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Effect of High Ammonia Concentration on UASB Reactor Treating Sanitary Landfill Leachate

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Abstract

Landfill leachate always contains high amounts of organic and inorganic waste which make its treatment hard. Combined biological and chemical treatment methods should be used to reduce high pollution loads to the discharge limits. Anaerobic digestion is the ideal method for removal of high organic carbon loads. However many inhibitory substances adversely affect the process stability and methane yield. High free ammonia concentration is primary cause of inhibition in anaerobic treatment. In this study leachate coming from Istanbul Komurcuoda Landfill was treated with upflow anaerobic sludge bed (UASB) reactor for 600 days. After inoculation of reactor, influent ammonia concentration was gradually increased from 100 mg/L to 2800 mg/L in order to observe the free ammonia effect on anaerobic treatment. Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) removal efficiencies decreased gradually from 95% to 15% while ammonia concentration was increased. Although anaerobic bacteria have been adapted to ammonia concentration, inhibitory effect of ammonia was observed at 1000 mg/L ammonia concentration.

Keywords: Leachate, Anaerobic Treatment, Free Ammonia Inhibition, UASB

Yüksek Amonyak Konsantrasyonunun Katı Atık Düzenli Depo Sahası Sızıntı Suyunu Arıtan YAÇY Reaktörü Üzerindeki Etkisi

Özet

Katı atık düzenli depo sahası sızıntı suyu her zaman arıtımını zorlaştıran yüksek miktarlarda organik ve inorganik atık içerir. Yüksek kirlilik yüklerini deşarj limitlerine kadar azaltmak için birleşik biyolojik ve kimyasal arıtma metotları kullanılması gerekir. Anaerobik parçalanma yüksek organik karbon yüklerinin giderimi için ideal bir metottur. Fakat birçok inhibitör madde prosesin kararlılığını ve metan üretimini olumsuz etkilemektedir. Yüksek serbest amonyak konsantrasyonu anaerobik arıtımda inhibisyonun birincil sebebidir. Bu çalışmada İstanbul Kömürcüoda Katı Atık Düzenli Depo Sahasından gelen sızıntı suyu yukarı akışlı çamur yatağı (YAÇY) reaktör ile 600 gün arıtılmıştır. Reaktörün aşılanmasından sonra, giriş amonyak konsantrasyonu anaerobik arıtımda serbest amonyak etkisini gözlemlemek için 100 mg/L den 2800 mg/L ye kademeli olarak arttırılmıştır. Amonyak konsantrasyonu arttırılırken, Kimyasal Oksijen İhtiyacı (KOİ) ve Biyokimyasal Oksijen İhtiyacı (BOİ) giderim verimleri %95 ten %15 e kadar kademeli olarak azalmıştır. Anaerobik bakteriler amonyak konsantrasyonuna adapte edilmelerine rağmen, amonyağın inhibitör etkisi 1000 mg/L amonyak konsantrasyonunda gözlemlenmiştir.

Anahtar Kelimeler: Sızıntı Suyu, Anaerobik Arıtım, Serbest Amonyak İnhibisyonu, YAÇY

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INTRODUCTION

Leachate by means of any liquid contains significantly high organic and inorganic waste material that drains from a solid waste landfill. The proper methods must be selected for leachate treatment due to complexity of waste material in leachate. In literature several chemical and biological treatment methods have been investigated for leachate treatment. One of these methods that could be used for COD removal is the anaerobic digestion which supplies both pollution control and energy recovery from generated methane yield [1]. In addition anaerobic digestion has low sludge production rate and requires low energy [2]. However operation of anaerobic digestion is difficult due to sensitivity of anaerobic bacteria to environmental conditions such as pH, temperature and toxic substances [3].

