



Comparison Between Biological Treatment and Chemical Precipitation for Nitrogen Removal from Old Landfill Leachate

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Abstract: The study reports the results of a laboratory scale investigation aimed at evaluating the effectiveness of mature municipal landfill leachate treatment by a biological stage (used SBBR as a biological treatment) and Chemical precipitation (Used MAP precipitation (magnesium ammonium phosphate)) to study the nitrogen removal capabilities for treatment of sanitary landfill leachate containing high ammonia concentration, and the comparison between them. The monitored sample taken from the Chang Sheng bridge landfill site in Chongqing city-China, has its concentrations of COD, BOD₅, and NH₃-N about 1650, 75 and 1100 mg/l respectively. The results from SBBR showed that after two months long period of domestication and one month period of stability, the ammonia nitrogen removal efficiency reached to 99% in the SBBR reactor, at nitrogen loading rate 0.51 kg TN/m³ per day and HRT was 9 hours, met to Chinese standards for discharge. The results of the MAP precipitation was technically effective to remove the high NH₃-N strength of over 1100 mg/l from the raw leachate at molar ratio of Mg²⁺: NH₄⁺: PO₄³⁻ of 1:1:1, they demonstrated a very satisfactory removal of ammonia; an initial NH₃⁺-N concentration of 1100 mg/l contained in the raw leachate was quickly reduced to 28 mg/l within 15 min, while the pH producing a maximum removal of ammonia was 9.0. The percent removal of ammonia after treatment by MAP was 97.5%.

Key words: Biological treatment, SBBR, MAP, struvite

INTRODUCTION

Sanitary landfill is an engineered of disposing solid wastes that minimizes environmental hazards^[1]. It has been suggested to be the most economical and environmentally acceptable method for disposal of municipal solid wastes^[2]. The sanitary landfill site is carefully selected. Since 1970 the design of landfill sites for disposal of municipal, industrial and commercial refuses include barrier systems as well as leachate collection system to prevent contamination of surrounding environment. Landfill leachate is a complicated waste, and it always contains high strength pollutants which have an adverse effect on the environment^[3]. It has been generally known as a high-strength wastewater that is most difficult to deal with. This is due primarily to its large variability of organic, inorganic and heavy metal contents, strongly depending on the age and type of solid wastes of a landfill site^[4]. Landfill leachate is formed by the percolation of rainwater through domestic refuses. The water causes leaching of soluble salts and partly biodegraded organic compounds, responsible for a foul-smelling, dark-colored leachate. It may also contain fine particles of

soil from the daily cover. Bacterial degradation starts under aerobic conditions as soon as the wastes are deposited in the landfill, generating high temperatures. The system becomes anaerobic following rapid depletion of oxygen, much cooler and for less reactive^[5].

Several factors affect the composition of landfill leachate. These include the age of the landfill, the nature of the waste (solid or liquid), the source of waste (municipal, industrial, commercial, mining) and the amount of precipitation. A young leachate in the acidogenic phase characterized by a high organic fraction and a BOD₅/COD ratio greater than 0.4, it can be easily biodegraded and it is weakly acidic, consequently mobilizing heavy metals. An older leachate in the methanogenic phase is not easily biodegrade as a young leachate. It contains refractory organic compounds, high concentrations of ammonia and is characterized by higher pH values^[6].

Many different techniques are currently in use to treat landfill leachates. The majority of them are adaptations of wastewater treatment techniques and can be divided in two main categories: biological treatment and physical / chemical treatments. The biological

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treatment was successfully used for leachate with a high organic strength and BOD/COD ratio (>0.5), particularly in leachates from recently placed wastes (less than 5 years) where readily biodegradable substances like volatile fatty acids comprise a large proportion of the organic material. Many small scale experimental studies showed that BOD and COD could be substantially reduced. However, leachates from older, more decomposed waste are less amenable to biological process, because a higher proportion of organic materials consist of relatively refractory materials like humic and fulvic acids^[7].

