Characteristics of MEG Removal from Industrial Wastewater by Sequencing Batch Reactor (SBR)

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ABSTRACT: *Background: MEG is extensively applied in the sour gas industry as hydrate inhibitor. It is toxic in oral drinking and serious injury or death may result from swallowing of pure ethylene glycol and poses a potential hazard to the environment through impact soil. Glycols are harmful to aquatic life. There is a little information about digestion of MEG in aerobic reactor. Therefore, the feasibility of MEG removal in aerobic reactor was investigated. Materials and method: Biodegradation of MEG was done in an aerobic SBR reactor with the capacity of 2000 mL and sanitary wastewater as primary required microorganism. The experiments were done in the three stages. In stages 1 and 2, 500 mL of reactor content was drawn-off and solutions contain 500 mL of 0.073 (wt %) of MEG (for first stage) and 0.201 (wt %) of MEG (for second stage) were added to reactor. In stage 3, 500 mL of wastewater of MEG removal unit in the 2nd refinery of South Pars Gas Company, Iran with the concentration of 4.021 (wt %) of MEG was added to 1500 mL of reactor content. Feed of stage 1 was pure MEG that was diluted in de-mineralized water but Feed of stage 2 was a dilution of industrial feed of stage 3. Results: In stage 1, after four days, removal efficiency more than 80% was obtained. In stage 2 after six days, efficiency of 20% was obtained. In stage 3, after seven days, more than 70 percent of MEG removal was obtained. Conclusion: by increasing residence time, the removal efficiency of the reactor could be increased acceptably. Therefore, the MEG solution of more than 4 (wt %) of MEG can be treated biologically.*

KEYWORDS: *SBR; Wastewater; Microorganism; DO, MEG; COD.*

INTRODUCTION

Glycols are extensively applied in the sour gas industry [1]. MEG is used as hydrate inhibitor in gas refineries in The South Pars Gas Company in Iran. A solution of 70% MEG is injected into the produced gas from wellhead to prevent hydrate formation during transfer of fluid to onshore facilities from sea. During the transformation of fluid, the water content of it (according to water in the well) will be increased and therefore, the MEG solution will be diluted. The Glycolated Water after separation from gas and condensate phase

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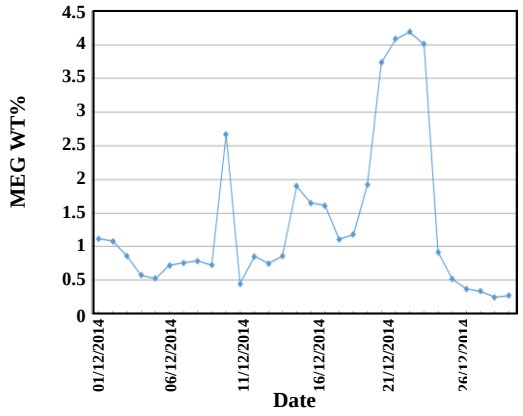

Fig. 1: MEG loss in the outlet of MEG regeneration unit (phases 2 & 3 South Pars Gas Company).

is concentrated in MEG regeneration unit based on packed bed distillation tower to re-inject to the sea line. Base on design case, maximum allowable amount of MEG loss in sour water stream from the top of the still column is 0.015 (wt %) to meet the environmental aspects. The sour water then is routed to sour water stripper unit for elimination of H_2S and then to the sea [2].

As shown in Fig. 1, because of any malfunctions that usually occur in the MEG regeneration unit, the MEG lost in the outlet of this unit is some of the time even more than 1 (wt %) and it is necessary to eliminate excess MEG to meet environmental standards for releasing to sea.

One of toxic and hazardous materials that are used in many industries is ethylene glycol [3]. Release of glycols into the subsurface soils poses a potential hazard to the environment through impact soil and groundwater [4], [5]. Ethylene glycol is also toxic in oral drinking and serious injury or death may result from swallowing of pure ethylene glycol [4],. Glycols are harmful to aquatic life. High values of COD in Glycolated water led to consumption of DO in receiving water [6], [7]. Maximum permissible concentration of glycol in water and chronic toxicity of ethylene glycol to small mammals was investigated by Plugin [8]. Fate, effects and potential environmental risks and toxicity of ethylene glycol are well characterized [9,10]. Ethylene Glycol is metabolized in the river by successive oxidation to a variety of compounds included: Glycolaldehyde, glycolic acid, Glyoxylic acid and oxalic acid. These compounds are more toxic than ethylene glycol and are cell toxins that cause central nervous system depression, and cardio-pulmonary and renal failure [11], [12] and [13].

