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Ammonium Removal from Landfill Leachate by Chemical Precipitation

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Abstract:

The landfill leachate in The Khajod Solid Waste Disposal Site, Surat usually contains quite high NH_4^+ -N concentration, which is well known to inhibit nitrification in biological treatment processes. A common pre-treatment for reducing high strength of ammonium (NH_4^+-N) is by an air-stripping process. However, there are some operational problems such as carbonate scaling in the process of stripping. For this reason, some technical alternatives for NH_4^+ -N removal from leachate need to be studied. In this study, a bench-scale experiment was initiated to investigate the feasibility of selectively precipitating NH_4^+ -N in the leachate collected from a local landfill in Surat as magnesium ammonium phosphate (MAP). In the experiment, three combinations of chemicals, $MgCl_2.6H_2O + Na_2HPO_4.12H_2O$, $MgO + 85\% H_3PO_4$, and $MgO + Na_5P_3O_{10}$, were used with the different stoichiometric ratios to generate the MAP precipitate effectively. The results indicated that NH_4^+ -N contained in the leachate could be quickly reduced from 1108 mg/l to 40 mg/l within short period of time, when $MgCl_2.6H_2O + Na_2HPO_4.12H_2O$ were applied with a $Mg^{2+}:NH_4^+:PO_4^{3-}$ mole ratio of 1:1:1. The pH range of the minimum MAP solubility was discovered to be between 8.5 and 9.0. Attention should be given to the high salinity formed in the treated leachate by using $MgCl_2.6H_2O$ + $Na_2HPO_4.12H_2O$, which may affect microbial activity in the following biological treatment processes. The other two combinations of chemicals $[MgO + 85\% H_3PO4 and MgO + Na_5P_3O_{10}]$ could minimize salinity after precipitation, but they were less efficient for NH_4^+ -N removal, compared with $MgCl_2.6H_2O + Na_2HPO_4.12H_2O$. COD had reduced up to 50% during this precipitation. It was found that the sludge of MAP generated was easily settled within 30 minutes to reach its solids content up to 50%.

Keywords: *ammonium* (*NH*₄⁺-*N*); *landfill leachate*; *precipitation*; *magnesium-ammonium phosphate* (*MAP*)

1. Introduction

The importance of good health necessitated the deposition of domestic and industrial solid waste in landfills at remote areas. Decomposing waste within the landfills create major environmental problems as a result of the emission of the greenhouse gases (methane and carbon dioxide) as well as the production of a liquid known as leachate when precipitation infiltrates. Leachate is highly polluted due to high content of ammonium ions and organic compounds ^[1]. High levels of ammonia cause, Eutrophication , Increased algal blooms, Increased BOD, Decreased DO ,Toxic to some organisms.

Leachate is any liquid that, in passing through matter, extracts solutes, suspended solids or any other component of the material through which it has passed. One of the major environmental concerns associated with land filling of municipal solid wastes is related to the discharge of leachate into the environment, which may cause serious pollution to groundwater aquifers as well as adjacent surface waters.

Leachate has a distinguishing characteristic, so it is necessary to remove from wastewater. Landfill leachate can be toxic, acidic, and rich in organic acid groups. They can contain sulphate ions as well as high concentration of common metal ions especially iron. However, the type of material put into a landfill, landfill conditions such as pH, temperature, moisture, age, climate and the characteristic of the precipitation entering the landfill are some of the factors affecting the actual composition of a land fill leachate. Leachate treatment technologies fall into two basic types, biological and physical/chemical.

Leachate consisting of mixtures of many chemicals is a potential risk to human health. Oxidative damage induced in brains and livers of mice by landfill leachate was studied ^[2]. The results show that leachate caused lipid peroxidation and change of antioxidative status in brains and livers of mice. It suggested that leachate exposure can cause oxidative damage on brains and livers of mice. Leachates of municipal solid waste incineration bottom ash from Macao: Heavy Metal Concentration and genotoxicity ^[3]. The study revealed that MSWIBA were genotoxic with the MN assay in vicia faba root tip cell. Genotoxicity of municipal landfill leachate on root tips of vicia faba ^[4]. The result confirmed that leachate might be a genotoxic agent in plant cells and this implies that exposure to leachate in the aquatic environment may pose a potential genotoxic risk to organisms. As a result of the potential health effect of leachate, landfills have to be designed to minimize both the formation of leachate and the amount of leachate that leaks out from it. Landfill should therefore undergo design and construction procedures that will provide safeguards for control of leachate migration into groundwater. There should be the lining system (low permeable soil or synthetic materials) to ensure low-permeability of leachate into groundwater. Consequently, leachate collected through piping systems installed above the liners should be pumped out and treated before discharging to the environment, otherwise our reservoirs, waterways and underground water will be exposed to contaminants from leachate.

