Simultaneous Removal of Chemical Oxygen Demand (COD) and Ammonium from Landfill Leachate Using Anaerobic Digesters

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ABSTRACT
BACKGROUND AND OBJECTIVE: Leachate, which contains large amounts of ammonium and hazardous organic compounds, can lead to the pollution of surface water and groundwater; consequently, leachate collection and treatment are essential before discharge into the environment. Anaerobic digestion is one of the most cost-effective methods of contaminated wastewater treatment. In this study, we aimed to evaluate the efficiency of an anaerobic digester in simultaneous removal of chemical oxygen demand (COD) and ammonium from landfill leachate.

METHODS: In this experimental study, a cylindrical anaerobic digester, made of Plexiglas sheets (with an inner diameter of 240 mm and useful volume of 10 L), was loaded with landfill leachate in Ghaemshahr, Iran. The effects of temperature (ambient temperature, 35°C, and 55°C) and various hydraulic retention times (1-5 days) on anaerobic digestion efficiency in COD and ammonium removal were assessed.

FINDINGS: At a hydraulic retention time of five days, maximum COD and ammonium removal (94% and 36%, respectively) was reported at thermophilic and ambient temperatures, respectively. The increase in hydraulic retention time had a positive impact on the efficiency of the digester in removing organic compounds and ammonium. Moreover, the rise in anaerobic digester temperature improved COD and ammonium removal.

CONCLUSION: According to our findings, the developed anaerobic digester could be used as a convenient and efficient tool for removing organic matters from landfill leachate. However, given the low efficiency of this digester in ammonium removal, an additional aerobic stage is required for wastewater treatment.

KEY WORDS: Waste, Leachate, Landfill, Anaerobic Digest, Organic Compound, Ammonium.

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Introduction

Leachate is a high-strength wastewater, which contains large amounts of organic and inorganic pollutants, ammonium (NH$_4^+$-N), heavy metals, hazardous organic matters, and pathogenic microorganisms (1,2).

The most important constituents of leachate include organic compounds, organic nitrogen compounds, and ammonium, which may pose serious environmental threats through landfill leachate discharge (3-5). The high concentration of nitrate in leachate (>10 mg/L as Nitrogen) significantly contributes to the pollution of groundwater and surface water. The organic compounds in leachate greatly influence the smell, taste, and oxygen depletion of groundwater and surface water (6).

The characteristics and discharge of landfill leachate are affected by different factors such as solid waste components, density, humidity, rainwater infiltration, season, temperature, and landfill operations. Overall, landfill age and waste stabilization rate are the most important factors influencing the composition of leachate (6).

The simple biodegradation of fresh leachate is attributed to the high concentration of volatile fatty acids. In this case, low pH, high biochemical oxygen demand (BOD$_5$), high chemical oxygen demand (COD), and large amounts of toxic compounds are among the characteristics of the produced leachate (7, 8). BOD$_5$/COD ratio of fresh leachate is much greater than that of old landfill leachate (9). In fact, BOD$_5$/COD ratio in old leachate is stabilized at < 0.2; consequently, biological processes are less efficient in the treatment of old leachate (4).

Old leachate contains a larger amount of resistant organic compounds, compared to fresh leachate; this hampers the treatment process and necessitates the use of advanced techniques (7). Landfill leachate can be treated, using various biological (i.e., aerobic or anaerobic methods) and physical-chemical (e.g., precipitation, oxidation, adsorption, and reverse osmosis) methods (5). Aerobic processes are only suitable for the treatment of biodegradable leachate with low concentrations of organic compounds (2), whereas anaerobic methods are prioritized for the treatment of leachate with high COD and BOD$_5$ (10).

