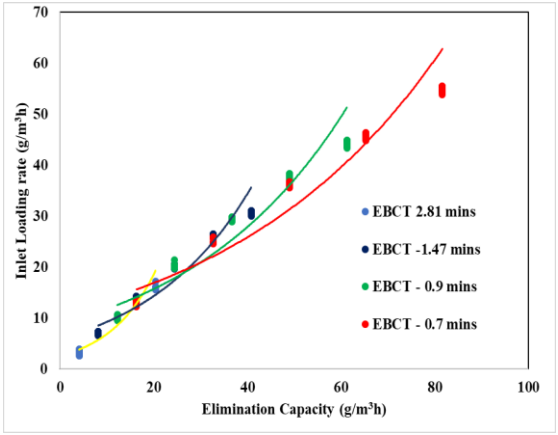


Fig. 2. *Effect of removal efficiency toluene by varying different inlet concentration and different EBRTs.*

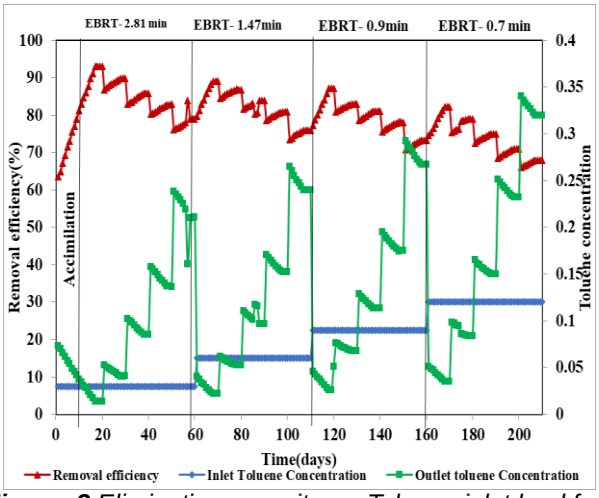


Figure. 3 *Elimination capacity vs. Toluene inlet load for various gas flow rates*

3.2 Performance Evaluation of the Toluene Membrane Bioreactor in Continuous Operation

After the startup experiment, the membrane bioreactor was operated continuously at 4 phases with different loadings rate for 200 days. Each phase was divided in to 5 stages. Figure 2 shows the performance evaluation of toluene membrane bioreactor during various phases and stages of operation in term of removal efficiency. In phase I operation, the membrane bioreactor was operated for 50 days at a concentration range of 0.2 to 1.2 g m^{-3} (EBRT = 2.81 min). In phase 1, stage 1 the Removal efficiency of membrane bioreactor was steadily increasing and reached a new steady-state value of 92% at a inlet concentration of 0.2 g m^{-3} . In stage 2, the removal efficiency of toluene decreased to 88 % at the inlet concentration of toluene increased to 0.2 to 0.6 g m^{-3}. In the stage 3,the removal efficiency of toluene decreased to 84 % at an inlet toluene concentration of 0.8 g $m^{-3.}$ In the stage 4, the removal efficiency of toluene decreased to 80 % at an inlet toluene concentration of 1.0 g m^{-3}. In the stage 5, the removal efficiency of toluene decreased to 76 % at an inlet toluene concentration of 1.2 g m^{-3}. In phase II operations, the inlet concentration range of 0.2 to 1.2 g m^{-3} with EBRT 1.47 min. In phase II operation, the membrane bioreactor was operated for 30 days at a concentration range of 0.2 to 1.2 g m^{-3} (EBRT = 1.47 min). In phase 1I, stage 1 the Removal efficiency of membrane bioreactor was steadily increasing and reached a new steady-state value of 90% at a inlet concentration of 0.2 g m^{-3} . In stage 2, the removal efficiency of toluene decreased to 90 % at the inlet concentration of toluene increased to 0.2 to 0.6 g m^{-3}. In the stage 3,the removal efficiency of toluene decreased to 88 % at an inlet toluene concentration of 1.2 g $m^{-3.}$ In the stage 3,the removal efficiency of toluene decreased to 84 % at an inlet toluene concentration of 0.8 g $m^{-3.}$ In the stage 4, the removal efficiency of toluene decreased to 80 % at an inlet toluene concentration of 1.0 g m^{-3}. In the stage 5, the removal efficiency of toluene decreased to 76 % at an inlet toluene concentration of 1.2 g m^{-3}. In phase III operations, the inlet concentration range of 0.2 to 1.2 g m^{-3} with EBRT 0.9 min. In phase III operation, the membrane bioreactor was operated for 30 days at a concentration range of 0.2 to 1.2 g m^{-3} (EBRT = 0.9 min). In phase I1I, stage 1 the Removal efficiency of membrane bioreactor was steadily increasing and reached a new steady-state value of 87% at a inlet concentration of 0.2 g m^{-3} . In stage 2, the removal efficiency of toluene decreased to 86 % at the inlet concentration of toluene increased to 0.2 to 0.6 g m^{-3}. In the stage 3,the removal efficiency of toluene decreased to 80 % at an inlet toluene concentration of 1.2 g $m^{-3.}$ In phase IV operations, the inlet concentration range of 0.2 to 1.2 g m^{-3} with EBRT 0.9 min. In phase IV operation, the membrane bioreactor was operated for 30 days at a concentration range of 0.2 to 1.2 g m^{-3} (EBRT = 0.7 min). In phase I1I, stage 1 the Removal efficiency of membrane bioreactor was steadily increasing and reached a new steady-state value of 85% at a inlet concentration of 0.2 g m^{-3} . In stage 2, the removal efficiency of toluene decreased to 82 % at the inlet concentration of toluene increased to 0.2 to 0.6 g m^{-3}. In the stage 3,the removal efficiency of toluene decreased to 78 % at an inlet toluene concentration of 1.2 g $m^{-3.}$ In the stage 3,the removal efficiency of toluene decreased to 84 % at an inlet toluene concentration of 0.8 g $m^{-3.}$ In the stage 4, the removal efficiency of toluene decreased to 80 % at an inlet toluene concentration of 1.0 g m^{-3}. In the stage 5, the removal efficiency of toluene decreased to 76 % at an inlet toluene concentration of 1.2 g m^{-3}. High removal efficiency of toluene of about 92% was obtained during I phase at stage 1 operations. In stage 2, increase in toluene concentration from 0.2 to 0.4 g m^{-3} the removal efficiency not only significantly dropped but also appeared obvious fluctuations. Similar results was obtained for the stage 2 and stage 4 at the phase 1.

