International Journal of Advance Research in Science and Engineering
Volume No.07, Special Issue No. (02), January 2018
www.ijarse.com
IJARSE
ISSN: 2319-8354

CONCEPTUAL DESIGN OF A BIOFILTRATION SYSTEM FOR TREATING VOC GENERATED IN REFINERY ETP

Srikumar Malakar[1], Papita Das Saha[2], Ravi Rajamanickam[3]

[1] *Environment, Water & Safety Division, Engineers India Limited, Gurgaon, (India)*

[2] *Department of Chemical Engineering, Jadavpur University, Kolkata, (India)*

[3] *Department of Chemical Engineering, Annamalai University, Chidambaram, (India)*

ABSTRACT

A conceptualised biofiltration system has been designed for treating organic and inorganic volatile compounds generated from refinery wastewater. The biofiltration system is consisting VOC collection and treatment sub-systems. Air emission rate of fourteen volatile organic compounds and two inorganic volatile compounds (NH_3 & H_2S) have been estimated by WATER9 software. VOC collection sub-system is consisted systematic volatile vapor collection from each ETP unit, mixing with air for dilution, transfer to biofiltration section. The hybrid biofiltration system are consisting of two numbers biofilters having 50% treatment capacity (flow rate: 6800 $Nm^3\ h^{-1}$ and volatile concentration: 33.5 kg h^{-1}). Inlet loading rate (ILR) and inlet concentration of contaminant for biofiltration are kept as 300 g $m^{-3}\ h^{-1}$ and 5 g m^{-3} respectively. Automatic control of overall system and vital parameters has been considered. In our previous experiment VOC (toluene) removal of 77-97% and 89%(average) was achieved. In this present study removal efficiency (RE) of 90% (minimum) is envisaged on continuous basis.

Keywords : Refinery, ETP, WATER9, VOC collection, Biofilter design.

I. INTRODUCTION

Treatment of off-gas containing volatile organics generated from refinery wastewater in Effluent Treatment Plant (ETP) is necessary to meet statutory norm and environmental requirement. For a typical refinery ETP, the VOC removal system consisted of VOC collection system and VOC treatment system. In addition to the VOCs, inorganics like NH_3, H_2S, mercaptans, amines are also constituents of off-gas generated in ETP. Removal of VOCs through granular activated carbon bed is popularly used in refinery across India. In this paper, a conceptualized design has been presented for VOC collection and treatment by biofiltration method. Though biofiltration was first came into picture many decades ago in Europe and numerous plants based on biofiltration are in operation in Europe, US, Japan, it is still a new area in India. Most of the biofilters are installed for treating off-gases for sewage water treatments plants, composting plants, livestock/ poultry industries. Most biofilters constructed till date are open, huge and using mostly compost as media. In open compost based biofilter, inlet loading rate and inlet contaminant concentration are less which result in requirement of high surface area and less process control. However, since 1990s, many researchers have carried out thorough research on biofiltration and presented scientific data on its efficiency, elimination capacity with different volatile components and conditions. The same helped further in development of closed and more efficient biofilters. The main benefit of biofiltration over the other VOC abatement processes is that it is environmentally safe and cost effective. Presently, there are many companies and institutes which are designing tailor made biofiltration systems for a particular application. However, the operating data and design parameters used for industrial biofilter design particularly in Refinery sector are not available for reference. Abatement of VOCs in refinery ETP is a comparatively new guideline, which require for 90% of volatiles and odor removal [1].

II. CONCEPTUALIZED VOC TREATMENT SYSTEM

The conceptualized VOC treatment system presented in this paper is designed based on the following pathways: (1) Estimation of volatiles, (2) Design of VOC collection system, (3) Removal of off-gas by biofiltration, (4) Venting of treated gas to atmosphere.

