Journal of Engineering Science and Technology
Vol. 8, No. 5 (2013) 578 - 587

METHANOL REMOVAL FROM METHANOL-WATER MIXTURE USING MUNICIPAL ACTIVATED SLUDGE

SALAM AL-DAWERY

Department of Chemical Engineering, University of Nizwa, Birkat Al Mouz, Oman
*E-mail: salam@unizwa.edu.om

Abstract

Methanol plants produce large volume of wastewater containing less than 10% methanol during the startup and shut-down operations, such amount is considered as an industrial waste problem. An experimental work has been carried out in order to examine the removal of methanol from methanol-water mixture using activated sludge. The results showed that the methanol was totally consumed by the bacteria as quick as the feed enters the sludge vessel. The bacteria indicated adaption and growth during experiment with adaptation time of 1 hour. However, an inverse effect on bacterial growth has been observed, when the methanol concentration is higher than 5%.

Keywords: Activated sludge, Methanol removal.

1. Introduction

There are several processes related to the production and usage of methanol which are directly responsible for the release of methanol and act as source of pollutants for atmosphere, soil and groundwater. For example; discharge wastewater from methanol plants during startup and shutdown, chemical process converts wood chips to cellulose pulp and the released organic compounds to air and water, that are naturally present in wood or produced during pulping manufacturing [1].

In 1998, the US Environmental Protection Agency (US EPA) passed the ''Cluster Rule" to regulate the release of these compounds, including hazardous air pollutants (HAP), chemicals that pose great risk to human or environmental health (US EPA, 1998). Methanol is the primary focus of these regulations, as it is released in quantities of over 44,000 tons per year and represents over 70% of the total HAPs emitted by this industry (US EPA, 2004), and can contribute to human health impacts such as cancer, respiratory irritation, and damage to the nervous system [2].

To prevent potential environmental and health impacts from methanol emissions, the Cluster Rule requires implementation of maximum available

control technology to collect and treat high-volume, low-concentration (usually less than 20% of the lower explosion limit of the gas mixture, or less than 12,000 ppm methanol) emissions from pulp washing and screening, oxygen delignification, and weak black liquor storage tanks [3].

Methanol in drinking water supplies can be remedied effectively through biological treatment. The type of technology used depends on the anticipated influent concentrations. For influent methanol levels of 1 ppm, a slow sand filter provides the required microbial activity for successful treatment for drinking water. Higher influent levels (on the order of 100 - 1000 ppm) would require treatment in a biologically activated filter (BAF) with counter air flow. Design of a BAF for methanol treatment would require pilot studies to determine the optimum design capacity and appropriate operating conditions for the desired methanol removal efficiency. In 1997, the University of Colorado at Boulder completed a pilot project for removal of nitrate in a biological process that utilizes indigenous bacteria [4]. The pilot plant consists of towers containing layers of bacteria that reduce the nitrates to nitrogen.

Real methanol released near drinking water supply would have an impact on the quality of the water. While it is unlikely that elevated levels of methanol will persist in groundwater due to the rapid rate of biodegradation, methanol releases near drinking water supply wells could impact negatively on the water supply source. Unlike certain gasoline additives, the taste and odor threshold concentration for methanol is high, ranging from 10 ppm to 20,000 ppm in air [5].

There are several treatments for the removal of methanol from water. These are; air stripping, adsorption process, advanced oxidation, membrane filtration, or biologically activated filters [6 - 8].

Many investigators consider methanol as an additional carbon source for denitrification in wastewater treatment and studied the carbon degradation activity in activated sludge [2, 9, 10]. However, activated sludge is used widely for the removal of many organic compounds [11], but little is known about removal of methanol using municipal activated sludge. Therefore, the goal of this work was to investigate the removal of methanol from wastewater that produced from methanol plants during the startup and shut-down operations.