Ammonia nitrogen is one of the most common toxic substances to bacteria when it is found in wastewater in large amounts. Ammonia is produced due to degradation of proteineous organic material and conversion of organic nitrogen under anaerobic conditions [3,4]. The following stoichiometric relationship gives the amount of ammonia generation of anaerobic biodegradation of organic substrate [5];

$$C_aH_bN_d + \frac{4a-b-2c+3d}{4}H_2O \rightarrow \frac{4a+b-2c-3d}{8}CH_4 + \frac{4a-b+2c+3d}{8}CO_2 + dNH_3 \qquad (1)$$

In aqueous phase two principal forms of inorganic ammonia, free ammonia (FAN) (NH_3) and ammonium ion (NH_4^+), found in equilibrium with hydrogen ion (H^+) are shown as following equation;

$$NH_4^+ \longleftrightarrow NH_3 + H^+ \qquad (2)$$

Ammonium ion and free ammonia are called total ammonia nitrogen (TAN). As can be seen from the equation (2), ammonium ion and free ammonia concentrations depend on pH. Since free ammonia has been suggested to be the actual toxic agent, at lower pH, ammonium and hydrogen ions are dominant species however when pH increases reactions shifts to right and increases the free ammonia concentration so it is result in increased toxicity.

While ammonium ion is an essential nutrient source by means of nitrogen for anaerobic bacteria, free ammonia has inhibitory effect since it is freely membrane permeable [6]. Proton imbalance, and/or potassium deficiency may occur by the diffusion of hydrophobic ammonia molecule into the bacteria cell [7]. Also free ammonia directly inhibits the activities of methane synthesizing enzymes which results in methane production failure. In literature ammonia concentrations lower than 200 mg/L are beneficial to anaerobic process since it is used in growth of anaerobic microorganisms. Other factors such as temperature, pH, acclimation periods and differences in substrates can influence the inhibiting ammonia concentrations [3].

Table 1. Effects of total ammonia concentrations

Total Ammonia	Effect
50–200mg/l	Beneficial
200–1000mg/l	No adverse effect
1500–3000mg/l	Inhibitory at pH > 7

Both microbial growth rates and free ammonia concentration are affected by changing in temperature. Not only increased process temperature in general has a positive effect on the metabolic rate of the microorganisms but also results in a higher concentration of free ammonia [1]. Certain ions such as Na^{+}, Ca^{2+}, and Mg^{2+} were found to be antagonistic to ammonia inhibition, a phenomenon in which the toxicity of one ion is decreased by the presence of other ion(s). Ammonia and sodium showed mutual antagonism, when each ion can antagonize the toxicity produced by another ion. [8].

Acclimation of anaerobic bacteria to ammonia concentration can influence the degree of ammonia inhibition. Predominant species of methanogens may be shifted into the methanogenic population by the adaptation [9]. Microorganisms that adapted to free ammonia have higher resistance to inhibition. Influent ammonia concentration of landfill leachate has been gradually increased to investigate the influence of free ammonia concentration on UASB reactor in this study. To determine the inhibitory effect of effluent COD concentrations and removal efficiencies have monitored for 600 days.

Material and Methods

Istanbul Komurcuoda MSW Landfill

Istanbul Komurcuoda MSW Landfill site has been accepting solid wastes since 1996 and constructed in 89 ha storage area. It is composed of six storage valleys and currently 17.000,000 m^3 solid wastes have been stored. The landfill has leachate treatment plant composed of ultrafiltration and nanofiltration processes that shown on figure 1, operated with average flowrate of 1100 m^3/day.