If landfill leachate is discharged directly to a receiving body (ground or surface water), the potential detrimental effects include toxic effects on fish and other aquatic organisms ^[5] and contamination of the groundwater or surface water with organic or inorganic contaminants. Consequently, prior to discharge, treatment to remove both organic and inorganic constituents is required.

In Surat , there is only one municipal landfill site; the high strengths of ammonium (NH_4^+-N) are a common feature of the local leachate generated at these landfills. Normally, those leachate generated at the domestic waste landfills contain 3,000 to 6,000 mg/L of NH_4^+-N ; the leachate generated at the mixed sites receiving both construction waste and domestic wastes may contain less NH_4^+-N in the range of 1,000 to 2,500 mg/L. Leachate with such high NH_4^+-N content are generally difficult of access to conventional biological treatment processes. A previous study ^[6] confirmed that the performance of a conventional activated sludge process could be significantly affected by a high concentration of NH_4^+-N . The COD removal declined from 95.1% to 79.1%, and the dehydrogenase activity of activated sludge decreased from 11.04 to 4.22 µg TF/mg MLSS, respectively, when the NH_4^+-N concentration in wastewater increased from 50 to 800 mg/l.

Under certain conditions, the leachate with a high concentration of NH_4^+ -N can be biologically treated, but a large amount of effluent needs to be recycled to the aeration tank so as to dilute the ammonia toxicity to a low level. This type of biological process with a high ratio of effluent recirculation causes a much higher operation cost and also occupies a much larger aeration tank than a conventional biological process does. Nowadays, the most common method for eliminating a high concentration of NH₄⁺-N (>3,000mg/l) involved in wastewater treatment technologies is the air stripping process. But a major concern about ammonia air stripping is the release of NH₃ into the atmosphere so as to cause severe air pollution. Ammonia is irritating and corrosive. Exposure to high concentrations of ammonia in air causes immediate burning of the nose, throat and respiratory tract. This can cause bronchiolar and alveolar edema, and airway destruction resulting in respiratory distress or failure. Inhalation of lower concentrations can cause coughing, and nose and throat irritation. Exposure to low concentrations of ammonia in air or solution may produce rapid skin or eye irritation. Higher concentrations of ammonia may cause severe injury and burns. Contact with concentrated ammonia solutions such as industrial cleaners may cause corrosive injury including skin burns, permanent eye damage or blindness^[7] if ammonia cannot be properly absorbed with either H_2SO_4 or HCl. The other concern is calcium carbonate scaling of the stripping tower, when lime is used for pH adjustment. Since the leachate from an aged landfill contains a high alkalinity just like a strong pH buffering system, the pH variation before and after stripping will consume a large amount of alkali (20 g/l of caustic soda is required to increase pH) and acid (10 ml/l of chloric acid is required to absorb NH₃ stripped out). A huge amount of carbonate precipitate is usually formed in the process and may cause severe operation and maintenance problems. Moreover, a large stripping tower will be needed due to foaming when NH₄⁺-N in raw leachate is stripped out.

For the above reasons, other technically effective alternatives to eliminate NH_4^+ -N in leachate need to be ascertained. The precipitation of NH_4^+ -N by forming magnesium ammonium phosphate (MAP) precipitate has been studied and practiced for different types of wastewater, such as tannery effluent in leather industries ^[8] digester supernatant ^[9] in wastewater treatment plants, wastewater from coke plants and nitrogen works ^[10] and also sludge liquor ^[11]. These studied results indicated very efficient removals of NH_4^+ -N. Cost estimates indicated that the cost of precipitation process is roughly similar to the cost of nitrification and de nitrification of 1 m³ communal wastewater ^[11], and similar to or about 20% more expensive than that of air stripping ^[9].

The removal of compounds containing nitrogen and phosphorus is a key element of the waste removal system and is intended to reduce and prevent Eutrophication of sensitive inland and coastal waters. With more stringent standards imposed regarding nutrient removal, treatment processes have been developed to remove compounds containing nitrogen and phosphorous. The result of removing greater concentrations of phosphorus from the wastewater is that the wasted sludge has a greater concentration of phosphorus, nitrogen and magnesium. This combination of ions found in sludge derived from nutrient removal processes, specifically biological nutrient removal (BNR), can result in the formation of a tenacious mineral. This mineral, composed of magnesium ammonium phosphate, is called struvite. Struvite is a white crystalline substance consisting of magnesium, ammonium and phosphorus in equal molar concentrations (MgNH₄PO₄ $6H_2O$). This product is also mineralogically known as struvite found in guano. Struvite forms according to the general reaction shown below:

$Mg^{2+} + PO_4^{3-} + NH_4^{+} + 6H_2O \Leftrightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow (1) \text{ pKs} = 12.6 (25^{\circ}C)$

However, this equation is a simplification of the chemistry involved in struvite precipitation. Struvite crystals have a distinctive orthorhombic structure and can be identified via X-ray diffraction (XRD). Struvite precipitation can be separated into two stages:

nucleation and growth. Nucleation occurs when constituent ions combine to form crystal embryos. Crystal growth continues until equilibrium is reached. In systems continuously replenished with struvite constituents; e.g. wastewater treatment plants, crystal growth may continue indefinitely. Struvite precipitation is controlled by pH, degree of super saturation, temperature and the presence of other ions in solution such as calcium and can occur when the concentrations of magnesium, ammonium and phosphate ions exceed the solubility product.

The formation of crystals (i.e. nucleation) usually occurs spontaneously (homogeneous nucleation) or can be aided by the presence of suitable nuclei, which may be either solid impurities in suspension or sites on the pipe walls (heterogeneous nucleation). The time taken for nucleation to occur (often termed the induction time) has been investigated to identify what controls the formation of a precipitate.

Chemical precipitation as MAP can form virtually or completely insoluble compounds that can be easily separated from the water phase. For example, its insoluble form of MgNH₄PO₄.6H₂Owith a low solubility of 0.023 g/100 ml-H₂O at 0°C is well known in analytical chemistry. The reaction is expressed below:

 $Mg^{2+} + PO_4^{3-} + NH_4^{+} + 6H_2O \Leftrightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow (1) \text{ pKs} = 12.6 \text{ (25°C)}$

Since the mole weight of MgNH₄PO₄.6H₂O is 245 g/mol, 17.5 g MgNH₄PO₄.6H₂O should be theoretically formed as precipitated sludge, when 1 g of NH₄⁺-N is removed. Because MAP has a similar composition of Mg, P and N to that of commercial fertilizers in soil, this product could have potential to be utilized as an additive to compost, garden soil or dried sewage sludge ^[9]. Besides, it can also possible be used as a fire retardant in fabrics ^[12].

The pH can be changed by dosing base commonly in the form of $Ca(OH)_2$, NaOH or Mg(OH)₂. Purely as a means of pH adjustment NaOH has been suggested as the more effective chemical. Systems that employ chemical pH adjustment include the Unitika process and the Kurita process. The distinct advantage of dosing with a magnesium-based chemical is that the precipitation potential of the liquor is increased and this may reduce the pH required to precipitate and recover struvite. Another method of pH adjustment that has been applied is aeration of liquors. Aeration strips carbon dioxide and thus alters the carbonate chemistry of the liquors resulting in an increase in pH.

In the precipitation process suitable chemicals are added to leachate to precipitate soluble contaminants as insoluble compounds which can be separated by sedimentation or filtration. Precipitation is used as pre-treatment to remove high strength ammonium nitrogen from leachate ^[13]. Chemical precipitation of NH_4^+ -N in its insoluble form of magnesium ammonium phosphate (MAP or Struvite) is a new option to selectively remove ammonium from liquid and has been studied for treating several wastewaters including tannery effluent, digester supernatant material, coke and nitrogen wastewater and also sludge liquor.

The experiment also demonstrated that the NH_4^+ -N in the leachate can be quickly precipitated as $MgNH_4PO_4 \cdot 6H_2O\downarrow$. There are three chemical combinations for these MAP process,

- $MgCl_2 \cdot 6H_2O + Na_2HPO_4 \cdot 12H_2O$
- MgO + 85% H₃PO₄
- $MgO + Na_5P_3O_{10}$

After addition of $MgCl_2 \cdot 6H_2O + Na_2HPO_4 \cdot 12H_2O$ the $NH_4^+ \cdot N$ concentration was reduced to 4 % when a mole ratio of $Mg^{2+}:NH_4^+:PO_4^{3-}=1:1:1$ was used. The optimum pH to reach the minimum solubility of $MgNH_4PO_4 \cdot 6H_2O\downarrow$ was found to be in the range of 8.5 and 9.0. Attention should be given to the high salinity formed in the treated leachate by using $MgCl_2 \cdot 6H_2O + Na_2HPO_4 \cdot 12H_2O$, which may affect microbial activity in the following biological treatment processes. Using other two combinations of chemicals [MgO + 85% H_3PO_4 and MgO + Na_5P_3O_{10}] could minimize salinity generation after precipitation, while they were less efficient for NH_4^+ -N removal.