In phase II, the gas flow rate was increased to 0.03 to 0.06 m^3h^{-1}. The removal efficiency was dropped to 81% and then gradually increased with the increase in time and attained a steady-state value by day 37. Similar results was obtained for the increasing the gas flow rate. The drastic change was possibly ascribed to part of gas channeling caused by great gas flow. The result suggested that the optimum EBRT and inlet toluene concentration should be 2.81 min and 0.2g m^{-3}, respectively in actual application of membrane bioreactor. Figure 2b. presents the effect of inlet loading rate on elimination capacity and removal efficiency in the toluene membrane bioreactor. The elimination capacity was linearly increased with the increase of toluene inlet loadings below 59 $gm^{-3}h^{-1}$ and maintained the removal efficiency nearly 90%, which indicated that the reaction was a gaseous diffusion-controlled first order process. When inlet toluene loading rate exceeded 59 $gm^{-3}h^{-1}$, the elimination capacity and removal efficiency was changed to non-linearly and presented a slow decrease with the increase of inlet loading rate up to 67 $gm^{-3}h^{-1}$. The maximum elimination capacity and removal efficiency for toluene in the whole operation was 43 $gm^{-3}h^{-1}$ and 90 % observed at an inlet load of 59 $gm^{-3}h^{-1}$. The increase in pollutant concentration did not affect the reactor performance immediately.

3.3 Factors on Gas Membrane Separation

The performance of toluene separation in the membrane bioreactor was monitored by varying inlet toluene concentration in the feed stream (C_f) and differences in pressure between the feed and permeate sides (P_d). The concentration of toluene varied from 0.2 to 0.6 g m^{-3}. The feed gas flow (Q_f), P_d and temperature were 0.06 m^3 h^{-1}, 5.0 kPa and 31˚C, respectively. As shown Figure 3 C_r was maintained

below 0.2 g m^{-3}, when C_f was less than 0.4 g m^{-3}. The removal efficiency of the membrane bioreactor reached over 75%. Then, Cr increased dramatically with the increase in C_f. When C_f was over 0.6g m^{-3}, Cr exceeded 0.2 g m^{-3}, and RE was reduced to 55%. This is probably because of the toluene penetrability through the PDMS membrane. In this study, with the increasing of C_f, constant increase of the toluene concentration in permeated stream (C_p) could be observed under the same experiment condition. Similar results were obtained by many research [8-11]. The gas permeability through a membrane is determined by solubility and diffusivity of the gas. High sorption uptakes of toluene will occur on organophilic polymers, such as PDMS, which resulted in membranes swelling. The enlarged interstitial spaces between polymer chains in the membrane due to membrane swelling not only favor the diffusion but also allow high solubility for toluene on membranes. Thus, an increase toluene concentration in the feed stream will enhance the toluene permeability through the membrane.

