Effect of Feammox on Landfill Leachate Treatment and Its Influence on pH

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Abstract. Feammox is a new biological nitrogen removal process which can synchronously achieve NH\textsubscript{4}+-N oxidation and Fe\textsuperscript{3+} reduction under the action of microorganisms. In order to investigate the starting of Feammox and the influence of different pH on the denitrification effect of simulated landfill leachate wastewater, the Feammox reaction was carried out by inoculating Anammox sludge under anaerobic conditions, and the N/Fe conversion pathway in the reaction was observed. On the 43rd day, the influent Fe\textsuperscript{3+} concentrations in the reactor was increased, and it was found that it promoted Feammox. Taking Feammox sludge in good operation as inoculation sludge, pH was set at 3.5-7.5, respectively. The results showed that the landfill leachate had the best denitrification effect when pH = 4.5, and the Feammox reaction almost did not exist in the reactor when pH = 3.5.

1. Introduction

The water quality of landfill leachate is complex, with high ammonia nitrogen content and rich organic matter and heavy metal content. It is considered to be a difficult pollutant with a large impact. In recent years, the Anammox process has attracted much attention for its advantages of low energy consumption and low sludge output. It can oxidize NH\textsubscript{4}+-N with NO\textsubscript{2}−-N as the electron acceptor under hypoxic conditions, but it is very harsh on environmental conditions. The nutrient ratio of landfill leachate is imbalanced and contains a large amount of toxic and refractory heavy metals, so the treatment effect of Anammox will be greatly restricted. Ygard et al\textsuperscript{1} evaluated the landfill leachate of four sanitary landfills in western Norway and found that the largest amount of heavy metal leaching was Fe, with a concentration of about 180mg/L. Li Dan and others also found that the most abundant heavy metal was iron when detecting compost leakage, with a concentration of 5.12-207.8mg/L.

Feammox is called iron reduction ammonia oxidation reaction, which refers to a method of removing ammonia that combines Fe\textsuperscript{3+} reduction and anaerobic ammonia oxidation under anaerobic conditions. The Feammox reaction can realize the simultaneous conversion of Fe\textsuperscript{3+} and NH\textsubscript{4}+. Yao Hainan et al. achieved a 52.73% nitrogen removal rate through Feammox treatment of landfill leachate. Scholars have found that the NO\textsubscript{2}− and NO\textsubscript{3}− produced by Feammox can oxidize Fe\textsuperscript{2+} to Fe\textsuperscript{3+}, which is called nitrate reduced iron oxidation (NDOFO). If NDOFO and Feammox can be connected to each other, Fe\textsuperscript{3+} can be regenerated by NDOFO and put into the next round of Feammox, thereby promoting the denitrification reaction cycle. However, Fe\textsuperscript{3+} regeneration in NDOFO is becoming less and less leading to the stagnation of Feammox cycle. Li et al.\textsuperscript{2} found that the addition of nitrate or aeration oxidation can promote the re-oxidation of Fe\textsuperscript{2+} to Fe\textsuperscript{3+}, which is good for promoting a virtuous cycle of Fe\textsuperscript{3+}/Fe\textsuperscript{2+}, the Feammox reaction can continue to occur and the denitrification effect is good. In this paper, Feammox reaction was initiated by inoculating Anammox sludge under anaerobic conditions.
sludge, and the changes of N and Fe concentrations during the process were observed, as well as the effects of increasing Fe$^{3+}$ concentrations on enrichment culture. The control groups were set to investigate the effect of different pH on the treatment of landfill leachate by Feammox.

2. Experimental apparatus and materials

2.1. Start of Feammox

2.1.1. The experimental device
The anaerobic ferrite fermentation tank (ASBR) with a total volume of 3.6L and an effective volume of 3L was used for sludge culture of Feammox. The reactor was controlled at 32 °C by heating the water tank. The influent pH was controlled between 7.4 and 7.6.