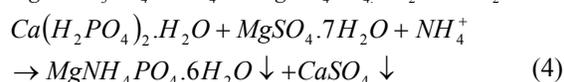
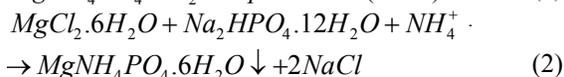
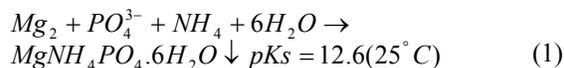
Conventional nitrification–denitrification biological processes, which have been widely utilized for ammonium removal from municipal and many industrial wastewaters, are not appropriate for treating landfill leachate because of the lack of sufficient electron donors in leachate and the high energy requirement for aeration. While new biological techniques like short-cut nitrification/denitrification and anaerobic ammonium oxidization have demonstrated potential in solving the above problems, they are still under study and it is not yet possible to constantly control the nitrification process in the nitrite-formation dominating step^[9].

The Sequencing Batch Biofilm Reactor (SBBR) is a system for wastewater treatment which combines the operating and performance advantages of the Sequencing Batch Reactor (SBR) and biofilm operation. This hybrid system provides the operational flexibility necessary for biological treatment of wastewaters containing volatile organic components with minimal fugitive emissions, treatment of low strength wastewaters which are difficult to treat in suspended growth reactors, and treatment of wastewaters containing surfactants. The SBBR also maintains the operational flexibility of the SBR for nutrient removal^[8].

The method of MAP precipitation has also been extensively studied to treat wastewater with high NH_3 content, and the NH_3 -N concentration could be reduced from 5618 mgL^{-1} to 112 mgL^{-1} within 15 min under a molar ratio of $\text{Mg}^{2+} : \text{NH}_4^+ : \text{PO}_4^{3-}$ of 1:1:1 for treating landfill leachate. Chemical precipitation as MAP can form virtually or completely insoluble compounds that can be easily separated from the water phase. The basic chemical reaction to form MAP has been expressed in Eq. (1). The theoretical amounts of chemicals needed to precipitate NH_4 -N can be calculated from the equations (2), (3), (4)^[10].

The objective of this study was to evaluate the possibility of using SBBR as a biological treatment and

MAP precipitation as a chemical treatment to remove the ammonia from old landfill leachate, and comparison between them.



MATERIALS AND METHODS

The leachate investigated in this experiment was taken from the ChangSheng Bridge Landfill inside Chongqing city. The composition can be showed in Table 1.

From Table 1, the landfill leachate is characterized as low C/N ratio, low BOD₅/COD ratio and high contents of NH_3 -N (1100 mgL^{-1}), which show the leachate can be classified as “old” and non-biodegradable.

The SBBR was carried out by a lab-scale SBBR made of a cylindrical reactor (geometric volume 24 L, working liquid volume 12 L). The SBBR reactors (12 l capacity) were made from acrylic plastic (5 mm thick). The dimensions of the reactor were 0.29 m (diameter) by 0.35 m (height). Air pump was used for supplying air for the reactor. The air diffuser for aeration was set up on the top of the settling zone to allow the biomass of large aggregates detached from the biofilm to settle during the aeration. The packing ratio of the carriers was 30%.

Figure 1 represents schematic diagram of the experimental apparatus. Units of fibrous carriers hung uniformly from the top of the reactor. Each unit of the fibrous carriers consisted of many bunches of fibers. The 24 hrs operation cycle comprised a 30 min filling period, during the acclimatization period.

Table 1: The Composition of the investigated landfill leachate

| Parameter | Unit | Value |
|------------------|--------------------|-------|
| COD | mg L^{-1} | 1650 |
| BOD ₅ | mg L^{-1} | 75 |
| NH_3 -N | mg L^{-1} | 1100 |
| TN | mg L^{-1} | 1350 |
| PO_4 -P | mg L^{-1} | 12 |
| SS | mg L^{-1} | 100 |
| pH | ---- | 8~9 |