High efficiency in COD reduction and removal, limited sludge production, energy renewal in form of methane, and reduced need for energy and chemicals are the major advantages of anaerobic processes (11). In fact, in recent years, use of anaerobic digesters has been taken into consideration due to significant methane production (12, 13). Several studies have been conducted on leachate treatment via biological methods in Iran and other countries. In this regard, Yang et al. used a simultaneous aerobic and anaerobic bio-reactor system to remove organic pollutants and ammonium from leachate. Based on their findings, the efficiency of this system in COD and ammonium removal was estimated at 94% and 95%, respectively (14).

Moreover, Sun et al. evaluated advanced leachate treatment, using a two-stage Upflow Anaerobic Sludge Blanket (UASB)- Sequencing Batch Reactor (SBR) system at a low temperature. The results showed that SBR plays the main role in ammonium removal (15).

Additionally, in another study, the efficiency of an anaerobic baffled reactor, modified by an anaerobic filter, in COD removal was reported to be 39-96% (16). Also, Kheradmand et al. used a combined activated sludge anaerobic digestion model for the treatment of leachate, generated from municipal solid waste (6). Overall, limited studies have been conducted regarding the simultaneous removal of COD and ammonium from landfill leachate in Iran. This study aimed to evaluate the efficiency of an anaerobic digester in simultaneous removal of COD and ammonium from landfill leachate at different temperatures and hydraulic retention times (HRT).

Methods

Design of the anaerobic digester: The anaerobic digester was composed of a Plexi glass cylinder with an inner diameter of 240 mm and net volume of 10 liters. Leachate was injected to the anaerobic digester from the bottom, using a pump (ProMinent® Concept Plus Series). To set the temperature and facilitate the mixing process in the anaerobic digester, an aquarium heater and an IKA C-MAG HS hot plate magnetic stirrer (with a 10 cm magnet) were used (10).
were collected from a landfill, located in Ghaemshahr, Iran (table 1).

**Seeding the anaerobic digester:** Approximately 50% of the volume of anaerobic digester was filled with the return activated sludge from the aerated lagoon of Ghaemshahr Wastewater Treatment Plant. The anaerobic digester system was ready for launch after 40 days of seeding. It should be mentioned that seeding is one of the most important procedures of anaerobic wastewater treatment for providing a suitable microbial population for the treatment process.

<table>
<thead>
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<th>Parameters</th>
<th>Unit</th>
<th>Amount</th>
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</thead>
<tbody>
<tr>
<td>pH</td>
<td>---</td>
<td>6.8-6.96</td>
</tr>
<tr>
<td>Biochemical Oxygen Demand (BOD)</td>
<td>mg/l</td>
<td>8070-8120</td>
</tr>
<tr>
<td>Chemical Oxygen Demand (COD)</td>
<td>mg/l</td>
<td>19300-19450</td>
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<tr>
<td>Total nitrogen (TN)</td>
<td>mg/l</td>
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</tr>
<tr>
<td>Nitrate</td>
<td>mg/l</td>
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<tr>
<td>NH4+ - N</td>
<td>mg/l</td>
<td>150-160</td>
</tr>
<tr>
<td>Total phosphorous (TP)</td>
<td>mg/l</td>
<td>13.5</td>
</tr>
</tbody>
</table>

**Reactor commissioning and operation:** The HRT of the anaerobic digester (with two liter discharge per day) was set at five days. Afterwards, different concentrations of COD (3250-19450 mg/l) were prepared by diluting raw leachate in water (1:1 to 1:5); eventually, pure leachate was collected. To provide the optimal conditions for microbial growth, COD:N:P ratio was set at 1:5:300 during the commissioning of anaerobic digester.

