Journal of Advances in Environmental Health Research

Effluent quality of ammonia unit in Razi petrochemical complex

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Original Article

Abstract

Establishment of great industrial centers and ports along the Khur-Musa Estuary in Mahshahr Port (Khuzestan, Iran) have been discharged a high volume of industrial and non-industrial pollutants to this estuary. The most important pollutants in Khur-Musa include industrial wastes and effluents including ammonia and urea units. This research aimed to survey the qualitative parameters of effluent of ammonia unit No. 3 in Razi petrochemical complex, and comparing these parameters to the allowable effluent discharge standards in Iran. The main objective of this study was to investigate the performance of this unit, and providing proper solutions to solve the existing problems. Thus, at first, the process of production and sources of pollutants in the effluent were recognized and sampling points were determined. The data were collected by examinations on parameters chemical oxygen demand (COD), total suspended solids (TSS), nitrite ion (NO_2), nitrate ion (NO_3), pH, and (ammonia ion) NH_4, during a consecutive six-month period. The results of the measurements were recorded monthly, weekly, and daily. The results showed that the COD and the concentration of ammonia and nitrate ions in the effluent of studied unit were considerably higher than allowable values stated in the national standards of Iran. Comparison between stated parameters in the six-month period of sampling indicated a more desirable trend for the value of studied parameters in the last month of the study (September). In order to upgrading effluent treatment system, an effective action plan could be provided to optimize the current status of effluent from ammonia unit in Razi petrochemical complex.

KEYWORDS: Ammonia Unit, Petrochemical Complex, Effluent, Qualitative Parameters

Date of submission: 29 Oct 2012, ***Date of acceptance:*** 28 Jan 2013

Citation: Alavi N, Amir-Heidari P, Azadi R, Babaei AA. **Effluent quality of ammonia unit in Razi petrochemical complex.** J Adv Environ Health Res 2013; 1(1): 15-20.

Introduction

Environment is a great and complex set of diverse elements which has been formed as a result of gradual evolution of organisms and components of the earth's crust; therefore it affects the human activities and is affected by them. Human activities for development, in any way, will have different impacts on the environment. This impact is mostly caused by industrial development.[1] Through the two recent centuries, global nitrogen cycle has been changed substantially due to different human activities. Today nitrogen compounds enter into water bodies, in addition to natural sources, from man-made sources such as industrial wastes, untreated sewage, and effluent from waste treatment plants.[2] The main problem with the presence of nitrogen compounds in the effluents discharged to environment is consumption of dissolved oxygen in water, which may create great risks for aquatic ecosystem and marine life.[3] Razi

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petrochemical complex is one of the old petrochemical complexes in Iran, with 40 years of history in producing chemical fertilizers. This complex now is located in Mahshahr special economic zone (SEZ) and produces 675 tons of ammonia per year.

Establishment of great industrial centers and ports along the Khur-Musa Estuary has been discharged a high amount of industrial and non-industrial pollutants to this estuary. The most important pollutants in Khur-Musa include industrial wastes and effluents, overflow of produced ammonia and urea, sewages containing chemicals, and oil spill resulted from accidents in oil tankers and rigs. Khur-Musa with a wide grid of small estuaries has provided a favorable condition for the presence of aquatics; so that many commercial and non-commercial species permanently live in this area. In addition, many of these species use this estuary as a suitable place for spawning and as nursery.[4]

In addition to having valuable aquatics, Khur-Musa accepts a lot of rare migratory and native birds. In order to preserve this valuable ecosystem, it is essential to have more supervision on performance of petrochemical units in this area, particularly the ammonia unit.

The activity of Razi petrochemical complex, in addition to impacts on valuable ecosystem in Khur-Musa, will affect the neighboring cities such as Bandar Imam Khomeyni (BIK) and Bandar-e Mahshahr, and it may affect the health of residents in these cities. Therefore recognizing the negative impacts of this complex on environment is very important.[5] Since the petrochemical industries in Mahshahr port and Mahshahr SEZ are established close to the Khur-Musa Estuary and discharge their effluents to this water resource, and since the Khur-Musa is one of the special ecosystems located at the north of the Persian Gulf, this estuary is very important mainly due to its geographical position and biodiversity.

