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METHANOL REMOVAL FROM METHANOL-WATER MIXTURE USING ACTIVATED SLUDGE, AIR STRIPPING AND ADSORPTION PROCESS: COMPARATIVE STUDY

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Abstract

An experimental research has been carried out in order to examine the removal of methanol from methanol-water mixtures using three different methods; activated sludge; activated carbon and air stripping. The results showed that the methanol was totally consumed by the bacteria as quickly as the feed entered the activated sludge vessel. Air stripping process has a limited ability for removing of methanol due to strong intermolecular forces between methanol and water; however, the results showed that the percentage of methanol removed using air pressure at 0.5 bar was higher than that of using air pressure of 0.25 bar. Removal of methanol from the mixture with a methanol content of 5% using activated carbon was not successful due to the limited capacity of the of the activated carbon. Thus, the activated sludge process can be considered as the most suitable process for the treatment of methanol-water mixtures.

Keywords: Activated sludge; Air stripping; Activated Carbon; Methanol removal.

1. Introduction

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. In chemical process industries, the most important issues are chemical discharge reductions, especially, minimizing organic and inorganic compounds in waste water as well as their effect on the environment. Such issues have become competent tasks to many petrochemical plants. However, many waste water treatment plants have become incapable of handling

Nomenclatures

C	Methanol concentration in the tank, g/l
C_o	Methanol concentration in the feed, g/l
F	Volumetric feed flowrate, l/s
t	Time, s
V	Tank volume, l/s

Abbreviations

GAC	Granulated activated carbon
VOC	Volatile organic chemicals

the waste treatment due to the stringent regulations and criteria that are set by government and industrial sectors.

There are several processes related to the production and uses of methanol which are directly responsible for the release of methanol as a pollutant in soil and groundwater, for example, discharge wastewater from methanol plants during operation of 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].

To regulate the release chemical compounds including hazardous air pollutants that pose great risk to human and/or environment, US Environmental Protection Agency (US EPA) has passed what is called the ‘‘Cluster Rule” on 1998 [2]. Methanol is the primary point of these regulations as it is released 70% of the total quantities of 44,000 tons/year that is emitted by chemical industries [3]. Methanol as hazardous material can contribute to considerable human health concerns [4].

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 [5].

Real methanol released near a 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 released near drinking water supply wells could impact a 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 [6].

Methanol in drinking water supplies can be treated 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 should provide 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. The design of a BAF for methanol treatment would require pilot studies to determine the optimum design capacity and appropriate operating conditions for the desired efficiency of methanol removal [7].

There are several treatment method for the removal of methanol from water such air stripping, adsorption process, advanced oxidation, membrane filtration, or biologically activated filters [8-11]. Many investigators consider methanol as an additional carbon source for de-nitrification in wastewater treatment and studying the carbon degradation activity in activated sludge [4, 12, 13]. Activated sludge is used widely for the removal of many organic compounds [14-16]. However, little is known about removal of the industrial methanol waste. Therefore, the goal of this work is to investigate the removal of methanol from industrial wastewater at concentrations of less than 10% that are produced from methanol plants during startup and shut-down operations. Three methods have been chosen for this task; activated sludge, air striping and activated carbon. Comparisons have been made based on the efficiency of each process.

2. Methodology

Methanol 99.99% was purchased from Fisher Scientific, UK. The diluted methanol solutions for all tests were prepared using distilled water available in the University of Nizwa lab.

2.1. Analytical techniques

During all the experimental runs, methanol was 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 and Siddiqui [17]. The optical density is then measured using UV spectrophotometer.

2.2. Activated sludge process design

Sewage sludge is a solid, semisolid, or liquid muddy looking residue that results after sewage is treated at a sewage plant. The sewage sludge includes: scum or solids removed in primary, secondary, or advanced wastewater treatment processes and a material derived from sewage sludge [18-21].