Moreover, to provide the phosphorus required for bacteria, potassium dihydrogen phosphate solution was used. In the next stage, we assessed the effects of HRT (range: 1-5 days) and temperature (i.e., ambient temperature, 35°C, and 55°C) on anaerobic digestion efficiency in ammonium and COD removal. In this study, all stages of sampling and testing were in accordance with the standard methods (17). COD test was based on closed reflux, colorimetric method (522OD method). Also, ammonia was measured through direct nesslerization (4500C method), using a Varian spectrophotometer (UV-120-02) at a wavelength of 425 nm (17). Also, pH and dissolved oxygen (DO) in the reactor were measured, using a pH meter (Testo 206) and DO meter (Hanna HI 9142), respectively. All the tests were repeated at least twice in order to reduce the possibility of errors and increase accuracy. The removal (rate) of pollutants (parameters) was calculated after determining the value of selected parameters.

Finally, one-way ANOVA was performed, using SPSS version 17.0 to compare anaerobic digestion efficiency in ammonium and COD removal at different temperatures and HRTs. P-value less than 0.05 was considered statistically significant.

**Results**

**Anaerobic digestion efficiency in COD removal:** By increasing HRT from one to five days, digestion efficiency in COD removal increased from 68% to 82% at ambient temperature, from 72% to 88% at mesophilic temperature (35°C), and from 80% to 94% at thermophilic temperature (55°C) (Figure 1). Minimum efficiency of the anaerobic digester in COD removal was 68% at ambient temperature with one-day HRT, while maximum efficiency in COD removal was 94% at a temperature of 55°C with a five-day HRT. Under these circumstances, COD concentrations of 6200 and 1160 mg/L were obtained, respectively. COD removal efficiency was 88% at 35°C and 82% at ambient temperature. Also, the highest COD removal efficiency was 94% at thermophilic temperature. Therefore, optimal HRT for COD removal was five days and the ideal temperature for this process was 55°C (p<0.05).

**Anaerobic digestion efficiency in ammonium removal:** The mean efficiency of ammonium removal by the anaerobic digester decreased from 29% to 24% and 14.5% by increasing the ambient temperature to 35°C and 55°C, respectively (p=0.00)(Figure 2).

Ammonium removal efficiency in the anaerobic digester diminished by decreasing HRT; consequently, the concentration of (disposed ammonium) (ammonium output) in the anaerobic digester increased. The minimum ammonium removal efficiency in the anaerobic digester was 7.6% at 55°C with a one-day HRT, while maximum efficiency was estimated at 36% at ambient temperature with a five-day HRT.
Simultaneous Removal of Chemical Oxygen Demand (COD)…; M. Tahmasbizadeh, et al

Discussion

In the present study, the anaerobic digestion efficiency in COD removal improved by increasing the temperature; in other words, the concentration of (outlet COD) (COD output) decreased in the anaerobic digester. Overall, the anaerobic digester showed higher efficiency in COD removal at thermophilic temperature, compared to mesophilic and ambient temperatures.

In this regard, Yilmaz and colleagues evaluated the treatment of paper industry wastewater by using anaerobic filters at mesophilic and thermophilic temperatures. The results showed that COD removal was more efficient at thermophilic temperature, compared to mesophilic temperature (18). Moreover, Ahn and colleagues reported similar findings (19). The results of the present study showed that COD removal improved by raising the temperature of anaerobic filter from ambient to mesophilic and thermophilic temperatures. Similar findings have been reported by Farzadkia et al., who found a significant decline in pathogens and fecal coliforms in anaerobic digesters at thermophilic temperature (20).

In the present study, reducing HRT from 5 days to 4, 3, 2, and 1 day in the anaerobic digester increased organic loading from 3.88 to 4.85, 6.47, 9.7, and 19.4 kg COD/m³/d, respectively. Moreover, COD removal efficiency improved by increasing HRT; in other words, the (outlet COD) (output COD) concentration in the anaerobic digester decreased. Overall, increased (contact) (exposure) of microorganisms to organic compounds in the reactor leads to greater consistency and increased consumption of COD as a source of carbon for these microorganisms.

