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The Influence of pH on the Removal of Ammonia from a Scheduled Waste Landfill Leachate

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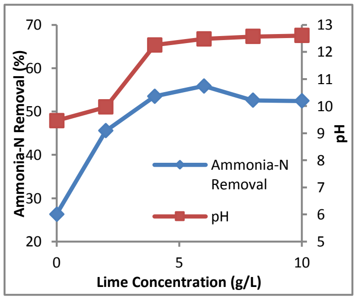
Graphical abstract



Abstract

Leachates are formed as the result of water or other liquid passing through the landfilled waste. These leachates contain high amounts of inorganic and organic matter such as ammonia which must be treated before being discharged into the environment. A pretreatment is required to increase the efficiency of the ammonia removal process. This paper presents the influence of pH on the removal of ammonia in leachate sample by lime precipitation. A raw leachate sample taken from a scheduled waste landfill was treated with different amount of lime (2, 4, 6, 8 and 10 g/L) to investigate the removal or release of ammonia. The removal of ammonia of raw leachate (average pH=9.43) was 26% and increases to the optimum dosage of 4 g/L with 54% removal at pH=12.39. However, addition of lime of more than 6 g/L does not show any significant effect on ammonia removal due to restabilization of colloids and re-dispersion of the colloidal particulates. An appropriate dosage of lime is an important factor that could save cost and time for the downstream secondary treatment.

Keywords: Scheduled waste landfill; ammonia removal; pH; leachate

■1.0 INTRODUCTION

One of the key challenges faced by the management of a landfill is the production of a highly complex and polluted leachate that brings harm to human health and the environment. Leachate is generated from sanitary or schedule waste landfills as a result of rain water percolating through the landfill site. It contains biodegradable organic matter, recalcitrant organic matter, heavy metals, inorganic salts as well as high concentration of ammoniacal-N.[1-4] Most leachate contains high amount of ammonia which imperatively must be treated before being discharged into surface water. A pre-treatment method by the addition of lime (or calcium hydroxide) through precipitation process is partially able to remove dissolved ammonia in leachate sample.[4, 6, 7] In addition, the use of lime reduces the temporary hardness of wastewater by decarbonation and at the same time it removes certain high molecular weight organic molecules such as humic and fulvic acids.[4]

Studies have been focused on the characterization of landfill leachate and treatment of leachate prior to its discharge to the environment. The new 2009 permissible limit of ammoniacal-N for domestic effluent discharged from treatment plants imposed by the Department of Environment Malaysia is 5 mg/L.[8] Many studies had been conducted on removal of ammonia from leachate originated from municipal solid waste landfill.[1-10, 12] However, there is very limited study on the ammonia removal taken from a secured scheduled waste landfill. Table 1 presents the characteristics of leachate from a scheduled waste landfill compared with other sanitary landfill sites[9] and average value of the standard discharge limit set by Department of Environment Malaysia.[7]

As in Table 1 shows that the schedule waste leachate has a higher pH, Biochemical Oxygen Demand (BOD5), Chemical Oxygen Demand (COD) and ammoniacal-N than other sanitary landfill in Malaysia. The high concentrations of ammoniacal-N (NH_3-N) in the leachate make the biological treatment impossible as it inhibited not only nitrite oxidizing bacteria (NOB) but also ammonia oxidizing bacteria (AOB).[10] Therefore, the study of lime application on removal of ammoniacal-N in scheduled waste landfill leachate was conducted and presented in this paper.

Table 1 Comparison on characteristics of raw leachate from sanitary leachate and scheduled waste landfill

Parameter	This study[a]	PBLS[b]	KLS[c]	AJLS[d]	KSLS[e]	Standard Discharge Limit
pH	9.92	8.3	7.8	7.5	8.1	6.0-9.0
BOD_5 (mg/L)	2873	358	515	48	85	20
COD (mg/L)	4633	1788	1593	599	990	400
NH_3-N (mg/L)	2403	1380	503	566	996	5.0
Total iron (mg/L)	0.4	3.6	6.0	3.0	5.0	5.0
Cu (mg/L)	0.3	0.01	0.2	0	0.7	0.20
Ni (mg/L)	0.4	0.1	0.2	0	0.3	0.20
Zn (mg/L)	0	0.3	0.3	0.01	0.2	2.0
Pb (mg/L)	0	3	1.6	0.3	0.4	0.10
Cr (mg/L)	0.065	0.2	0.1	0	0.05	0.20
Hg (mg/L)	0	0	0	0	0	0.005
Phenol (mg/L)	1.8	6	3	2	4	0.001
Cyanide (mg/L)	0	0	0	0	0	0.05

[a] Schedule waste landfill site, [b] PBLS: Pulau Burung landfill site, [c] KLS: Kulim landfill site, [d] AJLS: Ampang Jajar landfill site, [e] KSLS: Kuala Sepetang landfill site

The removal of ammonia within the scheduled waste facility complex will present a fundamental knowledge for the treatment of a leachate in a leachate treatment plant in saving cost and time for the next treatment downstream of a leachate treatment plant.