The overall goal of the activated-sludge process is to remove substances that have a demand for oxygen from the system. This is accomplished using 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 schematic diagram of activated sludge is shown in Fig. 1.

Most activated processes consist of aeration and settling tanks as shown in Fig. 1, however, an alternative design has been considered and constructed. The new design consists of a porous tank 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 an inner tank and placed inside a larger tank that holds and allows only the leakage of clear water from the porous tank. A rigid support ring was placed between inner and outer vessels helps to leave a gap between them. An air distributor was used for mixing and supplying oxygen. A schematic diagram and experimental rig is shown in Fig. 2.

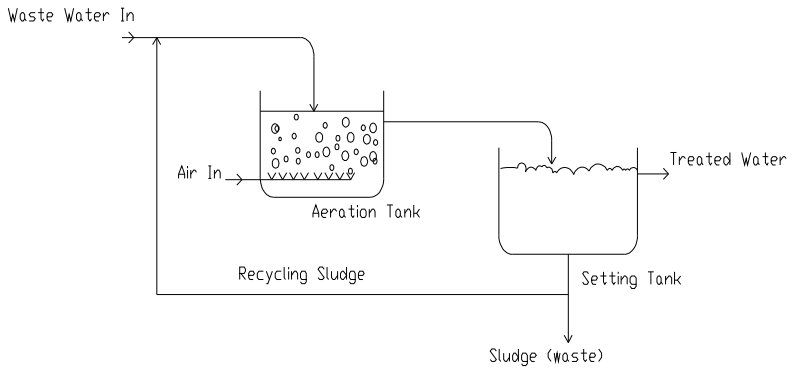


Fig. 1. Schematic diagram of an activated sludge process.

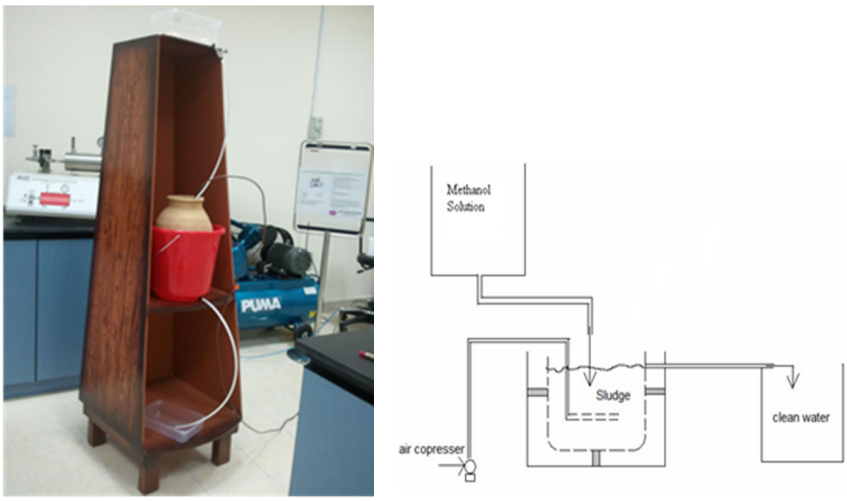


Fig. 2. Photo and schematic diagram of the alternative sludge process using a porous tank.

2.2.1. Materials

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 the feed stream to the wastewater plant.

In order to determine the type of bacteria present in the activated sludge, samples were analyzed for colony forming units (CFU) in the microbiology lab at the University of Nizwa. Firstly, a serial dilutions from the sample ($10^{\wedge-1}$, $10^{\wedge-2}$, $10^{\wedge-3}$) was made, then, incubate from each dilution. After incubation period, the CFU was calculated using the equation:

cfu/mL=(#colonies)*(dilution factor)/volume plated in mL.

2.2.2. Experiment

Experiments were performed in 6 liters porous pottery vessel containing 280 g of activated sludge. This pottery vessel was placed inside 20 liters 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 of; 5%v/v and 8%v/v. In order to have the same flow rate in and out of the sludge vessel, a 0.72 l/h methanol feed flow rate was chosen. Air was purged at low flow rate through the sludge vessel.