One of the most important processes for elimination of MEG is the biological treatment. In this case several investigations were done. The effect of oxygen concentration in the solution on the degradation of ethylene glycol by the Flavobacterium bacteria is considered [14]. In this end, a Biological batch reactor by controlled pH, temperature, Aeration and agitation was used. In addition, Degradation of ethylene glycol by Acinetobacter SC25 in a mineral salts medium was investigated [15]. Moreover, Study of biodegradation of ethylene glycol in the river water [16] and degradation of MEG by soil microorganisms [17] were done. Furthermore, Biodegradation of MEG, DEG and TEG and their breakdown products in natural soil and groundwater using indigenous microbes was considered [1].

In the present work, characteristics of MEG removal from industrial wastewater by SBR was done in bench scale.

EXPERIMENTAL SECTION

MEG measurement method

Concentration of MEG was determined by gas chromatography with these properties:

- Gas chromatography (Varin 3800) with capillary column WCOT Fused Silica (15 m*0.32 mm) ID, CP-Volamine coating
- Flame ionized detector (FID)
- Temperature of injector and flame detector was 280°C and 250°C respectively.
- Carrier gas was N2 and flame rate was 30 ml/min
- Calibration was done with internal standard method and propane diol used as internal standard

COD measurement method

COD test was done by spectroscopy method 435, set on 620 nm with (HACH DR2800), according to ASTM-D1252 that is suitable for range of 20-1500 mg/lit of COD.

Set-up

The SBR batch reactor was applied in this investigation. 2000 mL of mixed liquor of aeration tank of the sanitary wastewater treatment unit of the refinery was added to glassy reactor as a base of microorganisms. The magnetic mixer is used for mixing of suspended solids and preparing required DO for microorganisms' activities.

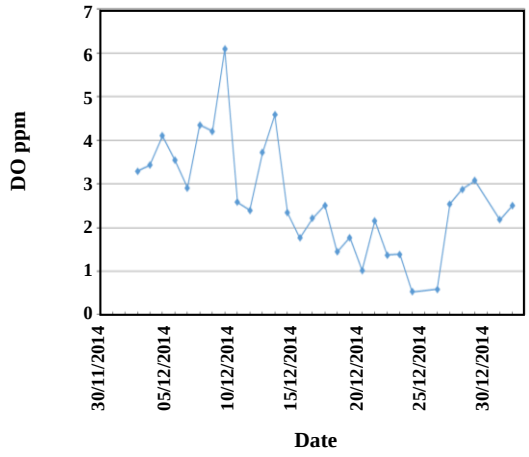

Fig. 2: Variation of dissolved oxygen in the reactor.

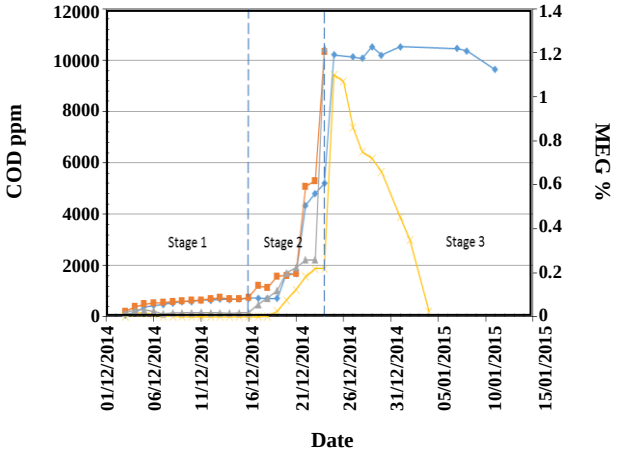

Fig. 3: Three stages of MEG removal in the reactor and changes in the MEG (wt %) and COD

As shown in Fig. 2, The DO was adjusted in the range of 1.5-4.5 ppm.