2.1 Estimation of volatiles

Before treatment of VOCs, identification of volatile compounds and their quantification is necessary. There are hundreds of components that can be constituent of refinery wastewater and volatilized. Some inorganic compounds like NH_3, H_2S, mercaptans, amines are also found in the wastewater. Among the numerous components, the following twelve numbers volatile organic components are very common in refinery wastewater: Benzene, Biphenyl, 1,3-Butadiene, Cresols, Cumene (Iso Propyle Benzene), Ethylbenzene, n-Hexane, Methyl tertiary-butyl ether, Naphthalene, Phenol, Styrene (Ethenylbenzene), Toluene, 2,2,4-Trimethylpentane, Xylene [2][3]. Among the inorganics NH_3, H_2S are mostly volatilized and need to treated along with the VOCs. Now for quantification of volatiles generated in Refinery ETP, there are 3 approaches: (1) Directly measure volatile concentration in ETP, (2) Measure volatile component concentration in wastewater and then estimate concentration in air, (3) Assume volatile compound concentration in wastewater and then estimate volatile concentration in air. For an operational ETP, the measurement of concentration in wastewater or air can be done, but for designing a new grassroot ETP, the wastewater component can only be assumed based on previous refinery data or literatures. Concentration of volatile compounds are estimated by WATER9 software developed by USEPA among other softwares and is very popularly used to estimate volatile emission rate [3][4]. In this paper, approach no. (3) has been adopted for quantification of VOCs and inorganics (NH_3, H_2S) which is a general approach for designing a new plant. It may be noted that, due to the different configuration of refinery process units both in terms of feed and product configurations worldwide, the wastewater produced are different and so are the constituent volatiles. The oily wastewater collection and routing system of system in refinery also plays a vital role on quantity of VOCs as many volatiles can be lost to atmosphere due to leakage or open collection system. In our previous study, we estimated VOC concentration for a 12 MMTPA refinery [3]. In present study, we have freshly estimated emission rate of NH_3 and H_2S. A flow diagram of a typical ETP emitting VOCs which is output of WATER9 software is shown in Fig. 1. The total air emission of the volatiles (including organics and non-organics) estimated as 67.1 kg h^{-1} using WATER9 software. The following assumptions have been made: (1) no volatiles loss during collection and routing to ETP and (2) no VOC emission from biological section (after oil removal section) of ETP. Concentration of individual volatile components in air has been shown in Table 1. While the concentration of organic volatiles has been taken from established literatures, the wastewater concentrations of NH_3 and H_2S which are most prevalent inorganic volatiles have been assumed.

Table 1: Emission rate of individual volatiles for a typical refinery ETP

Organic Volatile ➡	Benzene	Biphenyl	1,3-Butadiene	Cresols	Cumene	Ethylbenzene	n-Hexane	MTBE	Naphthalene	Phenol	Styrene	Toluene	2,2,4-Trimethylpentane	Xylene		
Inorganic Volatile ➡															NH_3	H_2S
Inlet Conc. in wastewater (ppmw) ➡	16.70	0.57	0.01	4.18	6.18	14.70	58.45	9.69	4.84	3.01	9.69	55.11	32.90	60.12	20	20
Emission Rate ($kg\ h^{-1}$) ➡	5.15	0	0	0	0.58	2.21	20.38	0.15	0.04	0.01	1.16	13.50	9.54	0.42	6.98	6.98
Total Emission Rate ($kg\ h^{-1}$)	67.11															

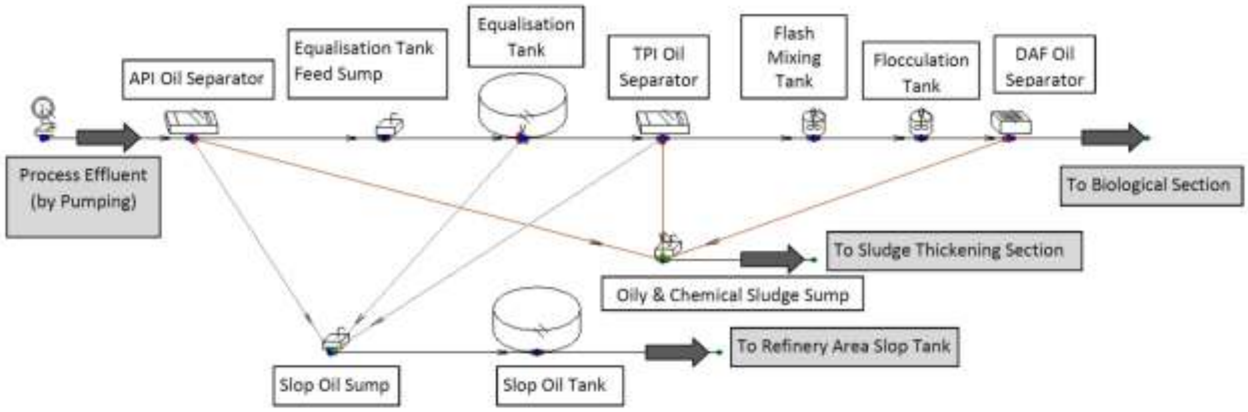

Fig. 1: Off-gas Emission block diagram [3]