3.4 Microbial Aspects

A day 10^{th}, the counts of fungi and bacteria present in the membrane surface is about 1.0×10^8 CFU g^{-1} and 0.9×10^8 CFU g^{-1}. The toluene degrading microbes increased by to an average count of 6×10^9CFU g^{-1} at day 100 of operation and then further increased to 8×10^8 CFU g^{-1} at day 200. The maximum count of 9.1×10^8 CFU g^{-1} and 9.8×10^8 CFU g^{-1} at day 210 for fungal and bacteria respectively. These values are higher than those reported for xylene degradation in the biofilters packed with pressmud [12] and Sugarcane bagasse based biofilter [13].

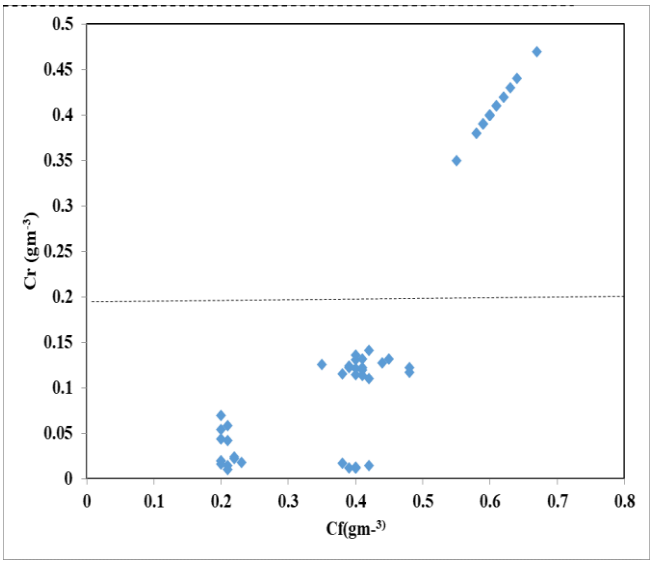


Fig 4*.Influence of toluene concentration in feed stream, Cr, concentrations of toluene in retentate stream*

3.5 Microbial Isolation and Identification

Numerous colony were obtained after sub culturing, from these colonies we selected two major colony for isolation of strain. These two colonies were further isolate and stored at 4^OC for this study. Several testes were studied for these tow isolated strain like biochemical tests including gram staining were performed. The results were showed in the table. From these results are consistent with the different phenotypic characteristic properties of Pseudomonas and Bacillus species. To further characterize the isolated organism, several biochemical tests including gram staining were performed. The results showed that the isolated organism is a rod shaped bacteria with gram-negative character (data not shown). In addition, the organism was found to be oxidase, catalase and lipase positive but negative in indole and hydrogen sulphide production and urease test (Table 2). All these results are To further characterize the isolated organism, several biochemical tests including gram staining were performed. The results showed that the isolated organism is a rod shaped bacteria with gram-negative character (data not shown). In addition, the organism was found to be oxidase, catalase and lipase positive but negative in indole and hydrogen sulphide production and urease test (Table 2).

3.6 Microscopic View

Figure 5 a shows the SEM image of before an after completion of membrane which exposed that very porous and raw exterior with big openings, which allowed the microbial attachment. In addition, a sample was taken at the end of operating period and analyzed using SEM. A dense biofilm covered the surface of the membrane and prolonged to the pores (Figure 5 b). While the morphology is difficult to be observed, some coccoid and rod shaped bacteria embedded in a matrix. Although such dense biofilm limits the diffusion of pollutants toward the inner particles, it may improve the resistance of microorganisms against high concentrations of toluene. Similar observation was seen in the biofiltration of xylene using tree bark as a packing material [13]

TABLE 2.
BIOLOGICAL CHARACTERISTICS OF ISOLATED STRAINS

Characteristics	Isolated -I	Isolated -II
	Morphology	
Cell type (Shape)	Rod	Slender, rod shape
Colour	Yellowish White	Greyish white
Size	0.4 -0.5 X 1.55 -2.7 µm	1.5–3 mm × 0.5 mm
Arrangement	Isolated	singly or in pairs
Surface	Smooth	Smooth
Density	Opaque	Translucent – Opaque
Motility	Positive	Positive
	Biochemical Test	
Gram,s reaction	+	-
Catalase Test	+	+
Spore	+ central	-
Indole Production	-	-
Starch hydrolysis	+	+
Citrate utilization	+	-
Methyl red	+	+
Vogas – Proskauer	+	-
Citrate	-	-
H2S Production	-	+
Urease	+	+
	Sugar Fermentation	
Glucose	+	+
Fructose	+	+
Maltose	-	+