Feed preparation

For three days, all parameters (DO, pH, Temperature), were kept constant to stabilize the condition of reactor content. In this period, two feeds with different concentrations were prepared. First was solution of 0.073 (wt %) of pure MEG in de-mineralized water that is nominated as FEED (I). FEED (II) was a solution of 4.021 (wt %) of wastewater of MEG regeneration unit. A mineral solution (Mineral Feed) was prepared consist of the materials with concentration as follow: KH_2PO_4 (8.5 g), K_2HPO_4 (6.5 g), $(NH_4)_2SO_4$ (35.5 g), $MgCl_2.6H_2O$ (17 g), $CaCl_2$ (2.6 g), $FeSO_4$ (0.06 g) that are solved in the de-mineralized water to reach 200 mL of volume.

Analytical method and parameters:

According to Fig. 3, the investigation has been done in three stages as below:

Stage 1: Every 24 hour, after 30 minutes of settling time, 500 mL of reactor content was drawn-off and filtered by GF/C (Whatman 4.7 cm). Then the tests of COD, MEG, pH and DO were done (nominated as "Before Feed Test"). Then 500 mL of FEED (I) was added to the reactor to compensate removal of 500 mL volume in the reactor and for adding of new feed. Again above tests were done (nominated as "After Feed Test").

In all three stages, 5 mL of mineral feed was added to the reactor to supply the required minerals. To inhibit the decrease of pH that was occurred in the reactor according to byproducts that were produced in the biodegradation process of MEG [4], sodium carbonate was used to stabilize pH.

Stage 2: In this Stage "Before Feed test", was done as same as stage 1 but for "After feed tests", 500 mL of diluted solution of FEED (II) (25 mL of FEED (II) was mixed with 475 mL of de-mineralized water for the final concentration of 0.201 wt%) was added to the reactor and similar to stage 1 the tests were done every day.

Stage 3: In this stage the feasibility study of microbiological treatment of high concentration of MEG and the effect of hydraulic resistant time were investigated in a batch reactor system. At the beginning of this stage, 500 mL of reactor content was drawn-off and the COD, pH, DO and MEG percentage tests were done. Then 500 mL of FEED (II) was added to 1500 mL of reactor content that increased the concentration of MEG in the solution up to 1.22 (wt %) (Feed of stage 3). Every 24 hours, residual MEG (wt %), COD, pH and DO were measured for nine days. The results of three stages are shown in Fig. 3.

Parameters

For first and second stage tests:

Removal efficiency of MEG (%) = (MEG (wt %) $_{\text{After Feed of yesterday}}$ - MEG (wt %) $_{\text{Before Feed of today}}$)/ MEG (wt %) $_{\text{After Feed of yesterday}}$ *100

For third stage tests:

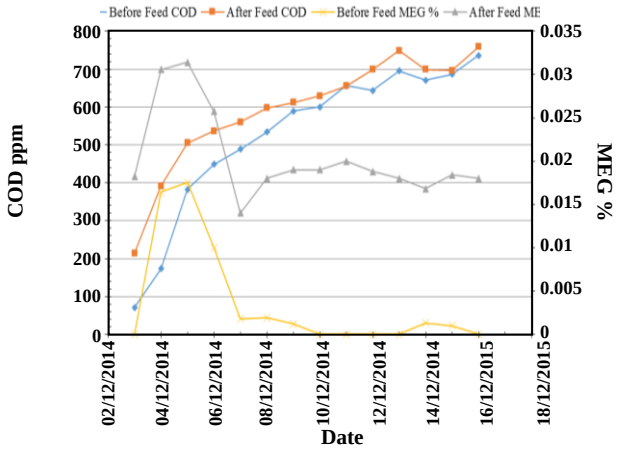

Fig. 4: Variations in the COD and MEG (wt %) in the first stage tests.

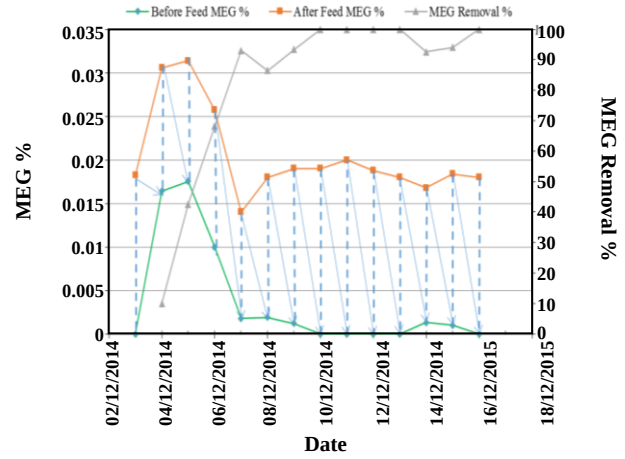

Fig. 5: Variation in removal efficiency of MEG in the first stage tests.