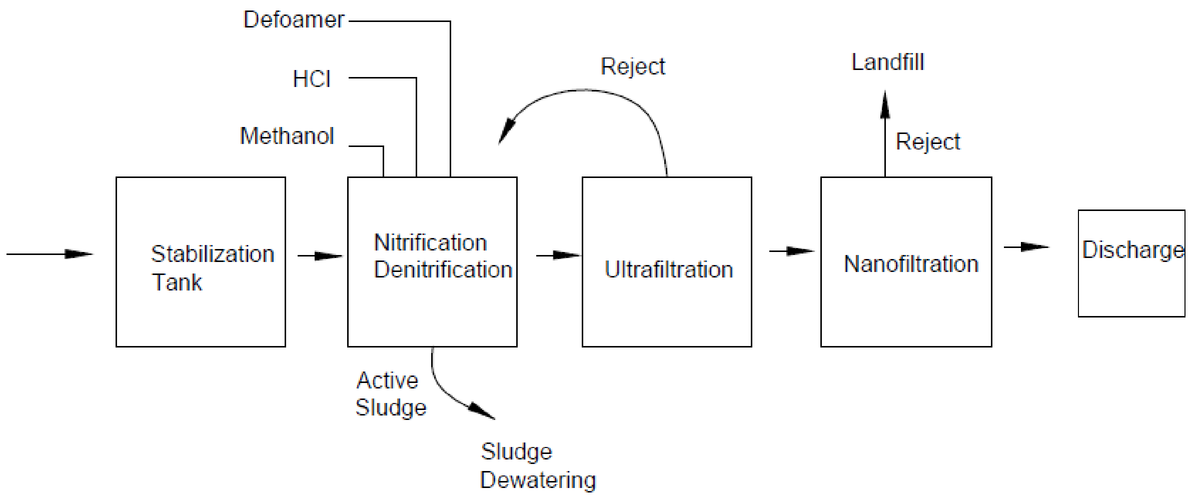

Figure 1 İstanbul Komurcuoda leachate treatment plant flow diagram.

Landfill Leachate

Leachate was originated from Istanbul Şile Komurcuoda Municipal Solid Waste Landfill with average COD concentrations 25800 mg/L and 2160 mg/L NH_4_N concentrations. Leachate was taken once in two months and stored at 4°C. Physical and chemical characterization analysis of leachate was performed immediately. Third times in a week influent analysis were performed while effluent analysis in each day. Samples were taken twice in a month from all sampling ports in order to observe bacterial activities inside the reactor (no data shown).

Seed Sludge

The anaerobic sludge was taken from UASB reactor of PAKMAYA Co. that treat wastewater containing yeast residues. The volatile suspended solid (VSS) concentration was measured as 16400 mg/L that was about 75 % percent of the total suspended solid (TSS) concentration.

Chemical Analysis

In the influent and effluent of the reactor total Kjeldahl Nitrogen (TKN), COD, BOD_5, TAN, pH and alkalinity were monitored every day. TSS and VSS analysis were conducted once in two weeks by taking samples from all ports. The reactor has been fed with leachate without making any pH adjustment. All analysis has been conducted according to the Standard Methods [10].

Reactor Configuration and Operation

The UASB reactor was made of plexiglas material and it had 7,4 l effective volume. It was 0,85m height and had 0,11 m diameter. There were four sampling ports vertically located on the reactor for taking samples. The reactor was fed with peristaltic pump to the funnel which connected to the bottom of the reactor. Leachate was given to the reactor with flow rate of 4,5 L/day by providing the hydraulic retention time 1,6 days. The reactor was held in incubator to adjust the temperature at 35 ± 2 ^{o}C. Reactor configuration is shown in Figure 2.