Samples were taken every hour from the sludge solution and the effluent was analyzed for both bacteria and methanol concentrations

2.3. Air stripping process

Air stripping is the process of forcing air through polluted water to remove harmful chemicals. The air causes the chemicals to change phase from a liquid to a gas phase. The gas is then collected and cleaned [22]. Volatile organic chemicals (VOCs) are common wastewater and groundwater contaminants that lend themselves to air stripping technology for water treatment. However, this section discusses the removal of VOCs with air stripping using the diffused aeration method.

The advantage of diffused aeration stripping is simple. It can handle high levels of suspended solids and thus it could be considered for many large and application [23].

2.3.1. Experiment

Batch experiments were performed in a glass tube of 1.2 m height and 10 cm diameter fitted with an air distributor disc of 8 cm diameter consisting of several holes each about 10mm in diameter, as shown in Fig. 3. At each experimental test, 5 liters of methanol-water mixture was prepared. The liquid height inside the glass vessel was about 75cm. Two methanol concentrations of solution mixtures have been prepared namely; 5 and 8% v/v. The air stripping unit was operated at two different gauge pressures; 0.25 and 0.5 bars. Samples were taken every 20 minutes and analyzed for methanol content.

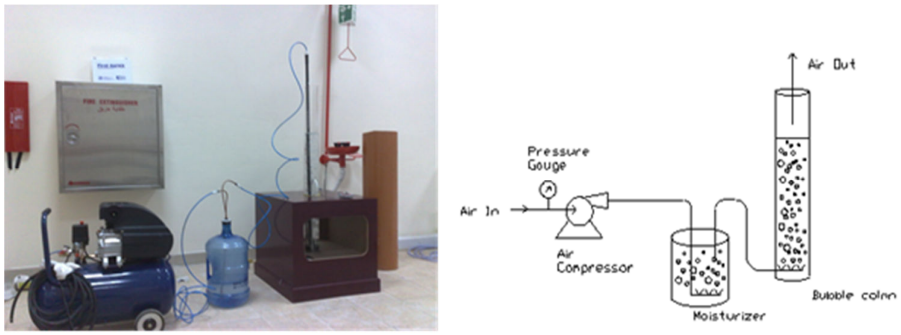


Fig. 3. Photo and schematic diagram of air stripping experimental setup.

2.4. Adsorption process

The water purification industry is currently one of the largest market for commercial activated carbon (CAC). In fact, CAC filters are used today in many drinking water and wastewater treatment plants to remove organic micro-pollutants and some metals by adsorption. The economics of the adsorption process greatly depends on the reuse of CAC. Two approaches have been considered by researchers to overcome the problems associated with the use of activated carbon adsorbents. One approach that has been investigated by many researchers is the development of low cost adsorbents based on carbonaceous waste products that can be used on a once through basis, hence eliminating the need for regeneration [24-28]. However, this merely transfers the pollutant from the liquid to the solid state. Adsorption beds containing activated carbon are widely used in industry to remove organics from water and air. One of the major disadvantages of this method is the difficulty of regeneration of the saturated carbon [29, 30]. Often the carbon must be removed from the bed and the organics burned off in regeneration furnaces.

Since granule activated carbon adsorption is generally utilized for the removal of organic compounds from wastewater and to remove the tastes and odors in water supplies, it is considered for the removal of the methanol compound from methanol-water mixture (less than 10% methanol).

2.4.1. Materials

The granular activated carbon (density 400 kg/m^3) particles of diameter 0.0015 m was supplied by the Haya Company-Sultanate of Oman, for water and waste water treatment.