2.0 EXPERIMENTAL

2.1 Leachate Sample Collection

The leachate sample was taken from a secured schedule waste landfill site. The sample was preserved according to the Standard Methods for the Examination of Water and Wastewater[11], and immediately transported to the laboratory. The sample was stored in a refrigerator at 4°C prior to use for experimental purposes to minimize biological and chemical reactions. The leachate sample was removed out of the refrigerator and left in the ambient temperature for approximately 3 hours before each experiment.[8] Then, the sample was agitated for re-suspension of settle able solids before the experiment was conducted.

2.2 Lime Precipitation

The lime sample used was in a form of powder that acts like a coagulant. The coagulation was performed in a conventional jar-test apparatus (VELP-scientifica, Model: J LT6, Italy), comprised of six paddle rotors (2.5 cm x 7.5cm), equipped with six beakers of 500 ml each. A 100 ml of leachate was filled in a beaker and dosed with a different amount of lime (0.2, 0.4, 0.6, 0.8 and 1.0g), which represents lime concentration of 2, 4, 6, 8 and 10g/L respectively in the leachate sample. Initially, a rapid mixing of 300 rpm was applied for the first 5 minutes, followed by slow mixing of 30 rpm for 30 minutes and finally, a settling period for 30 minutes.[4] Then, the sample was analyzed for ammoniacal-N according to Nessler method, along with pH and oxidation reduction potential (ORP) and temperature using a portable pH/pH-mV/ORP and temperature meter (Hanna Instruments, HI 991003).

2.3 Nessler Method

The ammoniacal-N (NH_3-N) was determined using Nessler method, 4500 NH_3 B & C.[11] The reaction of the reagent and the ammonia present in the sample (under strongly alkaline conditions) will produce a yellow-colored solution. The color intensity of the solution determines the ammonia concentration. The ammonia concentration was measured using the Ammonia High Range Portable Photometer (Hanna Instruments, HI 96733). The reaction between ammonia and Nessler Reagent produces yellow mercuric salt (Hg_2OINH_2). The instrument directly displays concentration in mg/L of ammonium ion (NH_4^+). The readings were converted to mg/L of ammonia (NH_3) by multiply with the factor 0.944 and multiply with factor 0.776 to convert the reading to mg/L of NH_3-N.

3.0 RESULTS AND DISCUSSION

3.1 Lime Precipitation

Figure 1 presents the pictorial view of the samples after addition of lime, which showed the condition of the sample after the settling period of 30 minutes. The first beaker on the most left is the raw leachate without addition of lime. While the second to the sixth beaker was added with 2 gL^{-1}, 4 gL^{-1}, 6 gL^{-1}, 8 gL^{-1} and 10 gL^{-1}, respectively. The original color of the raw leachate sample was dark brown and changed into a whitish brown upon addition of lime. In addition, sediment was formed at the bottom of the beaker as a result of the application of the lime.

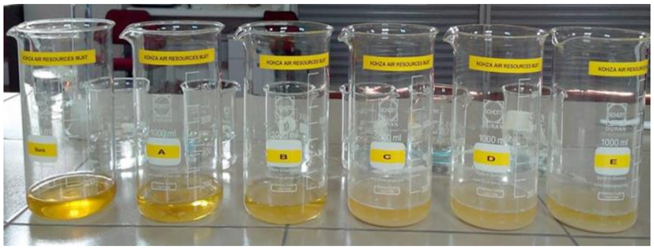


Figure 1 The color of the leachate sample after addition of lime with the most left is the raw leachate

3.2 Relationship between Lime, pH and Ammoniacal-Nitrogen

Coagulant dosage plays a significant role for the removal of target pollutants. Optimum dosage of coagulant can be defined as a value above which there is no increment in removal efficiency with further addition of the coagulant. Lime is an alkaline compound that can create pH levels as high as 12.4.[12]

Table 2 presents the average concentration, standard deviation and ranges of ammoniacal-N removed, which to a certain extend was proportional to the concentrations of lime added. The initial average concentration of the raw leachate was 2403_mg/L.

Table 2 Average concentration of ammoniacal-N remaining with different concentration of lime

Lime Concentrations (g/L)	Average ammoniacal-N (mg/L)	Standard Deviation	Range (mg/L)
0	1772	109	1684-1893
2	1309	225	1063-1505
4	1117	79	1032-1187
6	1061	105	939-1125
8	1140	128	1017-1273
10	1143	70	1063-1195

It is noteworthy that stirring promotes the release of ammonia from the leachate as can be observed in the study, where the remaining ammoniacal-N was 1772 mg/L from initially at 2403 mg/L. A reduction of 26% of ammoniacal-N even without addition of lime.

Figure 2 presents the plot on the effect of lime concentration on the pH and removal of ammoniacal-N, which showed the removal of ammoniacal-N increases with pH with the addition of lime. However as depicted in Figure 2, the removal of ammoniacal-N (i.e 54%) was the highest at 4g/L but remained relatively unchanged after this point compared to the raw leachate of merely 26%.