2. Basic Chemical Reactions

The basic chemical reaction to form MAP has been expressed in Equation (1). The theoretical amounts of chemicals needed to precipitate NH_4^+ -N can be calculated from following equations:

- $MgCl_2 \cdot 6H_2O + Na_2HPO_4 \cdot 12H_2O + NH_4^+ \Rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + 2NaCl (2)$
- $MgO + H_3PO_4 + NH_4^+ \Rightarrow MgNH_4PO_4 \cdot 6H_2O\downarrow + H_2O(3)$
- $MgO + Na_5P_3O_{10} + NH_4^+ \Rightarrow MgNH_4PO_4 \cdot 6H_2O\downarrow + H_2O$ (4)

To remove all NH_4^+ -N (1108/1028 mg/l) contained in the 500-ml leachate-ammonia source, the stoichiometric amounts of chemicals are either 8.03/7.45 g of MgCl₂.6H₂O and 14.16/13.14g of Na₂HPO₄.12H₂O, or 1.58/1.47 g of MgO and 4.56/4.23 g of 85% H₃PO₄, and 14.56/13.51 g of Na₅P₃O₁₀, when the Mg²⁺:NH₄⁺:PO₄³⁻ mole ratio of 1:1:1 is employed. From these calculations, the other stoichiometric amounts at the different Mg²⁺:NH₄⁺:PO₄³⁻ mole ratios can be easily obtained, as listed in Table 1 and 2.

Ν	MOLE RATI	0		REAGENTS USED									
Mg ²⁺	NH4 ⁺	PO ₄ ³⁻	MgCl ₂ Na ₂ HPC	MgCl ₂ .6H ₂ O + Na ₂ HPO ₄ ,12H ₂ O G		15P3O10 g	MgO + 85 g	% H ₃ PO ₄					
1.00	1.00	0.50	8.03	7.08									
1.00	1.00	0.75	8.03	10.62									
1.00	1.00	1.00	8.03	14.16	1.58	14.56	1.58	4.56					
1.00	1.00	1.25	8.03	17.71									
0.50	1.00	1.00	4.02	14.16									
0.75	1.00	1.00	6.02	14.16									
1.25	1.00	1.00	10.04	14.16									

Table 1: Amount of chemicals added in sample 1 (500-ml leachate) at various $Mg^{2^+}:NH_4^+:PO_4^{3^-}$ mole ratios * Raw leachate has $NH_4^+-N = 1108 \text{ mg/l}$

M	OLE RAT	Ю	REAGENTS USED							
Mg ²⁺	NH4 ⁺	PO ₄ ³⁻	MgCl ₂ .6H ₂ O+	MgCl ₂ .6H ₂ O+Na ₂ HPO ₄ 12H ₂ O g			MgO + 85% H ₃ PO ₄ g			
1.00	1.00	1.00	7.45	13.14	1.47	13.51	1.47	4.23		

Table 2: Amount of chemicals added in sample 2 (500-ml leachate) at various $Mg^{2+}:NH_4^+:PO_4^{3-}$ mole ratios * Raw leachate has $NH_4^+-N = 1028 \text{ mg/l}$

3. Methodology and Material

The raw leachate was collected from the Khajod landfill site Surat and stored in a cool room prior to the experiment. The basic characteristics of the leachate are summarised in Table 3. Two leachate samples collected for the study have NH_4^+ -N concentrations of 1108 and 1028 mg/l respectively. The MAP precipitation tests were carried out in 500-ml beakers with a batch mode and its procedure is outlined below: To weigh chemicals and to measure the 500-ml raw leachate for each test. To put the measured leachate samples and the weighed chemicals into beakers. To start magnetic stirrers at the bottom of beaker and to monitor pH of the samples. To react for 15 minutes until a stable pH indicated (equilibrium state). To stop magnetic stirrers and to settle for 15 minutes. To adjust pH for the minimum MAP solubility with 10 M NaOH solution. To collect the supernatant above the MAP precipitate for measuring the required parameters. To use mixed liquor for examining its characteristics.