2.2 Design of VOC collection system

For collection and routing of volatiles to the removal system, a well planned VOC collection network needs to be designed. Induced draft (ID) fans have been provided to transfer volatile vapors alongwith the dilution air to the biofiltration system. As the biofiltration system is effective for lower inlet volatile concentration, additional air dilution is needed. Total dilution air supplied is more than 13 times the amount of volatile vapor. Air dilution is also needed to keep VOC mixture below Lower Explosive Limit (LEL). The combined air flow rate was 13600 $Nm^3\ h^{-1}$ and due the higher volumetric flow rate the VOC treatment is envisaged in two parallel biofilters

 IJARSE
ISSN: 2319-8354

simultaneously. Exact sizes and length of VOC collection lines depends on the actual layout and placement of ETP units. VOC vapor generated are dependent on the wastewater flow rate, its concentration in liquid phase, temperature, pressure, vapor space in the units and vacuum pressure head of ID fans. A schematic diagram of VOC collection and treatment system is shown in Fig. 2. The following instrumentation is also envisaged: Flame arrestors on all individual collection lines from unit, one LEL detector on each header line, one number on the inlet line to biofilter, one number temperature indicator, hydrocarbon (HC) detector, flow meter on the inlet line of biofilters, pressure indicators on branch lines, header lines, fan discharge lines.