2. Methodology

2.1. Activated sludge process design

Sewage sludge is a solid, semisolid, or liquid muddy-like residue that results after plain old sewage (human and other waste from households and industries) is treated at a sewage plant. After being treated, the sewage sludge may be spread on non-organic agricultural land as a fertilizer or dust suppressant. The sewage sludge includes: scum or solids removed in primary, secondary, or advanced wastewater treatment processes; and a material derived from sewage sludge [12-15]. Primary sludge and material that settles out during primary treatment often have a strong odor which require treatment prior to disposal. Secondary sludge is the extra microorganisms from the biological treatment processes. The goals of sludge treatment are to stabilize the sludge and reduce odors, remove some of the water and reduce volume, decompose some of the organic matter and kill disease causing organisms and disinfect the sludge.

The overall goal of the activated-sludge process is to remove substances that have a demand for oxygen from the system. This is accomplished by the metabolic reactions (synthesis-respiration and nitrification) of the microorganisms, the separation and settling of activated-sludge solids to create an acceptable quality of secondary wastewater effluent, and the collection and recycling of microorganisms back into the system or removal of excess microorganisms from the system. The species of microorganism that dominates a system depend on environmental conditions, process design, the mode of plant operation, and the characteristics of the secondary influent wastewater. The following schematic diagram represents the general process of the activated sludge.

Most activated processes consist of aeration and settle tank as shown in Fig. 1. However, an alternative design has been considered and constructed. The new design consists of a porous pot in which the activated sludge can be held and only clean water leaks out, thus, no sludge circulation is required. This porous tank was considered as inner tank and placed in larger tank that holds and allowing only the leakage of clear water from the porous tank. A rigid support ring was placed between inner and outer vessels helps to leave space between them. Air distributor was used for mixing and oxygen supplying. Schematic diagram and experimental rig is shown in Fig. 2.

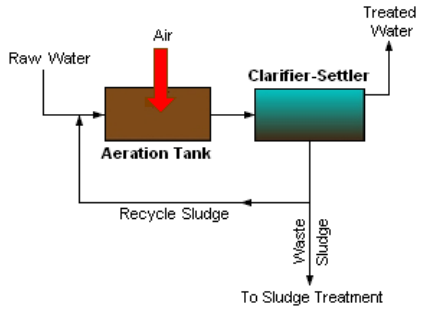

Fig. 1. A Generalized Schematic Diagram of an Activated Sludge Process.

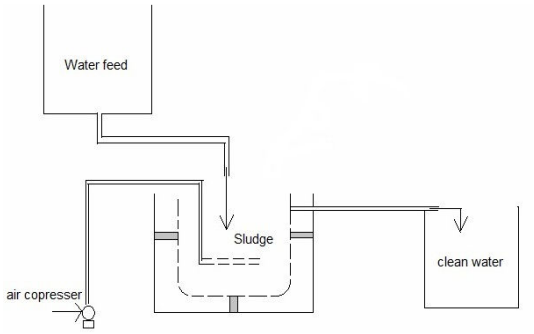

Fig. 2. Schematic Sludge Process Diagram using Porous Tank.

2.2. Materials

The samples of activated sludge and untreated wastewater were collected from wastewater treatment plant at Nizwa, Sultanate of Oman. The activated sludge was

collected from the recycling sludge container, while untreated wastewater samples were collected from feed stream to wastewater plant. In order to determine the type of bacteria present in the activated sludge, samples were analysed for colony forming unit (CFU) in the microbiology lab at University of Nizwa. The analysed samples showed that the bacillus positive bacteria type is present.

2.3. Experiment

Experiments have been performed in 6 L porous pottery vessel containing 280 g activated sludge. The porous pottery vessel is placed in 20 L plastic vessel for collecting the leakage liquid. Methanol solutions were prepared by adding the required amount of methanol to the untreated wastewater, two solutions were prepared; 5% v/v and 8% v/v. In order to have same flow rate in and out of the sludge vessel, 0.72 L/h methanol feed flow rate was chosen. Thus, the mean cell residence time maintained was 8.3 h. Air was purged at low flow rate through the sludge vessel. Samples were taken every one hour from sludge solution and effluents are analysed for both bacteria and methanol concentration.

2.4. Methanol estimation

The methanol is analyzed via the oxidation of methanol to formaldehyde with potassium permanganate, followed by condensation with 2,4-pentanedione to yield the colored product 3,5-diacetyl-1,4-dihydro-2,6-dimethylpyridine, this method proposed by Wood & Siddiqui [16]. The optical density is then measured using UV spectrophotometer.