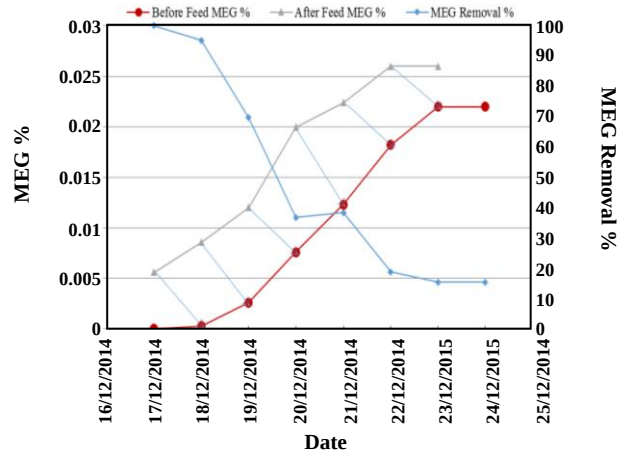

Fig. 6: Variation of MEG wt percentage and removal efficiency in the second stage test.

Removal efficiency of MEG (%) =

(MEG (wt %) $_{\text{Feed of Stage 3}}$ - MEG (wt %) $_{\text{Before Feed of today}}$)/ MEG% $_{\text{Feed of stage 3}}$ *100

RESULTS AND DISCUSSION

Stage 1 test

According to Fig. 4 with increase of FEED (I) (500 mL of 0.073 (wt %) of MEG), concentration of MEG in second day and third day increased in the after feed. This figure illustrates the sharp change in MEG concentration during first and second day and negative slope after third day that was according to low amount of MEG biodegradation microorganisms at the first day and increasing the amount of microorganisms in the next days. As it was seen, after the 3rd day before feed and after feed MEG (wt %) decreased sharply and before feed MEG decreased to near zero (100% conversion) after 5th day. Though the MEG concentration in the before feed was decreased very much after 4th day, the COD concentration in the before feed and after feed was increasing smoothly according to produce byproducts of MEG [7] and [1] that was produced in the reactor and there was not enough residence time to consume of them in the reactor by microorganism metabolism .

According to Fig. 5, the slope of MEG removal efficiency was sharp in the early days and decreased after 5th day that shows growth and stabilization of biodegradation metabolism. After 6th day, the removal efficiency is nearly 100% and the environment is ready for activity of microorganisms.

Stage 2 tests

As shown in Fig. 6, by changing the feed of reactor (FEED (I) with FEED (II) (50 mL 4.021 (wt %) MEG + 450 mL de-mineralized water)), the concentration of MEG in Before and After Feed increased smoothly and the efficiency percent of biodegradation of MEG decreased and fixed on 20% after 5 days. Therefore, the capacity of the reactor (include resident time and volume) is not enough for metabolism of this amount of feed.

According to Fig. 7 while the removal efficiency of MEG is decreasing, increase of MEG concentration in the solution raises the COD in the reactor especially when the removal efficiency of MEG is about 20%.

Stage 3 tests

According to low MEG removal efficiency in second stage, the influence of hydraulic residence time on MEG

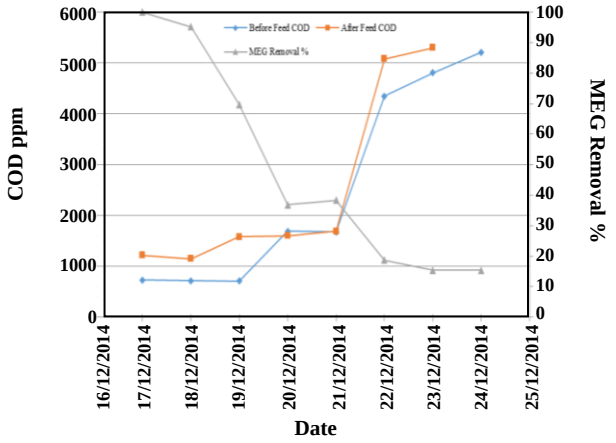

Fig. 7: Variation of COD and MEG removal efficiency in the second stage test.