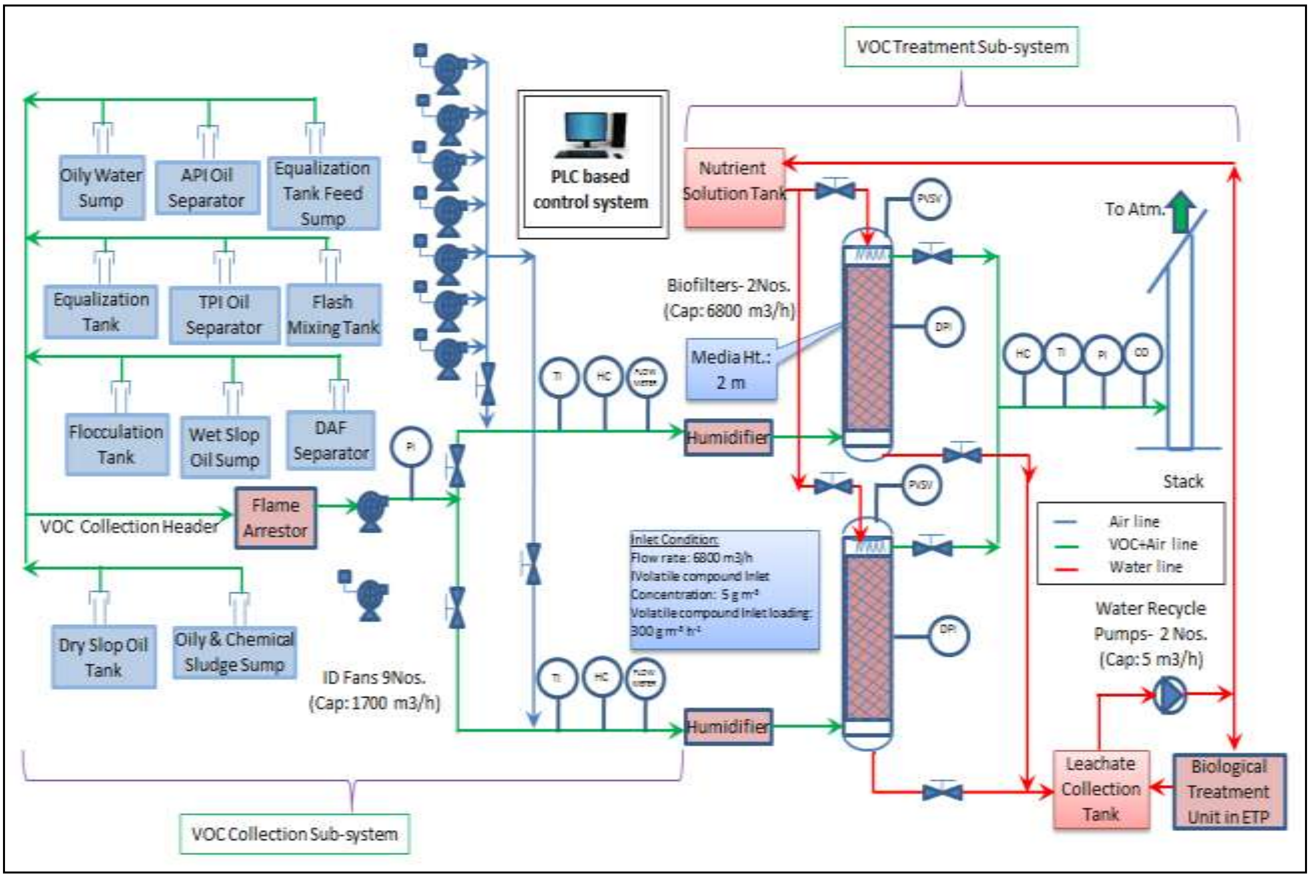

Fig. 2: VOC collection system and treatment through a hybrid biofiltration system

2.3 Removal of off-gas by Biofiltration

Biofiltration can remove VOCs and inorganic contaminants effectively. The removal efficiency in a biofilter generally more than 90% and up to 99% provided suitable conditions for microbial sustainability have been taken care of [5][6][7]. Selection of biofiltration process is necessary which is dependent on the property of contaminants and their concentration. Biofilter can also take load fluctuations and adapt itself to new environmental conditions. For effective biofiltration the compounds to be biofiltered should have some water solubility and can be biodegradable. The sixteen volatile components mentioned in Table 1 qualify these criteria. There are mainly 3 types of biofiltration methods: (1) Biofilter, (2) Biotrickling filter, (3) Bioscrubber. Detailed literature study and data have been provided in our earlier paper [5]. In this study we have designed a hybrid bioreactor combining the above three categories which involve: pre-humidification, periodically nutrient and water addition, vertical step-wise biodegradation, collection and routing of leachate to biological reactor in ETP. Before entering to biofilter, VOC stream has been humidified. Differential pressure indicator has been provided for each biofilter to measure the pressure head loss in the filter media. Nutrient solution dosing has been provided periodically for keeping bed humid and supplying nutrients. Nutrient solution dosing shall be provided based on N:P:K requirement of microorganisms. The leachate collected will be recycled back to nutrient dosing tank or sent to biological unit (activated sludge process) in ETP.

2.3.1 Design Parameters

The design parameters considered for designing the VOC collection system and biofiltration system for a typical refinery ETP having inlet wastewater flow rate of 350 m^3 h^{-1} is presented in Table 2. Design parameters of biofilters considered by other researchers have also been provided for comparison purpose.

Table 2: Design Parameters for VOC collection and biofiltration system

Design Parameter	Value Considered for Design (for each biofilter)	Literature Reference Value
Inlet Parameters		
Volumetric Flow rate, Q (Nm^3 h^{-1})	6800	10-300000 m3/h [8] <14000 cfm [9] <100000 scfm [10] 20000-100000 scfm [11]
Inlet Concentration of combined volatiles, C_{gi} (g m^{-3})	5	4 (Ethylbenzene); 4 (Xylene) [12] 0.2-1.7 [13] 3 (max.) (toluene) [14] 0.1-4.0 (toluene) [15]
Empty Bed Retention Time, EBRT (s) $EBRT = \frac{Q \ X \ 3600}{V_m}$	60	1.18-4.71 m [12] 1.13-2.81 m [16] 0.41-2.45 m [13] 0.7-2.9 m [14] 30-144 s [17] 30-120 s [18] 25-60 s [11]
Inlet Loading Rate, ILR (g $m^{-3}h^{-1}$) $ILR = \frac{Q \ X \ C_{gi}}{V_m}$	300	25-408 [12] 158 (benzene) [19] 151.1 (max.) [13] 289.8 (max.) [14] 8.1-1051.3 [17]
Volume of Media bed, V_m (m^3)	113.3	-