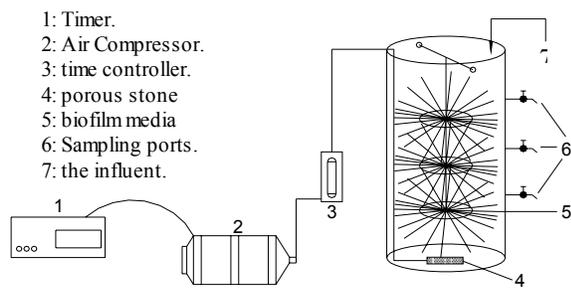


Fig. 1: Schematic diagram of the SBBR system

The MAP precipitating tests were carried out in 500-ml beakers as a batch mode. The experimental procedures were outlined below:

1. Weigh chemicals (see Table 2) to measure the 500-ml raw leachate for each test;
2. Put the measured leachate samples and the weighed chemicals into beakers;
3. Put the samples in the jar test device and start the mixing and monitor pH of the samples;
4. The reaction is 15 min until a stable pH indicated (equilibrium state);
5. Stop the mixing and leave the samples to settle for 15 min;
6. Adjust pH for the minimum MAP solubility with NaOH solution;
7. Collect the supernatant above the MAP precipitate to measure the required parameters;
8. Use mixed liquor to examine its characteristics.

Table 2: Amount of chemicals added in the 500 ml leachate at various $Mg^{2+}:NH_4^+:PO_4^{3-}$

| $Mg^{2+}:NH_4^+:PO_4^{3-}$ | $MgCl_2 \cdot 6H_2O$ | $Na_2HPO_4 \cdot 12H_2O$ (mgL ⁻¹) |
|----------------------------|----------------------|---|
| 1□1□0 | 7.975 | 0.000 |
| 1□1□0.5 | 7.975 | 7.032 |
| 1□1□0.75 | 7.975 | 10.548 |
| 1□1□1 | 7.975 | 14.064 |
| 1□1□1.1 | 7.975 | 15.470 |
| 1:1□1.25 | 7.975 | 17.580 |
| 1□1□1.5 | 7.975 | 21.096 |
| 0□1□1 | 0.000 | 14.064 |
| 0.5□1□1 | 3.990 | 14.064 |
| 0.75□1□1 | 5.980 | 14.064 |
| 1.1□1□1 | 8.773 | 14.064 |
| 1.25□1□1 | 9.969 | 14.064 |
| 1.5□1□1 | 11.963 | 14.064 |

RESULTS AND DISCUSSION

Use of SBBR system to remove ammonia (NH₃-N) as a biological treatment of the old landfill leachate:

Each cycle of the SBBR was divided into fill, react and draw periods. The react time for each cycle was the total cycle time less 1/2 hour for the fill and draw time (30 min). After 2 months acclimatization with a Nitrogen loading rate of 0.41 kg TN m⁻³ per day, the SBBR had reached a steady state. Then cycle time was reduced from 24 to 9 hrs and the loading rate from 0.41 to 0.51 kg TN m⁻³ per day. The data obtained from the operation of the SBBR at the last cycle time are summarized in Table 3 and 4.

During the reaction, the concentration of the NH₃-N decreased gradually in the reactor until reached to 11 mg L⁻¹ as shown in Fig. 2. In Fig. 3 observed that there was accumulation of nitrite significantly in the first 3 hrs, the concentration of nitrite (NO₂) inside reactor increased with time and this point represents the maximum of nitrite concentration. After that the nitrite was converted through reaction and decreased with time. The reason of the nitrite accumulation was the presence of a lot of free ammonia inside the SBBR reactor restrained the nitrifier bacteria. In Fig. 4 we observed that the concentration of nitrate (NO₃) increased gradually, because the ammonia nitrogen inside the reactor was removed under thorough aeration and there was no denitrification.

Use of MAP to remove ammonia NH₃-N as a chemical treatment of old Landfill Leachate:

Effect of pH: Struvite (MAP) precipitation reaction is highly dependent on pH. To study the effect of the solution pH on the ammonia removal by use the Struvite (MAP), the molar ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}$ was kept at 1:1:1. Fig. (5) demonstrated that the percent of ammonia removal increases, with the increase of pH, and the optimum pH value was 9.0. Various authors have reported optimum pH values for struvite precipitation was the range of between 8.5 to 9.0 for different type of wastewaters such as anaerobic digester effluent, swine wastewater, sludge, and livestock waste^[11-15].