2.4.2. Experiment

Two different methanol solution mixtures were treated using the granular activated carbon column. The experimental setup consisted of 5 liters glass vessel and an adsorption glass column of I.D = 5 cm and height= 1.2m. The column is filled up to 100 cm high with GAC. The methanol solution was fed to the column via a peristaltic pump at flow rate 3.75 L/h. The effluent liquid stream from the adsorption section is collected in a 5 liters plastic bottle. The schematic diagram of the process is shown in Fig. 4. Samples were taken every 15 minutes from the effluent solution and then were analyzed for methanol content.

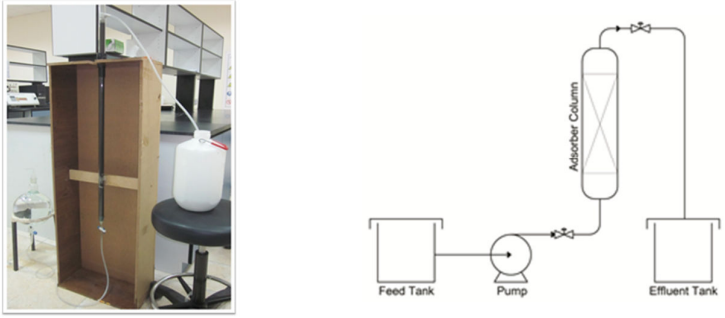


Fig. 4. Photo and schematic diagram of experimental adsorption set-up.

3. Results and Discussion

3.1. Activated sludge process

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 analyzed for methanol and bacterial content and the results are shown in Fig. 5. This result shows the decrease of methanol concentration due to the consumption of methanol by the bacteria during the experiment. The results indicate that the larger the amount of methanol in the feed the larger the amount is consumed.

However, if there was no activated sludge in aerated tank, this process may be considered as a normal mixing tank [31], and the response of the methanol can be modeled by Eq. (1) below. For the purpose of comparison, the result of normal mixing tank was compared with that of methanol obtained from the sludge process; the results are presented in Fig. 6. The results indicated that the methanol was increased exponentially in the tank without sludge due to the continuous feed of the methanol, while in the tank with activated sludge; the methanol concentration was decreased due to its consumption quickly by the bacteria.

$$C/Co = 1 - \exp(-(V/F)t) \quad (1)$$

where C is the methanol concentration in the tank (g/l), Co is the methanol concentration in the feed (g/l), V is the tank volume (l), F is volumetric feed flow rate (l/s) and t is time (second)

Also, bacterial growth was monitored during the experimental work and the results are shown in Fig. 7. This result shows that the bacteria first adapt themselves to the new conditions within 1 hour in both solutions and then start to grow, consuming more methanol, as shown in Fig. 7. The analyzed samples showed that the bacillus positive bacteria type was present.

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 had been consumed, see Table 1. It can be shown that the consumption of methanol was reduced slightly in the solution with a higher methanol concentration. This could be due to the inhibition of bacterial growth under a higher methanol concentration [32].

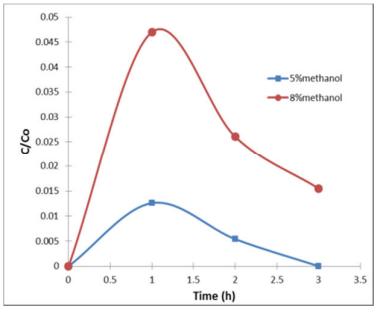


Fig. 5. Comparison between methanol removal in sludge vessel using 5% and 8% methanol feeds.

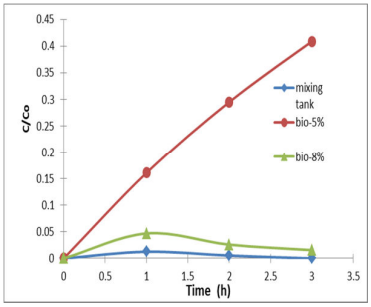


Fig. 6. Comparison between methanol concentration in sludge and mixing tanks.

