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AN INVESTIGATION ON THE NITROGEN CONTENT OF A PETROLEUM REFINERY WASTEWATER AND ITS REMOVAL BY BIOLOGICAL TREATMENT

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ABSTRACT
This investigation was performed on the biological removal of nitrogen from refinery's wastewater by the nitrification and denitrification process. In a petroleum refinery, removing of hydrocarbons is the main concern and nitrogen content is supposed to be negligible. The aim of this work was to search for nitrogen in Tehran Refinery wastewater and employing a biological technology to reduce this pollutant. Samplings were done in different points of wastewater treatment plant; influent to aeration unit, effluent of aeration unit and effluent of clarifiers. The results showed that despite of a high average removal efficiency of COD > 93%, the nitrogen removal during conventional activated sludge process was not efficient and sludge rising due to denitrification was observed within the clarifier. The analysis conducted in laboratory scale showed that a simultaneous nitrification and denitrification (SND) process could easily be realized in the same activated sludge plant by using the flocculating sludge and control of dissolved oxygen concentration. It was found that the higher MLSS value (10.0 g/L) and mixing rate (300 rpm) is effective in improving total nitrogen removal and overall SND performance. Our experimental results indicated that the SND process is very efficient for nitrogen removal from industrial wastewater.

Key words: Dissolved Oxygen; Industrial wastewater; Mixed Liquor Suspended Solid (MLSS); Nitrogen removal; Simultaneous Nitrification and Denitrification

INTRODUCTION
Nowadays, almost all wastewater treatment units in industrial societies that are involved with providing fresh water resources are contaminated with nitrate ion. Nitrogen contaminated water resources require larger amounts of oxygen. Eutrophication of water resources, destruction of aquatic animals, accession of maladies such as stomach cancer, blood pressure and also methoglobinemia are some other samples of the unfavorable effects of nitrogenous compounds (Lefevre *et al.*, 1993). Different physicochemical and biological processes are used for nitrogen removal (Kless and Silverstein, 1992). Since biological nitrogen removal is more effective and relatively inexpensive, it has been widely adopted in comparison to the physicochemical processes. The biological process for nitrogen removal consists of nitrification and denitrification. However, recent studies show that these two important steps can occur concurrently in the same reactor (Munch *et al.*, 1996; Helmer and kunst, 1998; Hao and Martinez, 1998; Menoud *et al.*, 1999; Wang *et al.*, 2005), and this process is termed as Simultaneous Nitrification and Denitrification (SND).

In Tehran Oil Refinery Co. (TORC), the water treatment plant inlet is the wastewater from different units of the refinery which consists of

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nitrogenous compounds. Mainly, condensates from fractional distillation column, condensates from catalytic cracking and reflux column consist of a large amount of ammonia. Condensates of these units are sent to the wastewater treatment plant after the stages of preliminary treatment consisting stripping operations. Large amounts of nitrogen in the wastewater are hazardous for the environment and have unfavorable effects on the operation system of the biological treatment. If the required predictions for nitrogen removal are not considered in designing and operation of a biological wastewater treatment, serious problems could arise such as sludge rising in the second clarifier.

At present, the treated wastewater in this unit is used for forest irrigation but at times that Tehran is in drought and lack of water, a part of water needed for cooling towers is supplied by that. The outlet of API separators enters the next stages of the treatment such as sedimentation tank, equalizing tank, floatation, biological oxidation and filtration. Wastewater will enter the sedimentation tank, equalizing tank and Dissolved Air Flotation unit (DAF). Before DAF, a diluted solution of poly electrolyte/ polymer is added to the wastewater. The wastewater mixed with polymer is sent to the cumulating tank and the mixture remains there until the bulks are formed. DAF process consists of a compressed water stream and dissolved air in it with a pressure about 60 psig. In this process, air is released in the form of bubbles. These bubbles adhere the suspended particles and take them to the surface of water. Flocculent materials will supply a larger surface for the bubbles and facilitate their performance. The retention time of this part is about 50 minutes. The outlet of this unit consists of 34.7 mg/L ammonia and 690 mg/L COD. Then, the wastewater will enter aeration vessels. At present, the mixed activated sludge process is used in this field, since this process can tolerate hydraulic and organic changes up to a higher level compared to the systems with plug flow. The outlet COD of this unit is 4440 mg/L. This high value of COD is due to biological suspended particles. After separation of solids in clarifiers the COD decreases to 340 mg/L. Four filters with sandy beds with the capacity of 350 gpm per each are used to decrease the suspended solids to 5 mg/L or less.