Lactose	-	-
Sucrose	-	+
Mannitol	+	+
Xylose	-	-
Probable Strain	B. sphaericus	Pseudomonas alcaligenes

3.7 Performance under transient conditions

Transient toluene loading experiment was conducted to understand the dynamics of pollutant removal performance in the membrane bioreactor. Experiments results for shutdown and fluctuating loading conditions are shown in figure 6. The membrane bioreactor subjected to a 30 days for shutdown period by stopping the toluene inlet flow to the filter bed. Clean air flow of 0.5 L / mim with no toluene supplied to membrane bioreactor and moisture content was maintained by nutrient medium from the one side. After operated for 30 days of starvation and then it restarted which initial loading condition. It was found within seventh day the reactor was able to recuperate well and recover from the starvation phase during restart. The removal efficiency was restored to 72% at the inlet loading of 43 g $m^{-3}h^{-1}$ and the corresponding elimination capacity is 36 g $m^{-3}h^{-1}$. Ganesan et al. 2019 studied the effect of xylene shock loading in biofilter, reveals that there was no inhibition zone around the reactor when raised the toluene concentration and is normally encountered in industry. Biomass in membrane bioreactor could maintain saprophytic activity with the products of dead cellular, co-products of toluene degradation and the exopolysaccharide of biofilm, but not multiply during starvation period. Thus, the rapid re-adaptation of the compost biofilter could be contributed to the activity retaining of its biomass. This could produce numerous physiological changes within the microbial cell body and makes to recovering activity of microorganisms(1) . Membrane bioreactor was subjected to minor shock loads on 52 day of run by increasing the inlet toluene concentration to 1.2 g m^{-3} after recovering steady state removal efficiency pattern. This shock loading not much affected the removal profile and is maintained the steady state very shortly around 68-70%. An experimental observation from this study shows that toluene The membrane bioreactor has a good capacity to tolerate shutdown and shock loading conditions.

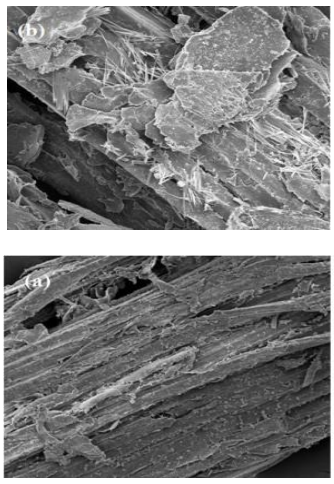


Fig.5*. Scanning electron micrograph of the filter media (a) before and (b) after experimentation*

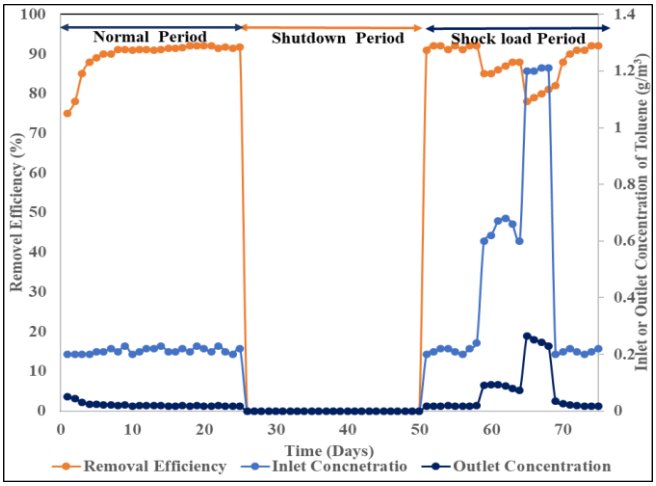


Fig 6 *Removal efficiency of the biofilter during transient operating conditions*

4 CONCLUSIONS

The results presented in this study illustrated the effective treatment by a lab-scale membrane bioreactor of waste gas polluted with toluene. A maximum removal efficiency and elimination capacity of 96% and 93 g/m^3h was observed when the system was operated at an EBRT of 2.81 min. At an EBRT as low as 0.9 min and inlet concentration of high as 1.0 g/m^3, waste gas contaminated with toluene can be successfully treated. Bacillus sphaericus and Pseudomonas alcaligenes isolate identified found to be active and potent microorganism for biodegradation of toluene .

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