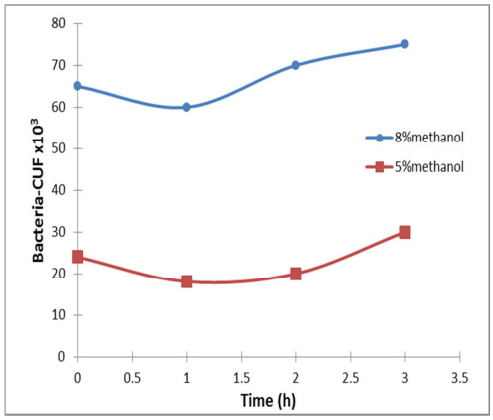


Fig. 7. Bacterial growths during experiments with 5% and 8% methanol feeds.

Table 1. Methanol concentration in wastewater after 24 hours.

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

3.2. Air stripping process

As mentioned in previous section 2.3.2, two types of tests were made for separating methanol from methanol mixture. Firstly, air stripping was carried out on solution with 5% methanol under 0.5 bar gauge and 0.25 bar gauge air flow rate separately, while the second test was carried out on solution with 8% methanol under 0.5 bar gauge and 0.25 bar gauge air flow rate separately. The obtained results are presented in Fig. 8. This result shows that the removal of methanol depends on the methanol content in the solution and the air flow rate.

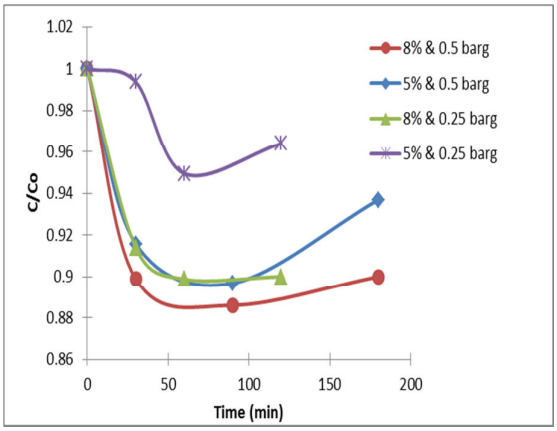


Fig. 8. Methanol removal using air striping at 0. 5 bar gauge.

The larger the air flow rate, the larger the methanol removal, such that for test of 5% methanol, about 10% of the methanol was removed under 0.5 bar gauge air flow rate, while only 5% is removed under 0.25 bar gauge. Also, it can be noted that the larger the methanol contents the larger amount is removed. For example, under 0.5 bar gauge air flow rate, about 12% is removed from the solution with 8% methanol compared to 10% from solution with 5%.

In addition, it can be seen from the results that the methanol concentration starts to increase after 70-80 minutes. The reason could be due to the strong intermolecular forces between water and methanol that resist further methanol removal when the water contents in the column starts to drop down due to evaporation by the air flow. The level dropped by about 4.1 cm.

The obtained results show that the efficiency of the air stripping would be higher for a high methanol concentration.

3.3. Adsorption using activated carbon

Granular activated carbon (GAC) has been used to remove methanol from the methanol water mixture. For this purpose, tests were carried out using two mixtures with a methanol concentration of 5% and 2% separately and the results are shown in Fig. 9. It can be seen that the average estimation of the break point of the adsorption process is about 100 minutes for both tests; 2% and 5% methanol contents. The fast saturation of the activated carbon reflect its good adsorption capacity, however, such fast saturation of would not be suitable for treatment of industrial solutions with high methanol content in respect to operation cost and the needs of frequent regeneration. The reason of hindering methanol adsorption may be referred to the formation of hydrogen bond between water and adsorbed methanol, consequently filling the pores of AC and resulting less space for adsorption. This reflects the short saturation limit of methanol.

Scanning electron microscopy is widely used to study the morphology of adsorbents. Scanning electron microscope (SEM) was used in order to observe the micrographs of fresh and the exhausted GAC after the experiments. Scanning for fresh GAC and exhausted sample from methanol adsorption column are shown in Figs. 10 and 11 respectively. Comparisons between these images indicate a rough structure on the surface and the presence of many pores on the fresh AC which is favorable for adsorption compared to that of exhausted sample.