The objective of this research is to investigate the effect of vital factors such as mixing rate and MLSS parameters on removal nitrogen from TORC wastewater.

MATERIALS AND METHODS

Experimental procedure

Experiments were done in a synthetic environment. Suitable feed should be prepared in a way that aerobic and anaerobic microorganisms can grow for nitrification and denitrification stages. Synthetic wastewater was made of glucose, NH_4Cl, K_2HPO_4, $CaCl_2$, $MgSO_4$, KOH, $FeCl_3.6H_2O$ and $NaHCO_3$ (Holman and Wareham, 2005). The feed consists of 50 mg/L initial ammonia. The feed used for sludge was prepared with different proportions of COD/NH_3 (2, 20) at similar compounds and conditions. Cultures were carried out in the 500 mL Erlenmeyer flask containing some feed, inoculated with a fresh and incubated at ambient temperature on the shaker-incubator (Unimax 1010, Heidolph Inkubator 1000) at 100 or 300 rpm. Values of DO and MLSS were measured during culture.

Analyzing methods

In WWTP of Tehran Oil Refinery, concentrations of ammonia nitrate and nitrite was measured in three points: aeration inlet, aeration outlet and the clarifier outlet. Since the most amount of nitrogen removal occurs in aeration unit, experiments were done on the inlet and outlet of this unit and the clarifier unit.

Ammonia nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^--N), total nitrogen (TKN) and MLSS were analyzed according to the standard methods for the examination of water and wastewater (APHA, 2005; ASTM, 2002). Measuring of ammonia and nitrate was done by spectraphotometer (Unicam 8700 series, UV/Vis). Measuring total nitrogen was done with kjeldahl method, using the related apparatus (KJELTEC Auto 1030 Analyzer). Nitrite concentration was also estimated based on the stoichiometry of nitrogen because the total nitrogen (TKN) was based on the sum of NH_4^+-N + NO_3^--N + NO_2^--N (Yang, 2009).

RESULTS

Characterization of water outlet from wastewater plant

The inlet average ammonia concentration to the aeration unit in which the biological treatment

occurs was 34.7 mg/L and reached to 16.7 mg/L in the outlet. This amount is still higher than the allowed standard amount which is 1.5 mg/L. Hence, other supplementary analysis was done on three spots of wastewater treatment unit on several days; results are presented in Table 1.
As it is observed above, the amount of ammonia in the unit's outlet was high, so several changes are required to improve the performance of this unit. The results of experiments related to the nitrogen removal in a synthetic medium, based on the statistical experiments design and SND process are mentioned below.

Table 1. Average amounts of nitrogen compounds in water treatment unit of Tehran Refinery

Nitrogen Type	Aeration inlet	Aeration outlet	Clarifier outlet	Allowed concentration (ISIRI, 1383)
Ammonia (mg/L)	34.7	16.7	15.6	1.5
Nitrate (mg/L)	3.51	0.76	1.05	5.4
Nitrite (mg/L)	0.0436	0	0.0002	4
Total Nitrogen (mg/L)	50.57	35.96	33.65	10

Effect of MLSS on nitrogen removal
Results of final concentration in different forms and two different amounts of MLSS are shown in Fig. 1.
According to Fig. 1, at higher MLSS concentrations, more nitrogen was removed. This effect is low for ammonia but remarkably high for nitrate. MLSS increase also caused more nitrogen removal for total nitrogen. It is obvious that high MLSS of 10 g/L causes more cellular bulk and better removal.