The three combinations of chemicals, $MgCl_2 \cdot 6H_2O + Na_2HPO_4 \cdot 12H_2O$, MgO + 85% H_3PO_4 , and $MgO + Na_5P_3O_{10}$, were respectively tested. Totally 12 tests with different $Mg^{2+}:NH_4^+:PO_4^{-3-}$ ratios were carried out. 8 sets by adding $MgCl_2 \cdot 6H_2O + Na_2HPO_4 \cdot 12H_2O$; the other 2 + 2 by adding MgO + 85% H_3PO_4 and $MgO + Na_5P_3O_{10}$). The effect of pH on the remaining NH_4^+ -N was also investigated in the study. After reaction and sludge sedimentation, supernatant was separated from the settled MAP sludge and collected as supernatant samples. Then 10 M NaOH solution was progressively added into the supernatant to explore the minimum solubility of MAP sludge. The pH and remaining NH_4^+ -N were carefully monitored during the addition of NaOH.

When the optimal $Mg^{2+}:NH_4^+:PO_4^{3-}$ ratio by using $MgCl_2\cdot 6H_2O$ and $Na_2HPO_4\cdot 12H_2O$ was determined, the additional batch tests with the same leachate were undertaken to investigate the effect of pH on the remaining NH_4^+ -N. After reaction and sludge sedimentation, the supernatant was separated from the settled MAP sludge and 10 M NaOH solution was progressively added into the supernatant to explore the minimum solubility of MAP sludge. The pH and remaining NH_4^+ -N were carefully monitored during the addition of NaOH. In the analysis, both the raw leachate and the supernatant were measured for the parameters of pH, NH_4^+ -N, conductivity, total dissolved solids (TDS), and COD. All parameters were measured by the standard methods ^[14].

4. Results and Discussion

4.1. Characteristics of landfill leachate sample

The collected leachate sample was characterized and its analytical results are shown in Table 3

PARAMETER	VALUES	LEACHATE DISPOSAL STANDARDS (IS: 2490, 1981) Inland Surface Water
Physical		
Color	8000 pt.sc.co	-
pН	7.85	5.5-9
Conductivity µs	51700	-
Turbidity NTU	16	-
Chemical		
Total COD mg/L	17820	250
BOD mg/L	7511	30
TSS mg/L	4020	-
TDS mg/L	22231	2100
NH4 ⁺ -N mg/L	1108	50
Alkalinity (as CaCo ₃) mg/L	16600	-
Chloride mg/L	8508	1000

Table 3: Characteristics of the raw leachate samples from the The Khajod Landfill, Surat.

The treated leachate sample was characterized and its analytical results are shown in Table 4 and 5.

4.2. MAP precipitation

s	REAGENTS	MOLE RATIO	Ν	NH₄⁺-N mg/I	2	COD mg/l		CONDUC	TIVITY µs	TDS mg/l	
T	USED	Mg ²⁺ :NH4 ⁺ :PO4 ³⁻	INITIAL	FINAL	% REMOV ED	INITIAL	FINAL	INITIAL	FINAL	INITIAL	FINAL
1		1:1:0.5	1108	750	32.31	17820	17000	51700	112300	22231	48289
2	MgCl ₂ .	1:1:0.75	1108	414.4	62.60	17820	12620	51700	120000	22231	49450
3	6H ₂ O +	1:1:1	1108	40	96.39	17820	9708	51700	133000	22231	57190
4	Na ₂ HPO ₄	1:1:1.25	1108	38	96.57	17820	9700	51700	132095	22231	57145
5	12H-0	0.5:1:1	1108	780	29.60	17820	17110	51700	112355	22231	48335
6	1211/0	0.75:1:1	1108	450	59.39	17820	13000	51700	122000	22231	50057
7		1.25:1:1	1108	35	96.84	17820	9695	51700	132115	22231	57120
	MgO+										
8	$Na_5P_3O_{10}$	1:1:1	1108	580	47.65	17820	8032	51700	54120	22231	25012
	MgO+85										
9	$\%H_3PO_4$	1:1:1	1108	644	41.88	17820	7960	51700	53600	22231	23048

Table 4: Characteristics of treated leachate sample 1 having 1108 mg/l NH_4^+ -*N.*

		MOLE RATIO	1	NH4 [*] -N mg/l	L	COD mg/l		CONDUCTIVITY µs		TDS mg/l	
s					%						
Ε	REAGENTS				REMOV						
Т	USED	Mg ²⁺ :NH ₄ ⁺ :PO ₄ ³⁻	INITIAL	FINAL	ED	INITIAL	FINAL	INITIAL	FINAL	INITIAL	FINAL
	MgCl ₂ .6H ₂ O										
	$+ Na_2HPO_4$										
1	12H ₂ O	1:1:1	1028	80	92.22	18400	11600	28000	57000	16369	28758
	MgO+		1000	607.6	12.20	10100	10000		10100	1000	10100
2	$Na_5P_3O_{10}$	1:1:1	1028	537.0	47.70	18400	12200	28000	49190	16369	18120
-	MgO+85%		1020	5.00	15.50	10400	12000	20000	40010	10000	17000
5	H ₃ PO ₄	1:1:1	1028	000	45.55	18400	12900	28000	48010	10309	1/900

Table 5: Characteristics of treated leachate sample 2 having 1028 mg/l NH_4^+ -N.