2.1.2. Inoculate sludge and test water
Anammox sludge, which was well run in the laboratory, was used as the inoculation sludge, and the influent NH$_4^+$-N 50mg/L and Fe$^{3+}$ 30mg/L were maintained.

2.2. Influence of different pH on denitrification rate of landfill leachate

2.2.1. Experimental device
Two 250ml serum bottles were used in the experiment, which was aerated with high purity nitrogen for 30 minutes before the reaction to remove the dissolved oxygen and sealed the bottle mouth. The temperature of the serum bottle was controlled at 28 °C through a thermostat and the stirring unit was operated at 120r/mins. The pH value of the simulated wastewater was adjusted to 3.5, 4.5, 5.5, 6.5 and 7.5 with 1mol/L dilute hydrochloric acid or 1mol/L sodium hydroxide. There were 5 parallel groups.

2.2.2. Sludge and experimental water
Through literature review, we believe that the quality of leachate of old landfill is as shown in Table 1. In this experiment, simulated leachate wastewater was used as the test wastewater. The main components were NH$_4$Cl:150mg/L, FeCl$_3$ 75mg/L, NaHCO$_3$ 600mg/L, KH$_2$PO$_4$ 27mg/L, CaCl$_2$·2H$_2$O 92mg/L, MgCl$_2$·7H$_2$O 16.5mg/L, and trace elements. Feammox sludge in good operation in experiment 1 was used as inoculation sludge.

| NH$_4^+$-N | NO$_2^-$-N | NO$_3^-$-N | Fe       | COD$_{CD}$ |
|------------|------------|------------|----------|------------|
| 100-350    | 1.1-3      | 2-12       | 0.6-130  | 100-400    |

2.3. Analysis method
Protein, NH$_4^+$, total nitrogen, NO$_3^-$, NO$_2^-$ Fe$^{2+}$, Fe$^{3+}$ volatile fatty acids were analyzed according to the report of Yang et al. 3

3. Results

3.1. Acclimation culture and N/Fe concentration change of Feammox
The whole process was carried out in an anaerobic reactor with influent NH$_4^+$-N concentration of 50mg/L and Fe$^{3+}$ concentration of 30mg/L maintained. As shown in Figure. 1-a, the reaction was divided into two stages: autolysis, acclimation and enrichment. In the autolysis stage (1-16 days), the effluent NH$_4^+$-N was greater than that in the influent, but the Fe$^{2+}$ concentration increased to some extent. This is because in thermodynamics, organic matter takes precedence over ammonium as the electron acceptor for Fe$^{3+}$ reduction 4, so the denitrification process of organic matter took place in the
faculty-oxygen condition at this stage. From the 17th day, the effluent ammonia nitrogen concentration began to decrease, which was the acclimation and enrichment period. From the 17th day to the 35th day, the effluent NH$_4^+$-N approached the influent water, indicating that the Feammox functional microorganisms began to enrich. From the 35th day, the effluent ammonia nitrogen was lower than the influent, and the amount of N loss increased with time. At this time, the Feammox reaction began to prevail. At the same time, the detection amount of organic matter was almost 0, which further indicated that heterotrophic denitrification was over and Fe$^{3+}$ began to act as the electron acceptor of NH$_4^+$. It is worth noting that the removal amount of NH$_4^+$ at this time was far beyond the theoretical value. According to the equation, when 30mg/L Fe$^{3+}$ participates in the reaction, the maximum loss of NH$_4^+$-N is 2.5mg/L. However, the decrease of NH$_4^+$-N at the 43rd day was 7.1mg/L, indicating that there were other reactions besides Feammox that caused the loss of N. As can be seen from Figure 1, both Fe$^{3+}$ and Fe$^{2+}$ fluctuated. For example, on the 16th to 25th day, Fe$^{3+}$ decreased from 14.31mg/L to 7.02mg/L. It then rose again to 15.67mg/L on the 35th day. Although Fe$^{2+}$ also fluctuated slightly, it still remained at a low concentration. For example, on the 42nd day, the decrease of NH$_4^+$-N was 7.1mg/L, while the effluent of Fe$^{2+}$ was 2.2mg/L, and the Fe/N ratio was much lower than the theoretical value of 3.