3. Results and Discussion

3.1. Test using feed of methanol

During the experimental runs, two different feeds were used; one with 5% methanol and the second with 8% methanol. For each test, several samples were collected and analysed for methanol and bacteria contents and the results are shown in Fig. 3. This figure shows the remaining methanol concentration in effluent after its consumption by the bacteria during the experiment, it can be seen that the larger the amount of methanol the larger the amount is consumed. For purpose of comparison, the results are compared with methanol concentration in a mixing tank with model equation;

$$C/C_o = 1 - \exp\left[-(V/F)t\right]$$

where V is the tank volume, F is volumetric feed flow rate and t is time.

Results from the model equation and that from biological reactor are plotted in Fig. 4. The large differences between these two results indicate that the methanol concentration dropped quickly due to the consumption by the bacteria.

Bacterial growth was monitored during the experimental work within the biological reactor and the results are presented in Fig. 5. This figure shows that the bacteria are firstly adapt themselves to the new conditions within 1 hour and then start to grow up consuming more methanol. This period of adaption of the bacteria was almost the same in both experimental tests using feed solutions with 5% and 8% methanol.

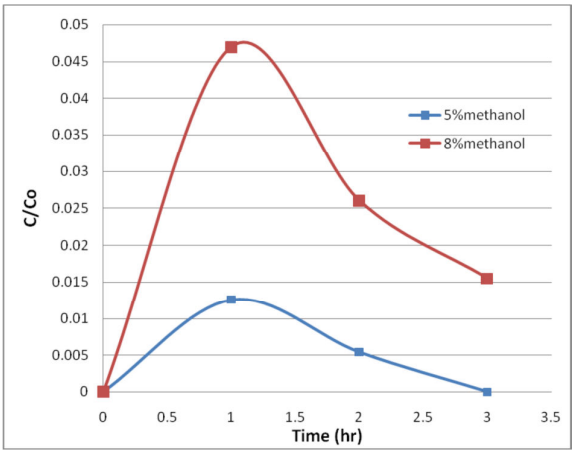

Fig. 3. Comparison between Methanol Removal in Sludge Vessel using 5% and 8% Methanol Feeds.

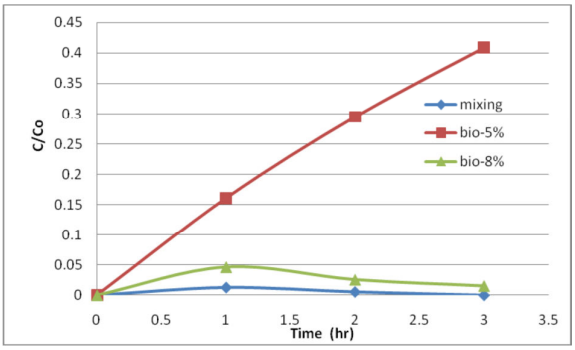

Fig. 4. Comparison between Methanol Concentration Response in a Mixing Tank and its Removal in Sludge Vessel using 5% and 8% Methanol Feeds.

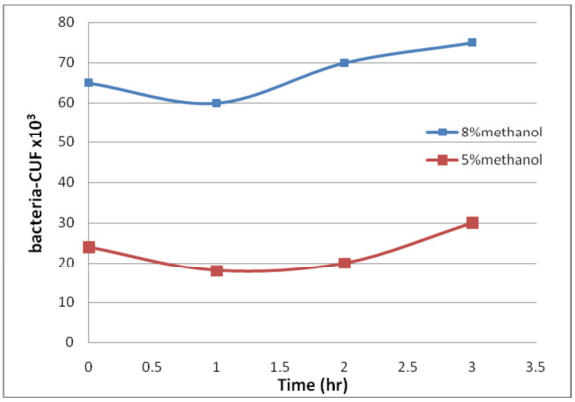

Fig. 5. Bacterial Growths during Experiments with 5% and 8% Methanol Feeds.