The leachate samples containing the NH_4^+ -N concentration of 1108 mg/l were tested by adding $MgCl_2.6H_2O$ and $Na_2HPO_4.12H_2O$ and the precipitation results are illustrated in Fig. 1 and 2. It was found that after adding $MgCl_2.6H_2O$ and $Na_2HPO_4.12H_2O$ into the leachate samples, white color precipitant was rapidly formed and it quickly settled at the bottom of beakers after stirring was stopped. The analytical results of supernatant demonstrated that NH_4^+ -N was efficiently decreased from an initial concentration of 1108 mg/l to as low as 40 mg/l at the $Mg^{2+}:NH_4^+:PO_4^{3-}$ mole ratio of 1:1:1. Overdosing either Mg^{2+} or PO_4^{3-} about 12.5% further lowered the remaining NH_4^+ -N concentration to 38 mg/l, respectively; any further over-dosages of $Mg^{2+}:NH_4^+:PO_4^{3-}$ mole ratio at 1:1:1 when the leachate needs to precipitate NH_4^+ -N as MAP, as expressed theoretically in Equation (2).



Figure 1: Determination of optimum mole ratio to precipitate NH_4^+ -N from the leachate with increase in Mg^{2+} ratio.



Figure 2: Determination of optimum mole ratio to precipitate NH_4^+ -N from the leachate with increase in PO_4^{3-} ratio

In the above test, pH of the leachate from an initial concentration of 7.85 was dropped to 5.21. To identify the solubility of MAP in the leachate affected by pH, 10 M NaOH solution was used to raise the pH of the treated leachate from 5.91 to 9.0 and the experimental results are plotted in Fig. 3. When the 10 M NaOH solution was dropped into the treated leachate, pH of the treated leachate was gradually increased, whereas the remaining NH_4^+ -N concentration was sharply decreased.

The above experimental results testified the excellent effectiveness of removing NH_4^+ -N from the leachate by the MAP precipitation. In this precipitation, however, an unwanted by-product, a high amount of salt, was generated in the treated leachate, according to Equation (2).

4.3. Comparable batch tests with three combinations of chemicals

To minimize the high amount of salt content in the treated leachate, the other two combinations of chemicals previously mentioned $(MgO + H_3PO_4 \text{ and } MgO + Na_5P_3O_{10})$ were also employed and the precipitation experiments were carried out under similar experimental conditions with the mole ratio of 1:1:1. In these batch tests, the leachate samples with the NH_4^+ -N concentration of 1108 mg/l were employed. The experimental conditions and dosage of NaOH used are summarized in Table 1, 2 and 6. The experimental results by comparing NH_4^+ -N residual concentrations with the additions of different chemicals are shown in fig 3.

SAMPLE	M	OLE RAT	OI	Precipitant]	рН	Volume of 10 M NaOH (ml)
	Mg ²⁺	$\mathbf{NH_4}^+$	PO ₄ ³⁻		Raw Leachate	Treated Leachate	
1	1.00	1.00	1.00	$\begin{array}{c} MgCl_2.6H_2O+\\ Na_2HPO_412H_2O \end{array}$	7.85	5.91	15.0
	1.00	1.00	1.00	MgO+ Na ₅ P ₃ O ₁₀	7.85	5.21	18.0
	1.00	1.00	1.00	MgO+85% H_3PO_4	7.85	5.25	24.0
2	1.00	1.00	1.00	$\begin{array}{c} MgCl_2.6H_2O+\\ Na_2HPO_412H_2O \end{array}$	7.31	4.98	24.0
	1.00	1.00	1.00	MgO+ Na ₅ P ₃ O ₁₀	7.31	4.04	27.6
	1.00	1.00	1.00	MgO+85% H ₃ PO ₄	7.31	4.56	36.0

Table 6: pH of leachate & the amount of NaOH added with different chemical additions.

* Sample 1 - Raw leachate has $NH_4^+ - N = 1108 \text{ mg/L}$

* Sample 2 – Raw leachate has NH_4^+ -N = 1028 mg/L



Figure 3: Efficiency of different reagents to precipitate NH⁺*-N from the Leachate*

The combination of $MgCl_2.6H_2O$ and $Na_2HPO_4.12H_2O$ was most efficient for removing NH_4^+ -N, but generated the highest salt concentration (see conductivity and TDS in Table 4).