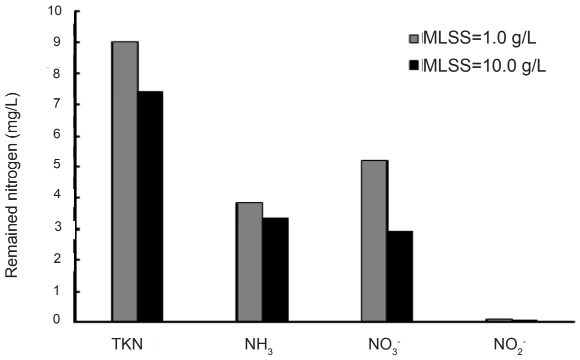

Fig. 1: Final remained amounts of TKN, NH_3, NO_3^- and NO_2^- measured in mg/L at two different MLSS concentrations of 1 and 10 g/L

In microscopic studies of samples at the end of culture time, significant differences were observed between outward morphologic properties of biologic sludge (Pochana and Keller, 1999). Fig. 2 (A, B) shows microscopic pictures of samples which had MLSS equal to 10 and 1 g/L, respectively.

As it could be observed in these microscopic pictures, cellular bulks were present in the form of coherent clods that resulted in a better removal.

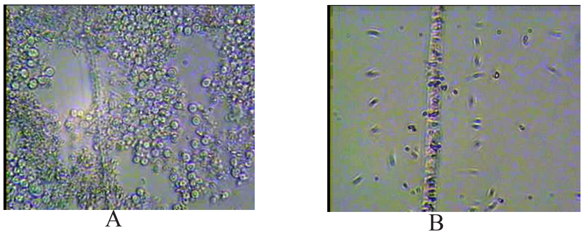

Fig. 2: Cellular clod concentration in biologic sludge with MLSS concentrations (g/L) of A: 10.0 and B: 1.0

Effect of mixing rate on nitrogen removal
Fig. 3 shows residual amounts of nitrogen at two different rates of mixing on the shaker.
This figure shows that in higher rates of shaking, the amount of total nitrogen removal has increased.

DISCUSSION
In most papers, MLSS of sludge is reported between 3-5 mg/L (Yoo *et al.*, 1999) while in this paper, samples with high MLSS concentration up to 10 g/L are studied. More nitrate removal in

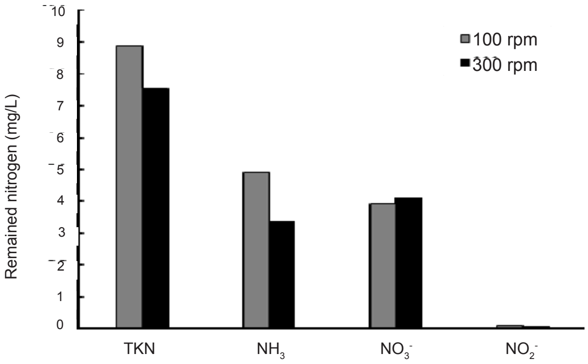

Fig. 3: Final remained amounts of TKN, NH_3, NO_3^- and NO_2^- measured in mg/L at two shaking rates of 100 and 300 rpm

high MLSS concentration could be due to larger bacterial clods formation and anaerobic areas in the center of these clods that results in better denitrification. Of course, the probability of nitrogen removal due to adsorption to biomass, especially in high concentrations of MLSS, should be considered. The results almost eliminate the probability of physical removal, because firstly, more biomass has not resulted in more ammonia removal and secondly, more removal of nitrite is not proportional to MLSS concentration increase of 10 times as an adsorbent.

Furthermore, by increasing the mixing rate, denitrifier microorganisms' activity and nitrate removal will decrease as denitrification occurs under anaerobic conditions. In fact, by increasing the intensity of mixing and also soluble oxygen, concentration nitrifier microorganisms will act better and ammonia removal will increase. By increasing the rate of shaker bacterial flocs are broken and SND process slows down, but in this study, the rate of shaking was not high enough to break flocs. In researches done by Weissenbachera *et al.* (2007) by increasing soluble oxygen concentration, the intensity of total nitrogen and ammonia removal increased and the intensity of nitrate removal decreased that is in accordance with results of this work.

The nitrogen removal from industrial wastewater using SND process has been experimentally proven to be an effective method in comparison with the traditional process. Based on our experimental results, nitrogen removal using SND method is potentially a novel process for wastewater treatment with almost 85% removal. This percent could be increased by optimization of conditions in treatment process. In this method, the biomass yield is very low, and consequently, little sludge is produced. Therefore, saving energy, costs and space than traditional process are benefices of this process. So, using this method for nitrogen removal from sanitary and industrial wastewater is so effective and will prevent release of nitrogen containing wastewater to the environment.

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