3.2. Bacterial contents during experimental works

The contents of bacteria that are living within the sludge and solution during the experiments have been analyzed and pictured as shown in Figs. 6 through 10. Figure 6 shows large bacterial contents within the freshly collected sludge material that was brought from conditioning tank at Nizwa wastewater plant. Figure 7 shows the bacterial growth in the diluted sludge solution which indicates bacteria are active at initial time before starting the experiment. Figs. 8, 9, and 10 show the bacterial growth in solution during experiment after 1, 2, and 3 hours.

Fig. 6. Bacterial Contents in Fresh Sludge Material.

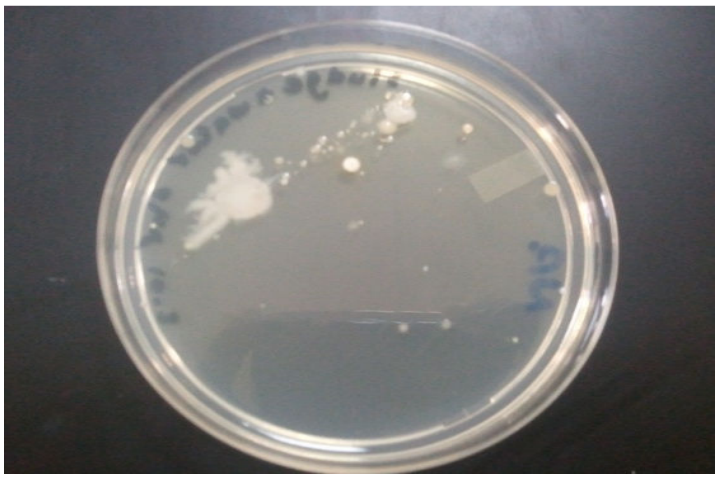

Fig. 7. Bacterial Contents in the Prepared Sludge Solution before Experiment.

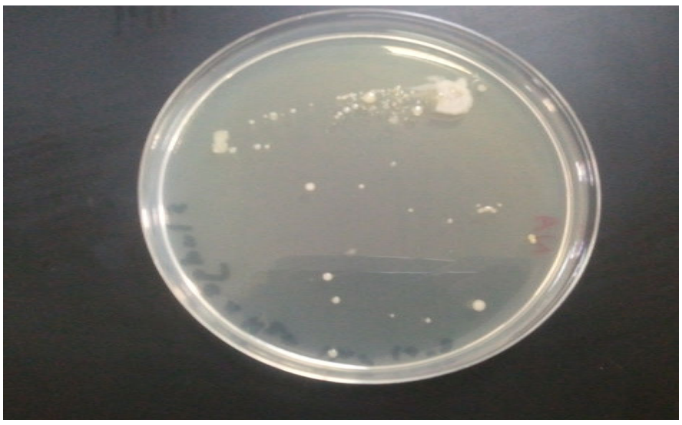

Fig. 8. Bacterial Contents in Sludge Solution after 1 hr Experiment.

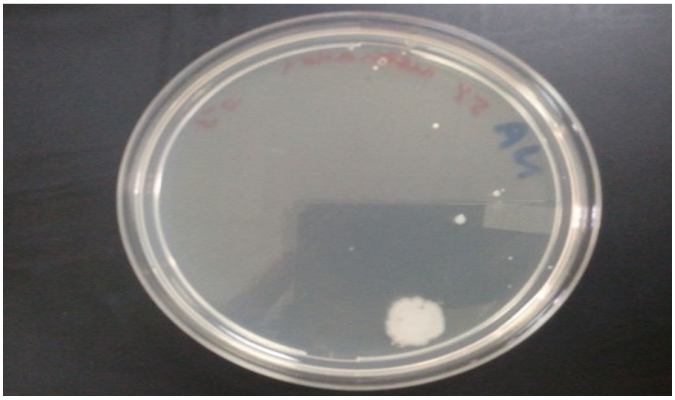

Fig. 9. Bacterial Contents in Sludge Solution after 2 hrs Experiment.