The comparison of the conductivity and TDS in the raw leachate and its treated supernatants by using the three combinations of chemicals are shown in Fig. 4 & 5. MgO + 85% H₃PO₄ generated the least TDS.



Figure 4: Conductivity comparison in raw & treated leachate with different reagents for Sample 1 NH_4^+ - N = 1108 mg/L (M.R-1:1:1)



Figure 5: TDS comparison in raw & treated leachate with different reagents for Sample 2 NH_4^+ - N = 1028 mg/L (M.R-1:1:1)

The very high salt content generated by using $MgCl_2.6H_2O+Na_2HPO_412H_2O$ may prohibit the activity of bacteria if a conventional biological treatment process is followed. Application of either MgO + 85% H3PO4 or $MgO + Na_5P_3O_{10}$ can significantly minimize the salinity of treated leachate. However, some research has been also carried out to enhance the activity of biomass to treat wastewater with high salt intensity^[15].

Total COD concentrations in the raw and the treated leachate were also measured and are shown in Fig. 6 and 7. There was 50% reduction in total COD in the experiment by using the three combinations of chemicals, which implies that this chemical precipitation technique has a significant selectivity to particularly remove ammonium from leachate, while it is a target of requirement in practice. After chemical precipitation, a biological treatment process can be followed to remove COD as a conventional process. In other words, MAP precipitation may be used as a pre-treatment process to minimize ammonia toxicity before biological treatment.



Figure 6: COD reduction with different reagents for Sample 1.



Figure 7: COD reduction with different reagents for Sample 2

4.4. Economic Analysis of the Process

The cost of ammonia recovery as struvite was studied based on the experimental results presented here, in order to assess the economical viability of the process in comparison to existing nitrogen removal technologies. In this preliminary assessment, investment and utility cost such as electricity and water etc. is not taken into account and only the cost of chemicals, Mg source, PO_4^{3-} source and caustic have been considered in the calculations. The commercial value of struvite was not considered, however, the market price of struvite will determine the applicability of this process in practice. The market prices of the chemicals used in the calculations are given in Table 7.

CHEMICALS	PRICE Rs/g
MgCl ₂ .6H ₂ O	0.3
Na ₂ HPO ₄ 12H2O	0.4
MgO	1.08
Na ₅ P ₃ O ₁₀	0.3
85% H ₃ PO ₄	0.488
10 M NaOH	0.320 (0.15 Rs/ml)

Table 7: The market prices of the chemicals used in the experiments at lab scale

The results of the economical analysis for the experimental results presented here are given in Table 8, 9 and 10, where the contribution of each chemical to overall cost of struvite precipitated is calculated.

S	MO	LE RA	TIO		R	eagent Cost I	Rs	Total	R	eagents Cost	%	NH4 ⁺ -N	NH4 ⁺ -N
M P L	Mg ²⁺	$\mathrm{NH_4^+}$	PO43-	NH4 ⁺ -N % Removed	MgCl ₂ . 6H ₂ O	$\begin{array}{c} Na_2HPO_4\\ 12H_2O \end{array}$	NaOH	Reagent Cost Rs	MgCl ₂ 6H ₂ O	Na ₂ HPO ₄ 12H ₂ O	NaOH	Removal Cost Rs/Kg	Removal Cost Rs/Lit
	1.00	1.00	0.50	32.31	2.41	2.83	3.45	8.69	27.72	32.59	39.69	24.28	0.024
	1.00	1.00	0.75	62.60	2.41	4.25	3.00	9.66	24.95	43.99	31.06	13.93	0.014
	1.00	1.00	1.00	96.39	2.41	5.67	2.25	10.33	23.34	54.87	21.79	9.67	0.010
1	1.00	1.00	1.25	96.57	2.41	7.08	2.12	11.61	20.76	61.02	18.22	10.85	0.011
	0.50	1.00	1.00	29.60	1.20	5.67	1.95	8.82	13.66	64.23	22.11	26.89	0.027
	0.75	1.00	1.00	59.39	1.81	5.67	1.77	9.24	19.55	61.30	19.15	14.05	0.014
	1.25	1.00	1.00	96.84	3.01	5.67	1.53	10.21	29.51	55.50	14.99	9.51	0.010
2	1.00	1.00	1.00	92.22	2.24	5.26	3.60	11.09	20.16	47.39	32.45	11.70	0.012