The objective of this research was surveying the qualitative parameters of effluent from ammonia unit No.3 in Razi petrochemical complex, in order to identify the current status of sources and values of pollutants emission, to decide on controlling strategies for minimizing pollutants in this industrial complex.

Materials and Methods

The ammonia unit is one of the most important production units in Razi petrochemical complex, whose main feed is sure natural gas, which is transmitted to this unit via a 174 km line from Masjed Soleyman gas wells. The unit produces 675 tons of ammonia per year. After mixing with steam and after reactions in the primary modifier, methane is converted to hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2). CO_2 is the by-product of ammonia unit, which is transmitted to urea unit after separation.

The complementary reaction is completed in the secondary modifier by injecting air; and the required nitrogen for ammonia production simultaneously enters into the process by this air. The mixture of nitrogen and hydrogen, which is called synthesis gas, following the compression at special pressure and temperature, is converted to ammonia in catalytic reactor.

The main amount of produced ammonia is used for production of urea and diammonium phosphate (DAP) fertilizers in the Razi petrochemical complex, and the remainder is supplied to international markets. Optimization of ammonia unit started in 1995 and the modernization operation of this unit was finished in 2000.[6]

After determining the boundary of the system, the sampling points were determined using existing maps and by consulting with industrial managers. According to the type of study process, since the system was closed, two sampling stations were selected for sampling and measurement of pollution parameters of effluent. In the first station, the inlet flow to the pretreatment system, corrugated parallel interceptor (CPI), and in the second station, the outlet flow from ammonia unit were selected for sampling. In these two stations, the qualitative parameters of the effluent, including pH, total suspended solid (TSS) (Method 2540D), ammonia ion (NH_3) (Method 4500-NH_3 F), nitrate ion (NO_3) (Method 4500-NO_3 B), nitrite ion (NO_2) (Method 4500-NO_2 B), and chemical oxygen demand (COD) (Method 5220 B) were measured according to standard methods for water and wastewater sampling and analysis.[7,8]

Grab and composite samplings were done during a continuous 6-month period, as the following:

a) Monthly sampling (from April to September), which was done once per month for each of the effluent polluting indexes.

b) Weekly sampling, which was done during 4 consecutivet weeks in the fourth month of study (July) for the polluting parameters of the effluent.

c) Daily sampling, which was done in 6 days of the last week of fifth month (August).

d) Composite sampling (hourly); due to fluctuations in the quality of effluent in the case of COD measuring this type of sampling was done just for measuring this parameter.

It should be mentioned that each composite sample is a mixture of samples which were collected in 4-hour intervals in each day, and this experiments were repeated in 3 consecutive days. After collecting the required data and performing the experiments, the results were compared to the standard values issued by The Iranian Department of Environment.

Results and Discussion

pH

The minimum and maximum values of pH were 7.6 and 9.2, respectively. The minimum and maximum values of this parameter were measured in September and June, respectively. The standard deviation of this parameter was 0.428 (Table 1 and 2).

Ammonia (NH_4)

The average value of measured ammonia ion during the six-month sampling period (monthly, weekly, and daily) was 152.36 mg/l. The minimum value (25 mg/l) and maximum value (426 mg/l) of ammonia in the sampling period were related to weekly sampling (2nd week of July) and monthly sampling (August), respectively. The value of this parameter in the sampling period had many fluctuations; and the standard deviation of that was 63.26 (Table 1).

Table 1. Average values of effluent qualitative parameters

Parameter / Time Period	Monthly average (mg/l)	Weekly average (mg/l)	Daily average (mg/l)	Compound average (mg/l)	Allowable value (mg/l)
pH	8.2	8.67	8.98	-	6.5-8.5
NH_4	101	102.75	132.83	-	2.5
NO_2	9.5	11.37	11	-	10
NO_3	65.3	77.25	78	-	50
COD	240	426.5	282.66	105	100
TSS	179	59	58.16	-	-

COD: Chemical oxygen demand; TSS: Total suspended solid

Table 2. Concentration of effluent pollutants during the total period of sampling

Parameter / Time Period	Total average concentration (mg/l)	Maximum concentration (mg/l)	Minimum concentration (mg/l)	Standard deviation (SD)
pH	8.61	10.5	7.8	0.428
NH3	112.19	528	25	63.26
NO2	10.62	15	6	1.56
NO3	73.51	162	40	29.79
COD	316.38	850	124	24.63
TSS	98.72	64	32	45.92

COD: Chemical oxygen demand; TSS: Total suspended solid

Nitrate (NO_3)

The minimum and maximum nitrate concentrations in the sampling period were 162 and 40 mg/l, respectively. The average value observed was 73.51 mg/l. The standard deviation of nitrate concentration was 29.8 (Table 1).