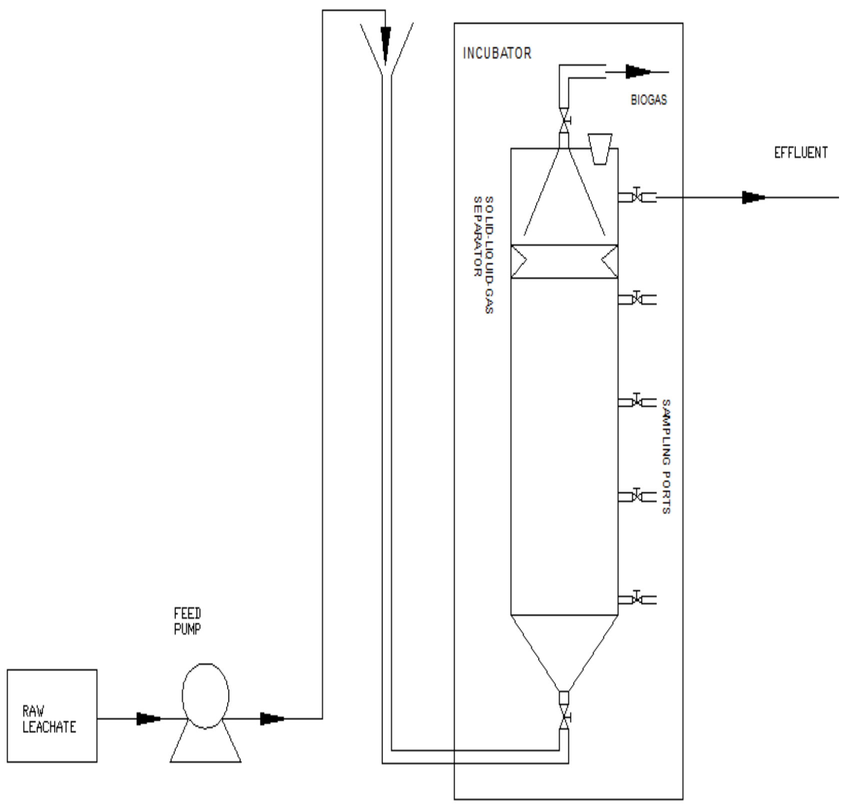

Figure 2 UASB reactor configuration

H_3PO_4 was added to raw leachate to prevent phosphorus deficiency and NH_4Cl was used to increase ammonia concentration up to 2800 mg/L .

Free Ammonia Calculation

The concentration of free ammonia nitrogen (FAN) was calculated by using the following equations; [11]

$FAN = \frac{TAN}{1+10^{(pKa-pH)}}$ $pK_a = 0.09018 + \frac{2729.92}{T+273.15}$ Where, pK_a is the dissociation constant for ammonium ion, 8.95 at 35 ^oC; T the temperature, °C

Results and Discussions

Komurcuoda landfill leachate exhibited variable characteristics during the operation of UASB reactor. COD concentrations have been decreased while the pH of leachate was increased. Also BOD and COD ratio has been decreased from 0.64 to 0.3 which indicates the age of leachate COD concentrations have ranged between 37760 and 9215 mg/L and BOD_5 between 24465 and 2910 mg/L. COD and BOD_5 values were higher at the beginning of the study but they decreased in time. The important parameter that effects the free ammonia concentration was pH and it has been increased from 7,5 to 8.3 as the time passes. The detailed characterization of leachate is shown in Table2.

Table 2 Characterization of MSW Landfill Leachate of Istanbul Komurcuoda

	Max.	**Min.**	**Avg.**
pH	8,3	7,5	7,8
Conductivity (µS/cm)	29900	24000	28033
Total Alkalinity (mg/L $CaCO_3$)	11800	8100	10408
TDS (mg/L)	18220	14070	16220
TSS (mg/L)	3440	685	1971
VSS (mg/L)	2100	450	1188
TS (mg/L)	30350	18140	24851
TVS (mg/L)	17970	5600	11974
COD (mg/L)	37760	9215	25817
BOD_5 (mg/L)	24465	2910	13188
TOC (mg/L)	10774	4830	8044
TKN (mg N/L)	3090	2115	2531
Ammonia (mg N/L)	2560	1830	2161
Color (Pt-Co)	45000	15600	29162
Chloride (mg/L)	5950	2600	4200
Sulfate (mg/L)	<20	<20	<20
Total Phosphorus(mgP/L)	27	12,3	18,2

In the start-up period of the reactor raw leachate was diluted with dechlorinated tap water before given to the reactor to maintain organic loading rate at 1kg COD/m^3.d. Influent COD concentration was adjusted to 2000 mg/L where ammonia concentration was 170 mg/L for two weeks. After this period, influent concentration of COD and ammonia concentrations were increased gradually. Maximum organic loading rate was 4 kg COD/ m^3.d during the operation.