Effect of molar ratio: The analytical results of supernatant demonstrated that NH₃-N was efficiently decreased from an initial concentration of 1100 mg/l to as low as 28 mg/l at the $Mg^{2+}:NH_4^+:PO_4^{3-}$ mole ratio of 1:1:1, as shown in Fig. (6) demonstrated that the maximum removal of ammonia was 97.5%. A high salinity formed in the treated leachate during precipitation using $MgCl_2 \cdot 6H_2O$ and $Na_2HPO_4 \cdot 12H_2O$, which may inhibit microbial activity in a following biological treatment process.

Table 3: Operation conditions for the SBBR for ammonia removal

| HRT(h) | Loading rate kg/(m ³ ·d) | Biofilm density to the total density | Effluent volume (L) | Temp.(°C) | Total volume (L) |
|--------|-------------------------------------|--------------------------------------|---------------------|-----------|------------------|
| 9 | 0.51 | 42% | 2 | 30-33 | 12 |

Table 4: The results of the SBBR effluent at the last cycle

| Time (hrs) | PH | NH ₃ -N (mg L ⁻¹) | NO ₂ -N (mg L ⁻¹) | NO ₃ -N (mg L ⁻¹) | TN (mg L ⁻¹) | DO (mg L ⁻¹) |
|------------|------|--|--|--|--------------------------|--------------------------|
| 0 | 8.61 | 121.275 | 89.90838 | 730 | 1248.5 | 4.7 |
| 1 | 8.34 | 98 | 79.92738 | 705 | 1243 | 4.7 |
| 2 | 8.1 | 83.3 | 93.65125 | 860 | 1259.5 | 4.7 |
| 3 | 7.91 | 66.64 | 96.97825 | 900 | 1245.75 | 4.6 |
| 4 | 7.68 | 49 | 89.90838 | 1005 | 1240.25 | 4.6 |
| 5 | 8.62 | 40.425 | 74.521 | 982.5 | 1239.5 | 4.5 |
| 6 | 7.82 | 33.565 | 59.5495 | 1092.5 | 1235.75 | 4.5 |
| 7 | 7.7 | 20.09 | 41.66688 | 1152.5 | 1233.25 | 4.7 |
| 8 | 7.64 | 14.7 | 22.9525 | 1145 | 1228.75 | 4.8 |
| 9 | 7.52 | 12.74 | 15.46675 | 1137.5 | 1225 | 4.7 |
| 10 | 7.43 | 11.025 | 11.308 | 1157.5 | 1219.5 | 4.9 |