Nitrite (NO_2)

The total average value of nitrite in the six-month period of sampling (monthly, weekly, and daily) was 10.62 mg/l. The minimum and maximum value of nitrite in the sampling period was related to monthly sampling (April) and weekly sampling (4th week of July), respectively. The standard deviation of this parameter was 1.56 (Table 1).

COD

COD is a criterion used for determination of power and level of pollution in domestic and industrial wastes. This parameter is also useful for analyzing industrial wastewaters and also for determination and control of organic matter content removal resulted in wastewater treatment plants. The average value of this factor in the sampling periods (monthly, weekly, and daily) was 100 mg/l. The average value of this factor in the composite sampling was 105 mg/l, which is nearly equal to the standard limit. It also should be mentioned that the value of this parameter had many fluctuations in the sampling periods. The minimum and maximum value of this parameter during the sampling periods was related to daily sampling and weekly sampling (the 1st week of July), respectively, and the standard deviation of this parameter in the six-month sampling period was 24.63 (Table 1).

Total Suspended Solid (TSS)

In this research, during the six-month sampling period, the average TSS was 98.72, and the maximum (179 mg/l) and minimum (59 mg/l) values of it were measured in September and April, respectively (Table 1).

Conclusion

pH

As shown in table 1, the total average value of pH is a bit higher than allowable range of discharge to surface waters (6.5-8.5). The six-month trend of changes in the pH of effluent in the studied unit indicates that in the 66% of the cases, this factor was higher than the allowable limits (Figure 1). pH of ammonia nitrate unit effluent in Shiraz petrochemical complex was high (average 10, and maximum 10.8), as well,[9,10] which indicated that the high volume of ammonia production in both of these two complexes increased the pH in their effluent.

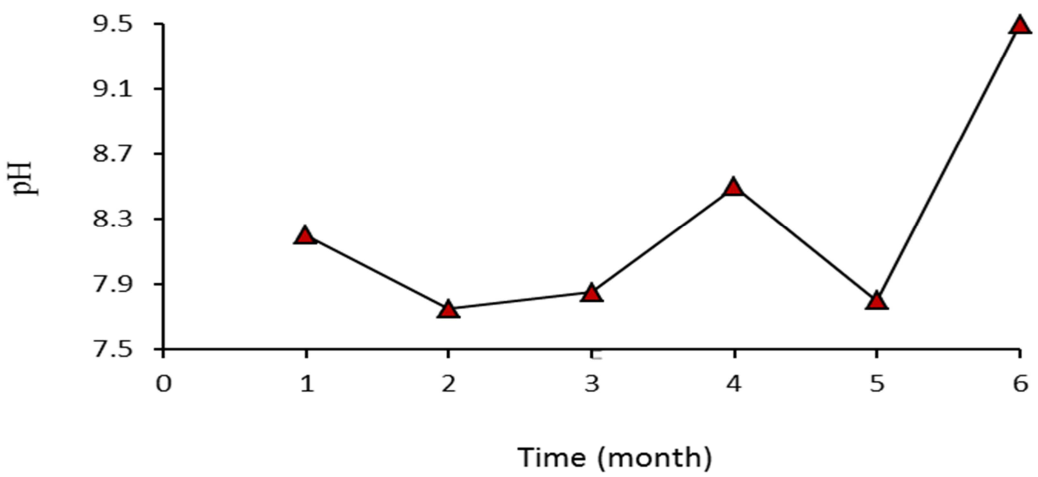

Figure 1. Monthly pH changes trend in effluent from ammonia unit in Razi petrochemical complex

Ammonia (NH_4)