After 60 days influent COD and ammonia concentrations increased to 5000 mg/L and 390 mg/L respectively. COD and BOD_5 removal efficiencies varied from day by day in the acclimation period. There was no free ammonia effect in this period so these variations caused by the acclimation of anaerobic bacteria to the leachate.

After day 100 COD removal efficiency increased linearly until day 250. In this period influent COD concentrations were increased by decreasing the dilution ratio with tap water. Maximum removal efficiencies were achieved in day 250. COD and BOD_5 removal efficiencies were 92% and 95% at that time. Generally, free ammonia inhibition in anaerobic treatment at mesophilic conditions has been reported in the range of 50–150 mg/l [12] however when the maximum removal efficiencies reached free ammonia concentrations were about to 100 mg/L as shown in Figure 3 and 4.

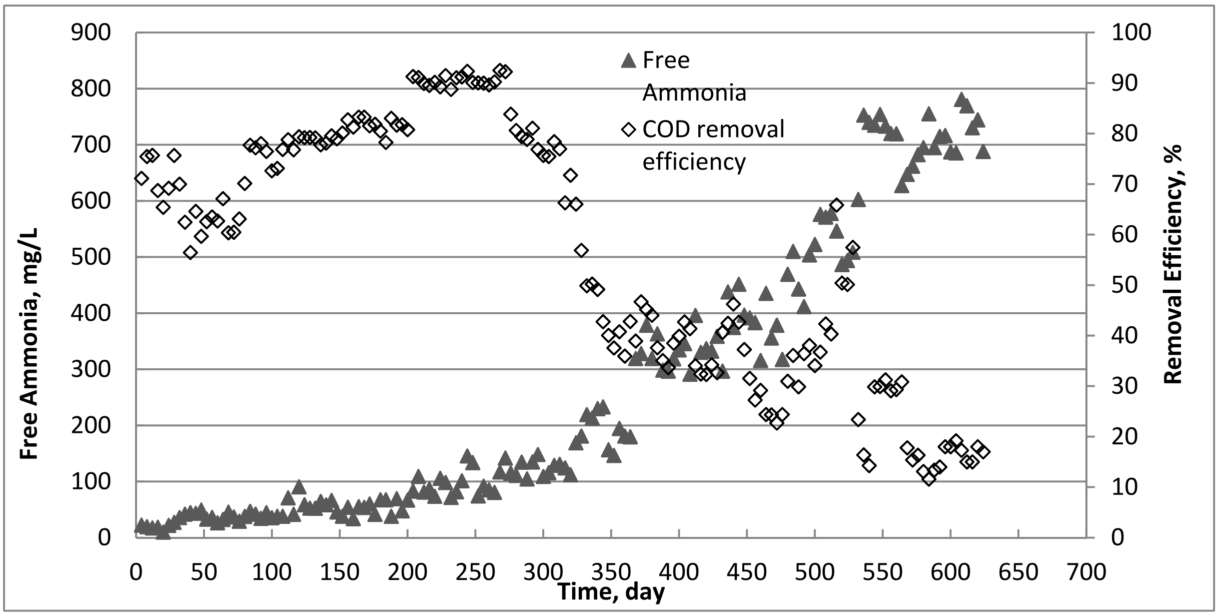

Figure 3 Change of COD removal efficiency and free ammonia

The UASB reactor had been fed with raw leachate after day 250. Sharp decrease was seen in COD removal efficiencies until day 350 because ammonia concentration was increased by the decrease of dilution ratio. After day 300 ammonia concentration was above the 1000 mg/L inside reactor. At this level COD removal efficiencies started to decrease from 80% to 40% and inhibitory effect of ammonia was observed clearly. Between the day 350 and 450 despite the free ammonia concentration had been increased continuously COD removal efficiencies did not show high differences.