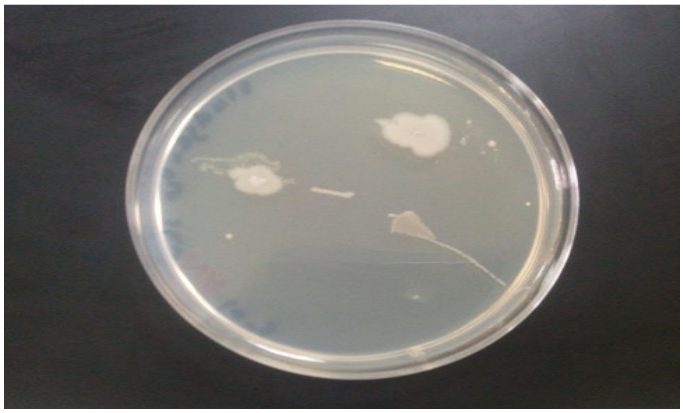

Fig. 10. Bacterial Contents in Sludge Solution after 3 hrs Experiment.

3.3. Effect of methanol concentration on bacterial growth

To study and examine the effect of methanol on bacterial growth, many samples were prepared by mixing different methanol concentration 1%, 3%, and 5% v/v with sludge solution, these samples were prepared and left 48 hours before the analysis steps. Then, samples were analyzed in the biological laboratory at University of Nizwa, picture of bacterial growth are shown in Figs. 11, 12 and 13. It appears in these figures that the increase of methanol concentration has a negative effect on the bacterial growth, as the methanol concentration increases the number of bacteria is reduced. The significant reduction of bacteria growth can be considered when concentration of methanol is large than 5%.

Batch experiments were also investigated using several samples of wastewater with different methanol contents; 1%, 3%, 5% and 8% v/v. samples were incubated at constant temperature for 24 hours before analysis for methanol. Results showed that the methanol content in these solutions has been consumed, as shown in Table 1. It can be seen that the consumption of methanol is reduced slightly in solution with a higher methanol concentration; this could be due to inhibition of bacterial growth under a higher methanol concentration.

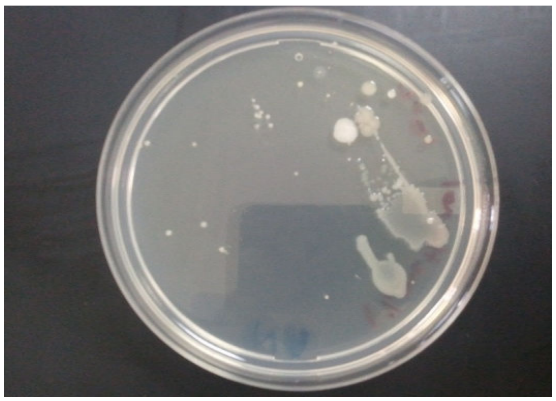

Fig. 11. Biological Growth in Sample with 1% Methanol after 48 hrs.

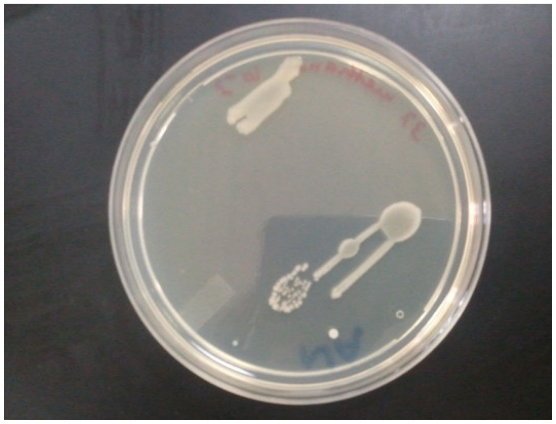

Fig. 12. Biological Growth in Sample with 3% Methanol after 48 hrs.

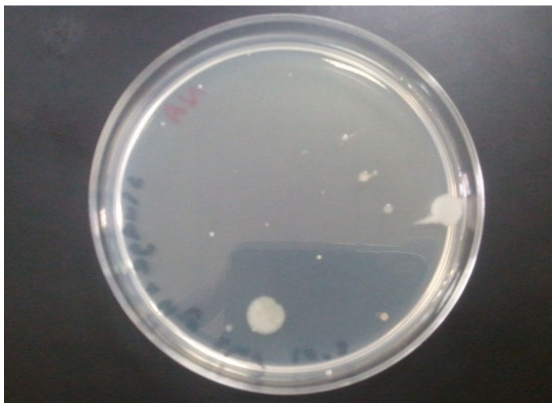

Fig. 13. Biological Growths in Sample with 5% Methanol after 48 hrs.