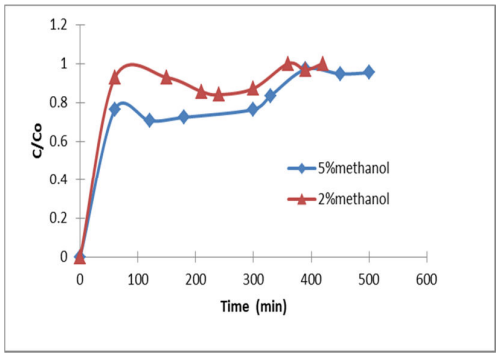
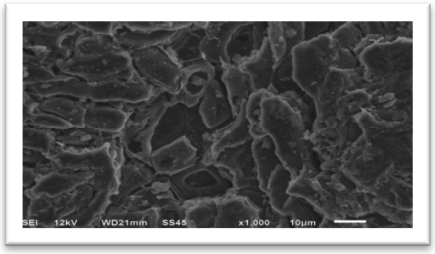
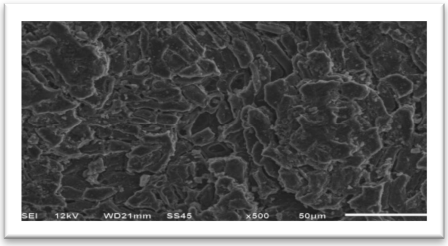


Fig. 9. Time profile of methanol output concentration from GAC.

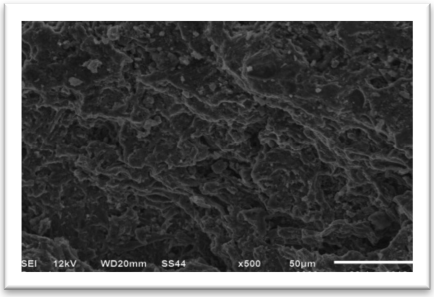


(a) Magnification = 500

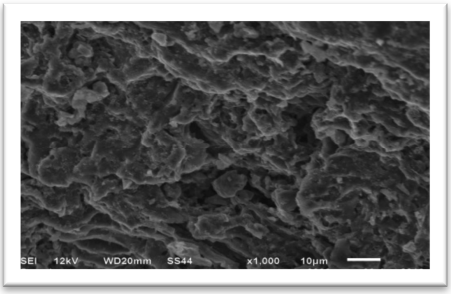


(b) Magnification = 1000

Fig. 10. SEM micrograph of fresh GAC.



(a) Magnification = 500



(b) Magnification = 1000

Fig. 11. SEM micrograph of exhausted GAC.

4. Conclusion

Methanol was removed from methanol-water mixture using activated sludge, air stripping and activated carbon. Based on the obtained results, it can be concluded that the methanol concentrations dropped and methanol was consumed quickly by the bacteria of the activated sludge as it entered to the sludge vessel. The bacteria within the sludge solution can adapt wherever an organic source such as methanol present. This is can be true for methanol concentrations up to as 5% within the sludge solution. The reduction of bacterial growth can be considered due to the increase of methanol concentration, especially if methanol greater than 5% within the sludge tank. This biological method proves its ability to remove methanol contaminant especially at low concentration.

It can be concluded that the air stripping process is not efficient for low levels of methanol concentration. However, it may be efficient for methanol removal with concentrations higher than 10 %.

It is well known that the activated carbon has the ability to adsorb organic material. However, such material was quickly saturated when using solutions with 2% and 5% methanol and thus, this method would not be recommended for the removal methanol from methanol water mixtures.

The comparisons between the three methods shows that the removal of methanol was about; 10-12% using method of air striping, 10-15 % using activated carbon and 98-100% using the activated sludge. This data indicates that the active sludge process is more efficient in removing methanol from the methanol-water mixture.

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