After day 500 free ammonia concentrations were increased above 500 mg/L and this was result in sharp decrease of COD removal efficiency. 10% of removal efficiency was seen at day 580 however 20 days later COD removal efficiency increased to 15% when the free ammonia concentration was 780 mg/L.

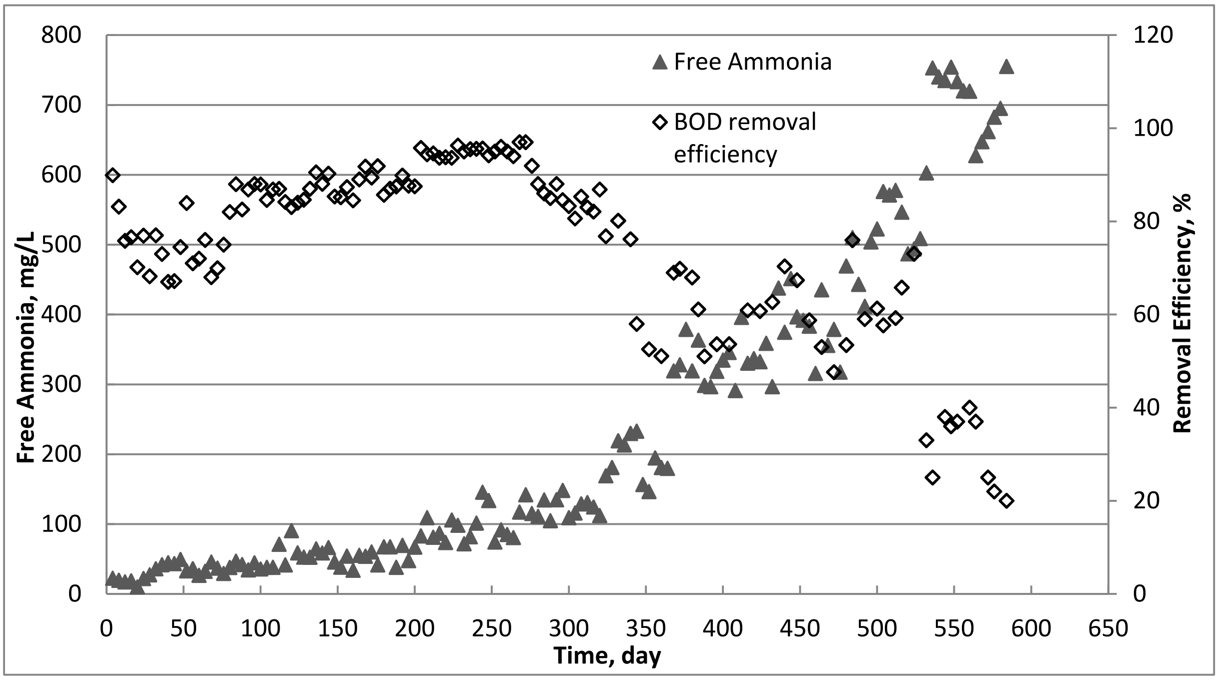

Figure 4 Change of BOD removal efficiency and free ammonia concentrations

Increasing of raw leachate pH and conversion of volatile fatty acids to the methane led to increase in pH inside the reactor. By the inhibition of methanogenic bacteria volatile fatty acid accumulate inside reactor. Sung (2003) was reported that increased in volatile fatty acid concentration caused a decrease in pH and alkalinity however high total alkalinity concentration had prevented pH decrease due to volatile fatty acid accumulation. Figure 5 shows the pH effect on free ammonia concentrations. The unionized fraction of ammonia was reported to have more toxic effect on anaerobic bacteria, increased by the pH rising [13]. COD removal efficiencies were too low at the high pH with respect to lower pH because of these phenomena.