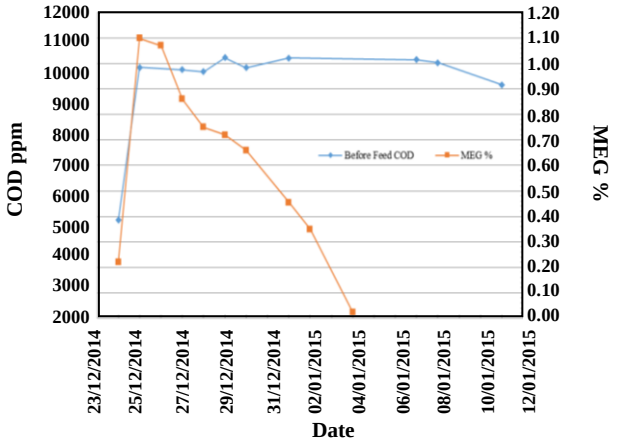

Fig. 9: The comparison between MEG concentration and COD in the reactor in the third stage tests.

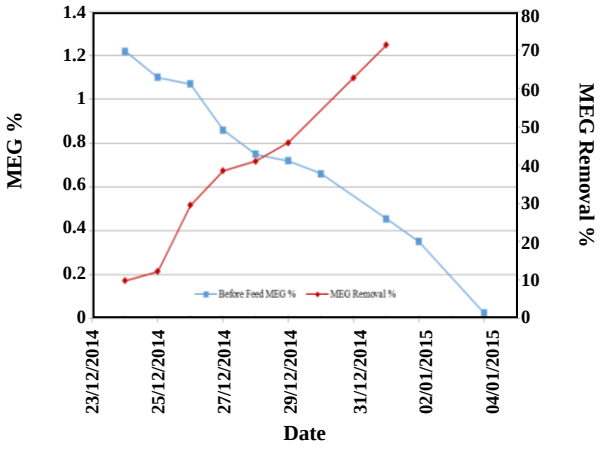

Fig. 8: Variation of MEG weight percent and removal efficiency in the third stage tests.

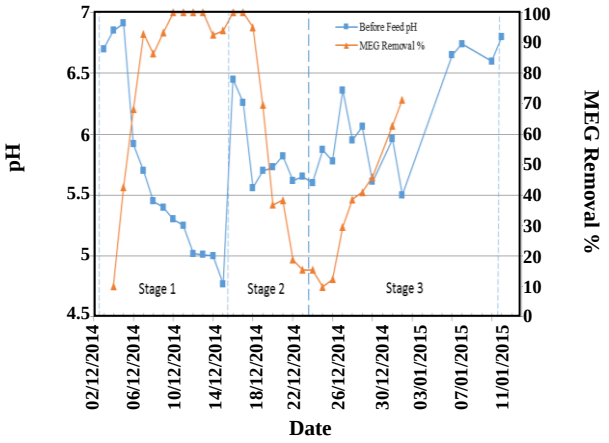

Fig. 10: Variation in the pH and removal efficiency of MEG in the reactor.

removal was investigated. Fig. 8 illustrates that the MEG removal efficiency was low at first day and then by increasing of bacterial metabolism, the slope of removal efficiency increased. Therefore, it is possible to eliminate high MEG concentration up to 10000 ppm by increasing hydraulic resident time in the aerobic microbiological reactor.

Fig. 9 compares MEG concentration and COD in the reactor during third stage. It is obvious that MEG was removed after 9 days by 80% but COD was constant. Since the high concentration of MEG was added to the reactor content at the first day as COD source, COD was increased and then was constant. It shows that MEG bacterial activities just change the nature of MEG and the byproduct materials as source of COD remained in solution. In this stage, MEG was converted to some soluble materials. Therefore, COD of the reactor content was constant during the test and no COD conversion was reached.

Fig. 10 illustrates the variation in the pH of the reactor content in three stages tests. According to high volume of the reactor and low removal of MEG, there are not large deviations of pH in two first days. But from third day by increasing of MEG removal up to 68% and production of byproducts, the pH decreased to 4.7 after 13 days. DO is one of the most important parameters that affects on pH. As it is mentioned in Fig. 2, DO was kept constant during all tests. Therefore, acidic byproducts of MEG metabolism were the only parameter that decreased the pH.