Type of Bed	Plastic structured packing	Polyurethane foam [16] Compost and Ceramic beads [20] Compost and PVC [18]
Height of Media bed, H_m (m)	2	100 cm [12] 0.5-1.5 m [11]
Temperature (deg. C)	Ambient	25.1-29.4 [12] 22-25 [21] 30 [19] 20-22 [22] 24-44 [16] 15-45 [11]
Operating Pressure, P (mm H_2O)	1000	Pressure drop: 2.7 cm H_2O/m [21] Pressure drop: 3.5-7 cm of H_2O/m of bed ht [23] 45.8-76.3 Pa [16]
pH	6.0-7.5	Neutral [22] 7.2-8.8 [16] 4.9-7 [17]
Inlet air mixture Relative Humidity, RH (%)	> 45	Moisture content of filter medium: 50-70% [22] 30->95% RH [17] 60-65% water content in bed [18] 90-100% RH [11]
Outlet Parameters		
Removal Efficiency, RE (%) $RE = \frac{C_{gi} - C_{go}}{C_{gi}} X\ 100$ Where, C_{go} is outlet concentration of combined volatiles, (g m^{-3}).	>90	89% (Ethylbenzene); 78% (Xylene) [12] 90% [21] 95% (avg.) (benzene) [19] 68.2-99.9% (toluene) [16] >90 [13] 96.1(max.) [14] >97 (max) [17] 96 [20] ~ 100 [18]
Elimination Capacity, EC (g $m^{-3}h^{-1}$)	>270	91.2 [23] 10.85-90.48 [16]

IJARSE
ISSN: 2319-8354

$EC = \frac{Q(C_{gi} - C_{go})}{V_m}$		2.6-687.8 [17]

2.4 Venting of treated gas to Atmosphere

The treated off-gas will be disposed off to atmosphere. Flame Ionization Detector (FID) based Hydrocarbon (HC) analyzer (or detector) are installed before discharging for continuous monitoring and to make sure 90% removal of VOCs and odor. Stack of adequate height shall be provided. The following instrumentation is also envisaged: one number temperature indicator, hydrocarbon (HC) detector, flow meter on the inlet line of biofilters, pressure indicators on outlet branch and main discharge lines.

III. ANALYSIS OF VOC TREATMENT SYSTEM

3.1 Safety Concerns

Any new plant is required to be safe both environmentally and operationally. In this system, adequate dilution has been provided for keeping volatiles concentration much below LEL of the most volatile component. Flame arresters have been provided adequately to arrest any spark/ flame in the upstream. Isolation valves shall be provided to isolate each and every individual units of this system. Suction side of ID fans i.e. the VOC collection and routing section is on negative pressure and the discharge side of ID fans i.e. biofilters and venting sections are on positive pressure. Hence one pressure vacuum safety valve will be installed on each of the biofilter. CO analyzer on biofilter outlet header line before discharging to atmosphere measures CO level in the treated air line. Adequate sampling ports shall be provided for measurement of gaseous components at inlet and outlet of biofilter. Measurement of collected samples shall be done by a Gas Chromatograph.

3.2 Operation of the System

The amount of VOC generation depends on the type of wastewater generated. Wastewater generation is not consistent due to some major intermittent effluent streams like draining of crude tanks, slop tanks. Hence the generation of VOCs and odors are not consistent. Hence, the biofiltration system needs to be designed to operate round the year and with turn-down capacity. For automatic control of the plant and data record, Programmable Logic Control (PLC) system has been considered. During operation & maintenance the following should be monitored: moisture content of the filter bed, volatile inlet and outlet concentration, off-gas temperature, pressure drop, humidity, inlet and outlet flowrate, checking if the inlet and outlet pipes of biofilters are clog-free.

3.3 Validation of Conceptualized System

There are numerous of biofilter plants installed worldover for treating a variety of organic and inorganic volatile vapor streams. Removal efficiencies for the most applications are 85%-95% for water soluble and biodegradable contaminants [11]. While designing the biofiltration system environmental parameters like temperature, humidity, nutrient needs to be optimized for adaptability of native microorganisms. Automatic control has been provided for better control of the vital parameters. The acclimatization period for microorganisms varies from weeks to months. In our recent study [20], the acclimatization period recorded as 20 days in a toluene biofilter.