According to the equation, indirectly increasing the concentration of Fe$^{3+}$ by adding nitrate can increase the loss of ammonia nitrogen. From day 43, gradually increased influent Fe$^{3+}$ concentration. As shown in Figure 1-b, it can be seen that the initial ammonia nitrogen loss increased with the increase of Fe$^{3+}$ concentration, and the effluent Fe$^{2+}$ concentration continued to rise, indicating that most of the influent Fe$^{3+}$ was involved in the reaction and was reduced to Fe$^{2+}$. When the concentration of Fe$^{3+}$ was 40mg/L, the effluent ammonia nitrogen was higher than the influent, and the effluent Fe$^{2+}$ concentration decreased. When the concentration of Fe$^{3+}$ was 30mg/L, the loss of ammonia nitrogen and the concentration of Fe$^{2+}$ increased again. The results indicated that the increase of Fe$^{3+}$ concentration within a certain range could promote the conversion of ammonia nitrogen, but too high concentration would affect the activity of functional microorganisms and thus reduce the denitrification rate.

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3.2. Influence of different pH on denitrification rate of landfill leachate

As shown in Figure 2-a, when the pH of simulated wastewater was 4.5 and 5.5, the concentration of ammonia nitrogen was significantly reduced after 20 days of operation of the reactor. When pH = 4.5, the concentration of ammonia nitrogen decreased from 150mg/L to 31.6mg/L, and the conversion of ammonia nitrogen was 78.9%. When pH was 5.5 and 6.5, the conversion of ammonia nitrogen was 73% and 70%, respectively. When pH = 7.5, ammonia nitrogen concentration decreased from 150mg/L to 31.6mg/L.
to 78mg/L, and the denitrification rate was only 48%. At the same time, as shown in Figure 2-b, when the pH of simulated wastewater was 4.5, 5.5, 6.5 and 7.5, the concentration of Fe$^{2+}$ had an upward trend. When pH was 4.5, the concentration of Fe$^{2+}$ increased the most, from 1.7mg/L to 32mg/L. When pH =7.5, the concentration of Fe$^{2+}$ increased the least, from 1.7mg/L to 10.9mg/L. The inversely proportional range of Fe$^{2+}$ and NH$_4^+$ concentration changes with pH value indicated that Feammox can take place between pH 4.5 and 7.5, but acidic environment is more conducive to nitrogen removal. In the natural environment, Feammox reaction was mostly found in acidic soils. It is worth noting that when pH =3.5 the concentration of ammonia nitrogen increased significantly after 20 days of reactor operation, while the concentration of Fe$^{2+}$ fluctuated at a low level. This is because Feammox bacteria did not adapt to the acidic environment and therefore die. Cell lysis released ammonia nitrogen. At this time, Feammox reaction almost did not take place. In conclusion, when pH was 4.5, Feammox of simulated landfill leachate wastewater had the best denitrification effect.

**Figure 2. Changes of NH$_4^+$-N(a) and Fe$^{2+}$(b) concentration under different pH conditions**

### 4. Conclusion

The Feammox experiment was started by inoculating Anammox sludge. On day 43, Fe$^{3+}$ concentrations of influents were increased. The results showed that this methods could increase the amount of nitrogen loss. The results showed that when pH =4.5, the landfill leachate had the best denitrification effect, and when pH =3.5, the reaction denitrification performance was the worst because of the inactivation of Feammox bacteria in the acidic environment.

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2. Food waste induces surplus sludge to enhance the fermentation performance of L-lactic acid bacteria (1nqn202011), Project of Education Department of Liaoning Province, 2020

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