In general it could be noticed that the percentage removal of parameters increased with an increase in coagulant dose until it reach to an optimum value. This might be due to the excessive amount of coagulant that causes re-stabilization of colloids and re-dispersion of the colloidal particulates. When lime alone is added as a coagulant, the principles of clarification can be explained by the following reactions:

$Ca(OH)_2 + H_2CO_3 \rightleftharpoons CaCO_3 + 2H_2O$ Equation (1)
Calcium hydroxide, Carbonic acid, Calcium carbonate

$Ca(OH)_2 + Ca(HCO_3)_2 \rightleftharpoons 2CaCO_3 + 2H_2O$ Equation (2)
Calcium hydroxide, Calcium bicarbonate, Calcium carbonate

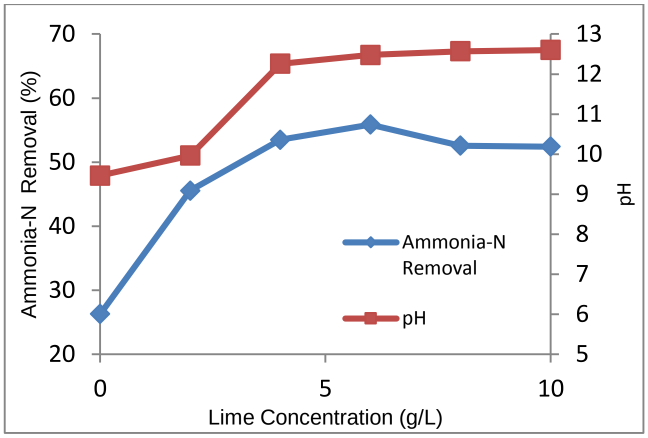


Figure 2 The effect of lime concentration on ammoniacal-N removal and pH

A sufficient amount of lime must be added in order to combine with all free carbonic acid and with the carbonic acids of the bicarbonates to produce calcium carbonate, which acts as the coagulant. In the other hand, the process of ammonia removal is based on the mass transfer, and follows the Equation (3).[13] In aqueous phase (liquid leachate), two principal forms of inorganic ammonia existed, namely free ammonia (NH_3) and ammonium ion (NH_4^+), found in equilibrium with hydrogen ion (H^+) as shown in equation below:

$NH_4^+ \rightleftharpoons NH_3 + H^+$ Equation (3)

Based on Equation (3), ammonium ion and free ammonia concentrations are dependent on pH. At lower pH, ammonium and hydrogen ions are dominant species, however when pH increases shifts to right and increases the free ammonia concentration. As lime is an alkaline, the additions of lime increase the pH of leachate. Hence, the reaction is shifted to the right, forming the ammonia (NH_3) gas. Generally, at pH 11, most ammonium ions are in the form of NH_3 gas, thus resulting in a higher removal of ammonia [7].

In addition, the gases frequently encountered in water treatment (with the exception of oxygen) do not behave in accordance with Henry's Law because they ionize when dissolved in water. For example:

$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^-$ Equation (4)
Water, Carbon dioxide, Hydrogen ion, Bicarbonate ion

$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$ Equation (5)
Water, Ammonia, Ammonium ion, Hydroxide ion

Ammonia and carbon dioxide are soluble in water under certain conditions. In a normal atmosphere, the partial pressure of each of these gases is practically zero. Thus, the establishment of a state of equilibrium between water and air by means of aeration results in saturation of the water with nitrogen and oxygen and nearly complete removal of other gases. Based on the Equation (4) and Equation (5), ionization of the gases in water is a reversible reaction. The common ion effect can be used to obtain almost complete removal of these gases by aeration. If concentration of one of the ions on the right side of the equation is increased, the reaction will be driven to the left, forming the gas.

In the case of carbon dioxide as in Equation (4), hydrogen ion concentration may be increased with the addition of an acid. Bicarbonate and carbonate ions in the water will form carbon dioxide, which can be removed by aeration. In the case of ammonia, an increase in hydroxyl ion concentration through the addition of lime or caustic soda will aid in the removal of ammonia. Based on Equation (5), when lime $Ca(OH)_2$ is added into the leachate, the hydroxide ion (OH^-) of the lime will react with ammonium ion (NH_4^+) that exist in leachate and increased the concentration on the right side (ammonium ion and hydroxide ion), hence the reaction will be driven to the left (water and ammonia) forming the ammonia (NH_3) gas.

■4.0 CONCLUSION

The study on the effect of lime on the removal of ammonia in a leachate sample through precipitation process had been presented in this paper. It was observed that the addition of lime increases the pH, which resulted in the increase the removal of ammoniacal-N to a certain point. The concentration of lime of 4g/L seemed to present the optimum dosage for leachate generated in scheduled waste landfill. The finding provides the necessary information on the best method for preliminary removal of ammoniacal-N from leachate of the scheduled waste landfill.

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