The RE during that period was recorded as 73% (average) though not consistent. Most laboratory experiments on biofiltration are done with organic or indigenous material as media. However, for industrial application plastic media is most suited because it is long lasting and does not get compacted easily. While designing biofiltration, peak load has been considered for designing and total volatiles load has been distributed into two equal streams for treating in two biofilters of equal capacity (6800 $Nm^3 h^{-1}$). When the load is less then only one biofilter can be used or both can be alternately put in service. ILR and Inlet concentration considered in this system are on the higher side to meet desired RE. For EBRT of 60 s, media height has been considered as 2 m. We recorded VOC (toluene) removal of 77-97% and 89%(average) in our recent study over a continuous run period of 22 days. However, as the biofiltration is a live process and entirely depends on the microorganisms to degrade contaminants, getting removal efficiency of more than 90% on continuous basis can be tough.

3.4 Advantages and Draw Back of System

The advantages and drawbacks of biofiltration system over the activated carbon adsorption process are given in Table 3.

Table 3: Advantages and drawbacks of biofiltration system over the activated carbon adsorption process

Advantages of system	Drawbacks of system
a) Biofiltration directly biodegrade the hazardous volatile vapor and produce non-harmful products whereas in activated carbon process, during regeneration, the adsorbed VOCs again emitted to atmosphere. b) Replacement of media is not frequent. c) Cost for this system in long run can be lower than the activated carbon adsorption process. d) ILR of inlet VOCs can be increased when the inlet VOC concentration is less and hence less operating cost.	a) During start-up of the plant the efficiency of biofilter might be low because of the acclimatization time required by the microorganisms to sustain and adapt. b) For varying component or load biofilter might not give the required efficiency though it can adapt to changing scenario very quickly. c) It requires a larger foot print than the adsorption by activated carbon process because of larger ILR requirement.

3.5 Costing

Popularity and development of any new technology in industry very much depends on its economic viability. A preliminary cost analysis (capital cost and operating cost) has been carried out for this conceptualized biofiltration system (VOC collection and treatment) done for both this conceptualized biofiltration system. It is to be noted that the cost of system depends on its configuration, location and it may vary when different makes of items with same specifications are used. The capital cost and operating of this biofiltration system are estimated (± 30%) as INR 4408 per $Nm^3 h^{-1}$ and INR 300 per $Nm^3 h^{-1}$ respectively.

IV. CONCLUSION

The conceptual design for collection and treatment of multicomponent VOCs have been studied along with design parameters. Comparison of biofiltration with adsorption by activated carbon process has also been studied. Costing analysis has also been carried out to check the economic feasibility of the conceptualized system. Though biodegradation of liquid wastewater is very popular in India, biodegradation of air contaminant is not. As most Indian refineries are in moderate climate zones which arevery much suitable for microbial sustainability, biofiltration will be a success. Like activated carbon filters, there is no need of media replacement and no chance of VOCs going back to the atmosphere during regeneration of carbon bed. However, it may be noted that biofiltration system is not a plug and play operation. Before installation at the site proper study of VOC generation and constituents are needed and environmental parameters like humidity, temperature, nutrient dosing shall be carefully considered. Proper acclimatization preferably with native microorganisms is required. The ILR and inlet concentration of VOCs need to be optimized for minimizing foot print area. This new "green" technology in Indian refineries can change the popular usage of adsorption method of VOC removal. In biofiltration technology, there are always scopes for improvement and up-gradation. In addition of plastic media which has been considered in this study, a layer of activated carbon may be provided which could help absorb the VOCs during the initial start-up or acclimatization period and help for speedier acclimatization.

V. ACKNOWLEDGEMENTS

Authors would like to acknowledge utmost cooperation and support of all members of Environment, Water & Safety Division of Engineers India Limited, Chemical Engineering Department of Jadavpur University and Department of Chemical Engineering, Annamalai University throughout the study.

REFERENCES

[1] G.S.R 186 (E), Ministry of Environment and Forests Notification, New Delhi, 18 March, 2008, Standard for oil refinery industry.

[2] RTI International, 2011. Emission Estimation Protocol for Petroleum Refineries, Version 2.1.1, Final ICR Version –Corrected.

[3] S. Malakar, and P.D. Saha, Estimation of VOC Emission in Petroleum Refinery ETP and Comparative Analysis with Measured VOC Emission Rate, The International Journal of Engineering and Science, 4(10), 2015, 20-29.

[4] E. Fatehifar, D. Kahforoshan, L. Khazini, J. S. Soltanmohammadzadeh and H.R. Sattar, Estimation of VOC Emission from Wastewater Treatment Unit in a Petrochemical Plant Using Emission Factors, Proc. WSEAS Conf., Spain, September 2008.