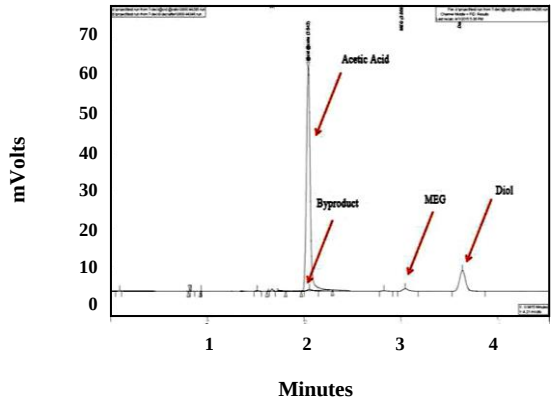

Fig. 11: GC curve 3th of December 2014.

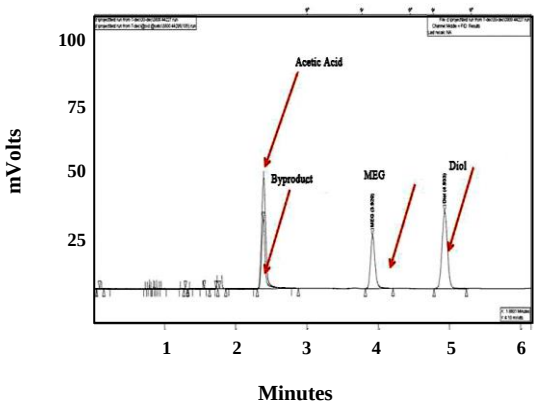

Fig. 12: GC curve 30th of December 2014.

Byproducts

Figs. 11 and 12 compare the GC curves of MEG, Propane Diol and Acetic acid in Before Feed solution in the 3th and 30th days. The pure acetic acid curve is coincident with byproduct curve that demonstrates that the most byproduct of MEG metabolism is acetic acid.

In the figure of 3th of December, the MEG concentration of GC is very higher and larger than byproducts curve, but in the 30th of December GC test, the increase in area and length in byproduct curve reveals the influence of byproducts on high amounts of COD and conversion of MEG to acetic acid.

Biodegradation of MEG in an aerobic SBR reactor with the capacity of 2000 mL was investigated. The experiments were done in the three stages. In stage 1, after drawing-off of 500 mL surface liquid after 30 minutes settling in the reactor, 500 mL of 0.073 (wt %) of MEG was added every day. MEG removal efficiency was obtained more than 80 % after four days. In stage 2, 50 mL wastewater of MEG regeneration unit with the concentration of 4.021 (wt %) of MEG with 450 mL de-mineralized water (diluted to 0.1) was added to the reactor and 500 mL was drawn off as before. The MEG removal efficiency of 20% was obtained after 6 days because of low residence time in the reactor. In the third stage 500 mL of wastewater of MEG regeneration unit of refinery with the concentration of 4.021 (wt %) of MEG was added to 1500 mL of reactor content and MEG removal was investigated with time. After seven days, more than 70% of MEG removal was obtained. Therefore, by increasing residence time, the removal efficiency of the reactor could be increased acceptably though the feed concentration is more than 4 (wt %) of MEG. In all the stages of tests, the COD did not decrease according to production of byproducts that remain in the system.

Recommendation

The hydraulic and sludge residence time should be increased to consider the influence of it on the MEG and COD removal efficiency for the elimination of byproducts. All these tests could be done in the anaerobic SBR reactor to measure MEG and COD removal efficiency of anaerobic systems.

Competing interests

The authors declare that they have no competing interests.

Authors' Contribution

Authors participated in this research including design, experiments and data analysis, and manuscript preparation. All authors read and approved the final manuscript.

Nomenclatures

MEG	Mono Ethylene Glycol
ppm	Part per million
DO	Dissolved Oxygen
SBR	Sequencing Batch Reactor
COD	Chemical Oxygen Demand
GC	Gas chromatography

Acknowledgements

This research was supported by 2nd refinery of South Pars Gas Company, Iran. The object of the present work

was removal of MEG from wastewater with biological system to meet environmental aspects

Received : Mar. 23, 2018 ; Accepted :Jan. 1, 2019

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