According to a study by Chen et al., by reducing HRT in leachate treatment via Moving Bed Biofilm Reactor (MBBR), concentration of the (outlet COD) (as the output of) in the anaerobic and aerobic units increased (2). Additionally, based on a study by Timur et al., COD removal efficiency decreased from 83% to 72% in the anaerobic sequencing batch reactor at mesophilic temperature by reducing HRT from 5 days to 1.5 days (21).

According to a study by Farzadkia et al., COD removal efficiency decreased from 96% to 79% in an aerobic reactor by reducing HRT from 8 to 2 hours (22). Also, the effect of HRT on the performance of up-flow septic tanks was evaluated in a study by Moussavi and colleagues. The results showed that the efficiency of this system significantly diminished by decreasing HRT (23).

Based on the findings of the current study, the anaerobic reactor showed high efficiency in COD removal, which was partly due to the high ratio of biodegradable substrates in leachate. BOD₅/COD ratio was 0.4 in the raw leachate sample from the landfill. Comparison of this ratio with the values reported by Metcahf (0.3 to 0.8 in raw urban sewage) represents the significant biological decomposition of organic compounds in leachate. If BOD₅/COD ratio is less than 0.3, toxic substances are present in wastewater, causing difficulties in the biodegradation of waste (11).

In the present study, mixture of leachate with sludge in the digester led to proper contact and distribution of microbes and organic compounds, which can be quite useful in COD removal. Similar results were reported by Chen et al., who reported 80-91% efficiency of an anaerobic reactor in COD removal (2). Also, the study of anaerobic digestion
efficiency in ammonium removal showed that the average efficiency of the anaerobic digester decreased from 29% to 24% and 14.5% by increasing the ambient temperature to 35°C and 55°C, respectively. Therefore, the highest efficiency of the anaerobic digester in ammonium removal was observed at ambient temperature. The results reported by Liang et al. on the control agents in nitrogen (removal) treatment of landfill leachate showed that ammonium removal efficiency remained unchanged by increasing the temperature (20-30°C); however, a decline was reported at temperatures higher than 35°C (24). In the present study, ammonium removal efficiency in the anaerobic digester diminished by reducing HRT; therefore, the concentration of the (outlet ammonium) of anaerobic digester increased. This finding was confirmed by a study by Chen and colleagues, which reported a decline in ammonium removal efficiency from 97% to 20% by reducing HRT from 3.8 to 2.3 days (2).

Moreover, in a study by Chakraborty et al. on the effect of HRT on ammonium removal in an anaerobic-anoxic-aerobic system, ammonium removal efficiency increased by decreasing HRT. Based on their findings, ammonium removal efficiency decreased from 97% to 93%, 90%, and 68% by decreasing HRT from 3.5 days to 2, 1.5, and 1 day, respectively (25). In the present study, maximum efficiency of the anaerobic reactor in ammonium removal was estimated at 36%. As indicated by previous studies, this may be related to the low consumption of ammonium by bacteria via anaerobic microbial uptake (2, 26). Agdag and colleagues employed the upflow anaerobic sludge blanket technology, modified with continuous stirred tank reactors, for the treatment of landfill leachate. The rate of ammonium removal was reported at 15-34%, 90%, and 99.6% in the anaerobic reactor, aerobic reactor, and the total system, respectively (27). Also, according to a study by Kettunen et al., the maximum capacity of the anaerobic unit in ammonium removal was 10%, while the aerobic unit was able to remove about 80% of ammonium (26). In conclusion, under specific circumstances, i.e., proper setup, high HRT, and high temperature, anaerobic digesters are relatively efficient in the removal of organic compounds. COD removal was at its highest (94%) with a five-day HRT at thermophilic temperature; however, at ambient temperature, the maximum efficiency of ammonium removal was 36% under optimal conditions.

Despite the proper treatment of organic compounds in the anaerobic digester, this method has some limitations in ammonium removal, according to environmental standards. Therefore, additional processes such as aerobic treatment should be applied for efficient removal of ammonium.

Acknowledgments

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References