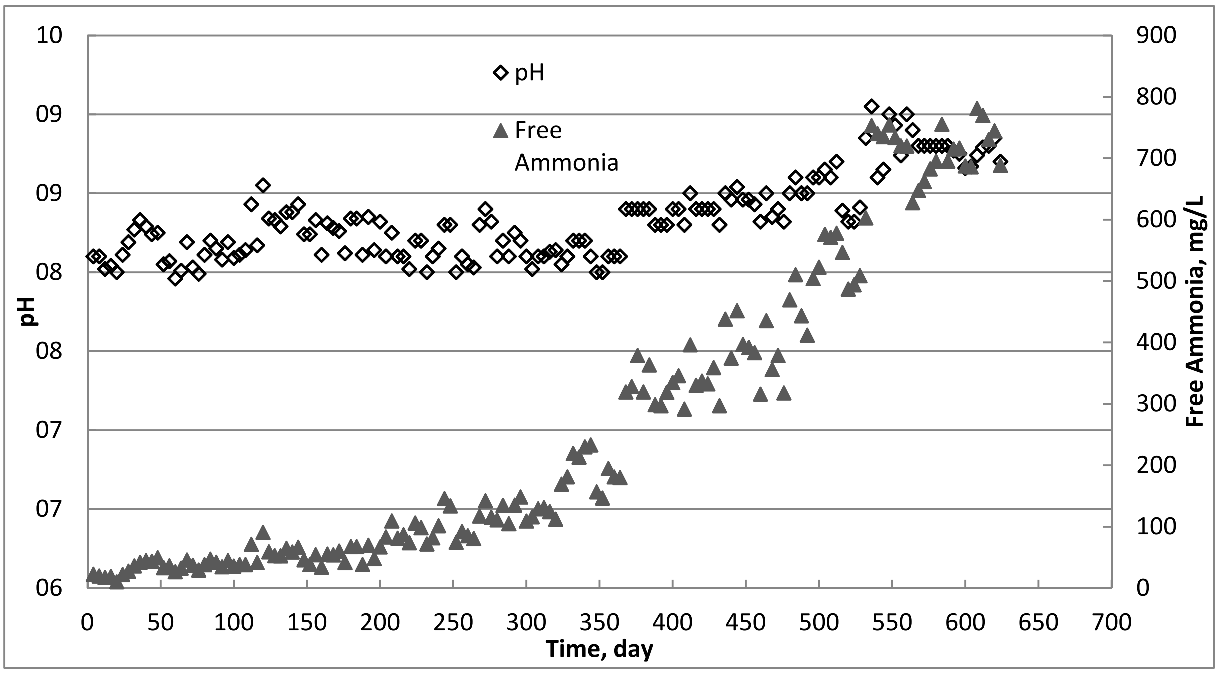

Figure 5 Free ammonia and pH concentrations inside the UASB reactor

In addition to this, Oz Eldem (2006) reported that methane production in anaerobic treatment was significantly decreased above pH 7.8 due to effect of total ammonia nitrogen [14]. In our study when the influent NH_4_N concentration was increased to 2800 mg/L free ammonia concentration was reached to 780 mg/L with influence of high pH inside reactor and COD removal efficiency decreased to 10% at this point. It was reported in literature this level was the maximum free ammonia concentration that anaerobic bacteria could survive [15, 16].

As a result high free ammonia concentrations adversely affect the anaerobic treatment's efficiency at high pH levels. Raw leachate needs to be treated or diluted with other wastewaters to reduce the ammonia concentration.

CONCLUSION

Consequently, anaerobic treatment is an effective way of the removal of high COD concentration in leachate. Respectively 95% and 92% COD and BOD_5 removal efficiencies were obtained during the operation. However, anaerobic bacteria are susceptible to high ammonia concentrations. The decrease in COD removal efficiency was observed above 1500 mg/L ammonia concentration and anaerobic bacteria were completely inhibited at 780 mg/L free ammonia concentration. Operational parameters should be controlled and several precautions should be taken in order to counteract the ammonia inhibition.

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