The average value of the measured ammonia ion during the six-month sampling period (monthly, weekly, and daily) was much higher than the standard allowable value (2.5 mg/l) for discharge to surface waters. The results of sampling (monthly, weekly, and daily) indicated that in 100% of the cases, the value of this parameter in the effluent was higher than the standard allowable limit (Figure 2). Discharging this effluent without treatment is a threat to receiving waters. The results of similar researches on quality of effluent from ammonia nitrate unit in Shiraz petrochemical complex showed that the effluent of zone 2 in that complex had a high concentration of ammonia. The average concentration of ammonia of effluents discharging to water body was also 600 mg/l; and in the effluents discharging to lagoon this value was 910 mg/l, which can be returned to water treatment unit, if its ammonia is separated.[10] Therefore, since the outlet effluent from the under study unit and the other units of Razi petrochemical complex, after a primary treatment, are directly discharged to sea, this treatment is not enough ever, and the outlet effluent contains high value of NH_4 and COD.

Nitrate (NO_3)

According to figure 3, the total average value of nitrate in the sampling period (monthly, weekly, and daily) was also higher than allowable standard value (50 mg/l) for discharge to surface waters. According to the results of measuring nitrate parameter in the six-month sampling period (monthly, weekly, and daily), in the 62.57 % of the cases, the value of nitrate was higher than the standard allowable limit. According to a comparison between the value of nitrate in the studied unit and that in the ammonia nitrate unit of Shiraz petrochemical complex (average 1830 mg/l and maximum 3040 mg/l),[10] the discussed parameter in Razi petrochemical complex was much closer to standard allowable limit. Furthermore, the fluctuation of this parameter in the sampling period was not considerable.

Nitrite (NO_2)

As illustrated in figure 4, the total average value of nitrite in the six-month period of sampling (monthly, weekly, and daily) was almost equal to the standard allowable value (10 mg/l) for discharge to the surface waters.

According to the US Environmental Protection Agency (EPA) guidelines, the concentration of nitrite in drinking water should be less than 1 mg/l based on nitrogen. Moreover, its value in the effluent discharging to water sources must be less than 10 mg/l based on nitrogen. The average value of measured nitrite in the six-month sampling period was less than the standard allowable value (10 mg/l) for discharge to surface waters. One reason for the low value in effluents is its instability in the aqueous environments, and its conversion to nitrate.

COD

Chemical oxygen demand is a criterion used for determination of power and level of pollution in domestic and industrial wastes. This parameter is also useful for analyzing industrial wastewaters and also for determination and control of organic matter content removal resulted in wastewater treatment plants. The average value of this factor in the sampling periods (monthly, weekly, and daily) was higher than the standard allowable limit (100 mg/l) for discharger to surface waters; and the value of this parameter in all of the sampling periods was higher than the standards limit (Figure 5).

It should be mentioned that this parameter had many fluctuations in the sampling period, and this was probably due to process and equipment failure, operation errors, occasional or annual maintenance, etc. In the similar researches in the Bandar Imam petrochemical complex, the monthly average value of COD was reported 328 mg/l, which was higher than measured values in Razi petrochemical complex and the allowable standard limit.[5] In other researches in this complex, the annual average of COD was reported 220 mg/l.[11]

Total Suspended Solids (TSS)

The changing trend of this parameter in the sampling period had many fluctuations (Fig. 6). In a similar research in Bandar Imam petrochemical complex, in 2008 and 2009, the annual average value of this parameter in the outlet effluent from that complex was reported less than 100 mg/l, which is relatively less than that of Razi petrochemical complex.

Management Strategies

Following actions and management strategies are recommended for control of pollutants in the effluent of studied unit:

- Establishing and commissioning of waste treatment plant, considering the quality of outlet effluent from different units
- Performing actions to increase the performance of pollutants removal, including:

- Recovery of ammonia from effluent, through concentration and returning to ammonia production unit
- Diluting with hygienic waste to decrease the concentration of dissolved solids
- Establishing a treatment unit for ammonia removal at the beginning of the system
- Establishing a system to increase nitrification at the beginning, and then removing nitrate by de-nitrification processes at the end.

Decreasing the volume of effluent in the studied units.

Recommendations

Based on the results of experiments on qualitative parameters of the effluent during the six-month period of sampling (monthly, weekly, and daily), the results of measurement of ammonia, nitrate, and chemical oxygen demand were several times greater than the standard allowable limits obligated by Iranian Department of Environment for discharge to surface waters.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

The authors would like to thank the Research and Technology Deputy of Ahvaz Jundishapur University of Medical Sciences for their financial support.

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