Table 8: Economic analysis of the process when MgCl₂.6H₂O is used as Mg source

S	MOLE RATIO				F	Reagents Cost	t %	Total	Reagents Cost %			NH4 ⁺ -N	NH4 ⁺ -N
M P L	Mg ²⁺	$\mathrm{NH_4^+}$	PO4 ^{3.}	NH4 ⁺ -N % Removed	MgQ	$Na_5P_3O_{10}$	NaOH	Reagent Cost Rs	MgO	$\mathrm{Na}_5\mathrm{P}_3\mathrm{O}_{10}$	NaOH	Removal Cost Rs/Kg	Removal Cost Rs/Lit
1	1.00	1.00	1.00	47.65	1.71	4.37	2.70	8.78	19.48	49.76	30.76	16.62	0.017
2	1.00	1.00	1.00	47.70	1.59	4.05	4.14	9.78	16.22	41.44	42.34	19.94	0.020

Table 9: Economic analysis of the process when MgO is used as Mg source with $Na_5P_3O_{10}$

S	MOLE RATIO		NH. ⁺ N		agents C	ost %	Total	Re	agents Cos	NH4 ⁺ -N	NH4 ⁺ -N		
A M P L	Mg ²⁺	$\mathrm{NH_4^+}$	PO43-	% Removed	MgQ	85% H ₃ PO ₄	NaOH	Reagent Cost Rs	MgO	85% H ₃ PO ₄	NaOH	Removal Cost Rs/Kg	Removal Cost Rs/Lit
1	1.00	1.00	1.00	41.88	1.71	2.23	3.60	7.54	22.68	29.54	47.77	16.24	0.016
2	1.00	1.00	1.00	41.88	1.59	2.07	5.40	9.05	17.52	22.82	59.66	19.34	0.019

Table 10: Economic analysis of the process when MgO is used as Mg source with $85\% H_3PO_4$

The cost of ammonia removal is the function of removal ratio and cost of the chemicals added per ammonia present in the effluent. The relative cost of $MgCl_2$ is lowest compared to those of H_3PO_4 and caustic when it is used as Mg source, amounting to approximately 20-24% of the overall cost. However the cost of the process per ammonia fixed as struvite depends on removal as well as stoichiometric ratio of chemicals used.

Main cost factor is the cost of MgO since the prices of Mg from $MgCl_2$ is relatively cheaper compared to that of MgO. The cost of the process per ammonia removed as struvite does not change much since the recovery of ammonia is relatively low in comparison to that of $MgCl_2$ is used. In order to reduce the overall cost of the process cheaper caustic source such as $Ca(OH)_2$ can be used for pH adjustment. In this case there is a risk of calcium phosphate precipitation, which eventually reduces the availability of phosphate for struvite thus increases the need for phosphate. Removal cost is between 9.67-11.70 Rs/Kg NH_4^+ -N at high ammonium concentrations. In all these works, the commercial value of struvite is not taken into account. When the market price of struvite is deduced from the cost, the actual cost comes down. As a result, local availability and price of chemicals and use of struvite determine whether this process can potentially compete with existing nitrogen removal and recovery technologies currently available in the market.

5. Conclusion

As a pre-treatment process, the MAP precipitation was technically effective to remove NH_4^+ -N strength of over1100 mg/l from the raw leachate collected at The Khajod Landfill site, surat. When MgCl₂.6H₂O and Na₂HPO₄.12H₂O were employed at the Mg²⁺:NH₄⁺:PO₄³⁻ mole ratio of 1:1:1, a very satisfactory removal of ammonium; an initial NH₄⁺-N concentration of 1108 mg/l and 1028 mg/l contained in the raw leachate was quickly reduced to 40 mg/l and 80 mg/l i.e 96.39 % and 92.22 % removal within short period of time.

Attention should be given to high salinity formed in the treated leachate during precipitation using MgCl₂.6H₂O and Na₂HPO₄.12H₂O, which may inhibit microbial activity in following biological treatment process. Other chemical combinations such as MgO + 85%H₃PO₄ and MgO + Na₅P₃O₁₀ were conducive to lowering salinity, but they produced lower removal efficiencies of NH₄⁺-N compared with using MgCl₂.6H₂O and Na₂HPO₄.12H₂O. Moreover, MgO + 85% H3PO4 generated the least dissolved salts, whereas MgCl₂.6H₂O and Na₂HPO₄.12H₂O generated the least TDS.

During the MAP precipitation, COD was significantly reduced up to 50%. Thus, a biological treatment process may need to be followed to remove COD. MgCl₂ is cheapest source of Mg²⁺ then MgO. The cost of ammonia recovery is around 9.67 to 11.7 Rs/Kg NH_4^+ -N as a function of removal ratio and amount of chemicals added. This process can be viable when the value of struvite is taken into account.

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