[5] S. Malakar, P.D. Saha, D. Baskaran, R. Rajamanickam, Comparative study of biofiltration process for treatment of VOCs emission from petroleum refinery wastewater—A review, Environmental Technology & Innovation, 8, 2017, 441-461.

[6] G. Leson and A.M. Winer, Biofiltration: an innovative air pollution control technology for VOC emissions, Journal of the Air & Waste Management Association, 41(8), 1991, 1045-1054.

[7] A.F. Mohamad, T. Amirreza, P. Mohanadoss, M.Z. Abd Majid, H. Tony, G. Amin, Biofiltration process as an ideal approach to remove pollutants from polluted air, Desalination and Water Treatment 52(19-21), 2014, 3600–3615.

[8] R. Govind, Biofiltration: An innovative technology for the future, University of Cincinnati, 2009. http://www.prdtechinc.com/PDF/PRDBIOFILTERR%26DMAGAZINEPAPER.pdf.

[9] I.K. Faisal and K.G. Aloke, Removal of volatile organic compound from polluted air, Journal of loss prevention in the process industries, 13(6), 2000, 527–545.

[10] C.M. Edward, Reduce VOC and HAP Emissions, Chemical engineering progress, 98(6), 2002, 30–40.

[11] S.F. Adler. Biofiltration- a primer, Chemical engineering progress, 97(4), 2001, 33–41.

[12] R. Natarajan, J. Al-Sinani, S. Viswanathan and R. Manivasagan, Biodegradation of ethyl benzene and xylene contaminated air in an up flow mixed culture biofilter, International Biodeterioration & Biodegradation, 119, 2017, 309–315.

[13] E.R. Rene, D,V.S. Murthy and T. Swaminathan, Steady- and transient-state effects during the biological oxidation of gas-phase benzene in a continuously operated biofilter, Clean Technologies and Environmental Policy, 12(5), 2010, 525–35.

[14] X. Chen, W. Qian, L.J. Kong, Y. Xiong and S.H. Tian, Performance of a suspended biofilter as a new bioreactor for removal of toluene, Biochemical Engineering Journal, 98, 2015, 56-62.

[15] M. Zilli, A. Del Borghi and A. Converti, Toluene vapour removal in a laboratory–scale biofilter, Applied microbiology and biotechnology, 54(2), 2000, 248–254.

[16] R.S. Singh, B.N. Rai and S.N. Upadhyay, Removal of toluene vapour from air stream using a biofilter packed with polyurethane foam, Process Safety and Environmental Protection, 88(5), 2010, 366-371.

[17] E.R. Rene, B.T. Mohammad, M.C. Veiga and C .Kennes, Biodegradation of BTEX in a fungal biofilter: influence of operational parameters, effect of shock-loads and substrate stratification. Bioresource technology, 116, 2012, 204-213.

[18] D. Reza, R. Babak, A. Mahzar, F. Mohammad and A. Ahmad, Confirmation of monod model for biofiltration of styrene vapors from waste flue gas, Health promotion perspectives, 2(2), 2012, 236–243.

[19] C.T. Davidson and A.J. Daugulis, The treatment of gaseous benzene by two-phase partitioning bioreactors: a high performance alternative to the use of biofilters, Applied microbiology and biotechnology, 62(2-3), 2003, 297–301.

[20] S. Malakar, P.D. Saha, D. Baskaran and R. Rajamanickam, Microbial biofilter for toluene removal: Performance evaluation, transient operation and theoretical prediction of elimination capacity, Sustainable Environment Research, December 2017 (Article in press).

[21] S.M. Zamir, R. Halladj and B. Nasernejad, Removal of toluene vapors using a fungal biofilter under intermittent loading, Process safety and environmental protection, 89(1), 2011, 8–14.

[22] L. Sene, A. Converti, M.G.A. Felipe and M.Zilli, Sugarcane bagasse as alternative packing material for biofiltration of benzene polluted gaseous streams: a preliminary study, Bioresource technology, 83(2), 2002, 153–157.

[23] E.R. Rene, S. Kar, J. Krishnan, K. Pakshirajan, M.E. Lopez, D.V.S. Murthy and T. Swaminathan, Start-up, performance and optimization of a compost biofilter treating gas-phase mixture of benzene and toluene, Bioresource technology, 190, 2015, 529-535.