Table 1. Methanol Concentration in Wastewater after 24 hrs Time.

Sample	% methanol in influent	Temperature ℃	% methanol in wastewater
1	1	22	0.025
2	3	22	0.105
3	5	22	0.175
4	8	22	0.295

4. Conclusions

Following results of the experiments, it can be concluded that the methanol concentration dropped quickly as a result of its consumption by the bacteria immediately they enter into the sludge vessel. The bacteria within the sludge solution can be adapted wherever an organic methanol source. The bacterial adaptation can be true for methanol concentration up to 5% within the sludge solution. The reduction of bacterial growth can be considered due to the increase of methanol concentration especially of methanol greater than 5% within the sludge tank. This biological method proves its ability to remove methanol contaminant especially at low concentration.

References

1. Someshwar, A.; and Pinkerton, J. (1992). Wood processing industry. In: *Air pollution engineering manual: Air and waste management sssociation*. New York, Chapter 3, 835-849.
2. Babbitt, C.W.; Pacheco, A.; and Linder, A.L. (2009). Methanol removal efficiency and bacterial diversity of an activated carbon bio-filter. *Bioresource Technology*, 100(24), 6207-6216.
3. Varma, V.K. (2003). Experience with the collection, transport, and burning of kraft mill high volume low concentration gases. *Special Report No. 03-03*. National Council for Air and Stream Improvement.

4. Scott, J. CU-Boulder, (1997). *Colorado town wrapping up pilot drinking water treatment project.* http://www.eurekalert.org/pub_releases/1997-08/UoCa-CCTW-290897.php.
5. US Environmental Protection Agency. Office of pollution prevention and toxics (USEPA OPPT). (1994). Chemical summary for methanol. *Report No. EPA 749-F-94-013a*.
6. Malcolm Pirnie, Inc. (1999). Evaluation of the fate and transport of methanol in the environment. *Technical Memorandum*. American Methanol Institute, 800 Connecticut Avenue, NW, Suite 620, Washington DC 20006. Report number 3522-002.
7. Soltanali, S.; and Hagani, Z.S. (2008). Modeling of air stripping from volatile organic compounds in biological treatment process. *International Journal of Environmental Science and Technology*, 5(3), 353-360.
8. Mandal, S.; and Pangarkar V.G. (2003). Development of co-polymer membranes for pervaporative separation of methanol from methanol-benzene mixture- solubility parameter approach. *Separation and Purification Technology*, 30(2), 147-168.
9. Hagman, M.; Nielsen, J.L.; Nielsen, P.H.; and Jansena, J.C. (2008). Mixed carbon sources for nitrate reduction in activated sludge-identification of bacteria and process activity studies. *Water Research*, 42(6-7), 1539-1546.
10. Premkumar, R.; and krishnamohan, N. (2010). Removal of methanol from waste gas using biofilteration. *Journal of Applied Science Research*, 6(11), 1898-1907.
11. Falas, P.; Baillon-Dhumez, A.; Andersen, H.R.; Ledin, A.; and Jansen, J.C. (2012). Suspended biofilm carrier and activated sludge removal of acidic pharmaceuticals. *Water Research* 46(4), 1167-1175.
12. Junkins, R. (1983). *Activated sludge process: Fundamentals of operation*. Ann Arbor Science Publishers, Michigan.
13. Wanner, J. (1994). *Activated sludge bulking and foaming control*. 1st Ed., CRC Press.
14. Sorour, M.T.; Abd EL Rassoul, F.A.; and Ibrahim, B.A. (2001). Final settler performance as a bio-reactor in activated sludge process. *Proceedings of the Sixth International Water Technology Conference*, *IWTC 2001*, 378-387.
15. Dominguez, M.V.L. (2007). *Study of sludge conditioning processes*. Ph.D. Thesis, School of Chemical Engineering & Analytical Science, University of Manchester.
16. Wood, P.J.; and Siddiqui, I.R. (1971). Determination of methanol and its application to measurement of pectin ester content and pectin methyl esterase activity. *Analytical Biochemistry*, 39(2), 418-428.