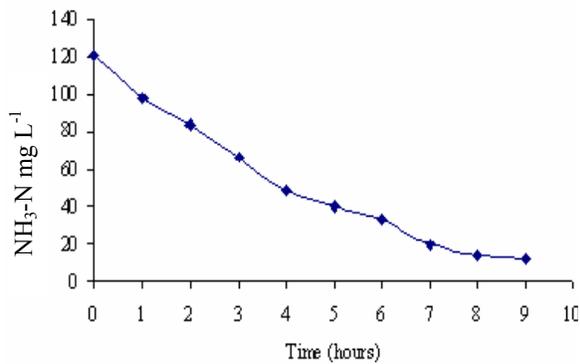


Fig. 2: The change of ammonia with time at the last cycle

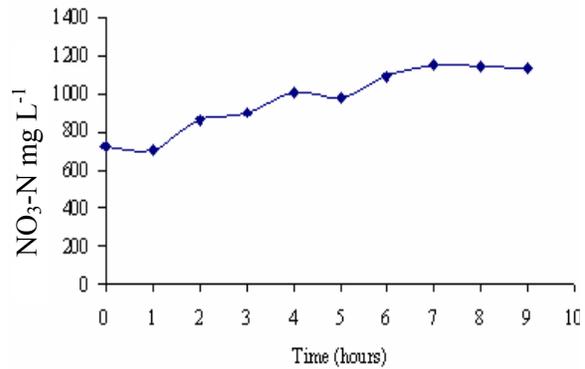


Fig. 4: The change of the nitrate with time at the last cycle

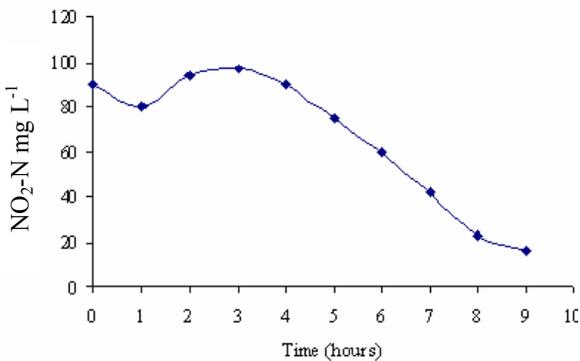


Fig. 3: The change of the nitrite with time at the last cycle

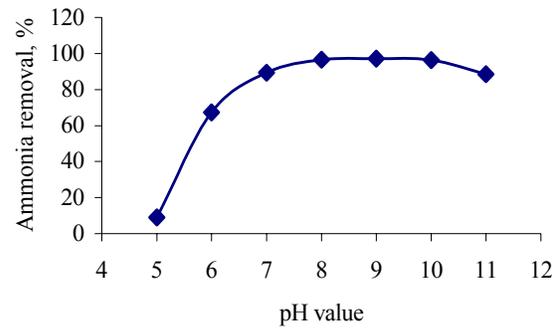


Fig. 5: Effect of pH value on the ammonia removal by using MAP precipitation at mole ratio 1:1:1

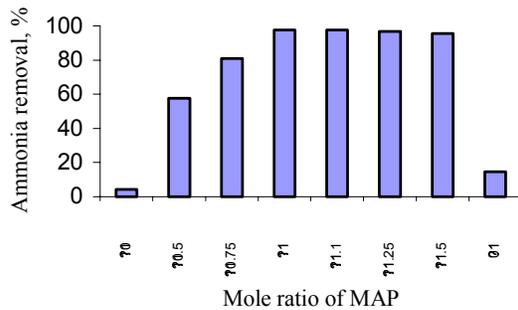


Fig.: 6 Percent of ammonia removal with different mole ratio at pH value is 9.0

CONCLUSION

- The SBBR was shown to be a viable reactor system for treating the leachate. The laboratory study on the sequencing batch biofilm reactor (SBBR) resulted in the following conclusions:
 - * The SBBR can remove the ammonia effectively using adequate operation conditions.
 - * The highest ammonia removal was obtained with a nitrogen loading rate of 0.51 kg TN/m³ per day, and cycle time at 9 hours. The ammonia removal percent after treatment was 99%, or 11 mg/l and met with Chinese standards for discharge.
- As a pre-treatment process, the MAP precipitation was technically effective to remove the high NH₃-N strength of over 1100 mg/l from the raw leachate at the mole ratio of 1:1:1, they demonstrated a very satisfactory removal of ammonia; an initial NH₃-N concentration of 1100 mg/l contained in the raw leachate was quickly reduced to 28 mg/l within 15 min, while the pH producing a maximum removal of ammonia was 9.0. The percent removal of ammonia after treatment was 97.5%.
 - The comparison between the two methods for removing ammonia from the old landfill leachate is as the following:
 - * The biological SBBR method is cheaper than the chemical method by using the MAP.
 - * For MAP precipitation method, a high salinity formed in the treated leachate during precipitation using MgCl₂.6H₂O and Na₂HPO₄.12H₂O, which may inhibit microbial activity in a following biological treatment process.
 - * The MAP precipitation method (just 15 minutes) is very faster than biological treatment that need more than 3 months.
 - * The two methods proved that they were very effective to remove the ammonia from old landfill leachate as shown in their results.

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