



Review Paper on Ammonical nitrogen removal from organic industrial effluent

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ABSTRACT

Human society always trend to elaborate itself towards the progress during this journey of progress it needs to mitigate industrialization as well as look after environmental issues equally this concept is popularly known as sustainable development for achieving sustainable development green technology cleaner production & social responsibility plays an very important role.

To plunge into an initiative towards the sustainable development one parent industry invited us to reduce one of the pollutant parameter named Ammonical Nitrogen by Treatability study and designing on-site plant along with economical viability. Ammonical Nitrogen is a major problem for modern industries as it will hamper biological treatment and the lethal for many micro-organisms responsible for bio degradation. The statutory requirement for Ammonical Nitrogen is 100 mg/lit while as this industry is tipping out Effluent have concentration of Ammonical Nitrogen from 800 – 4000 mg/lit which is varying.

Keywords: Ammonical nitrogen, MAP Process, Air stripping tower, Design, Packed tower

1. INTRODUCTION

With the dramatic development of economy and improvement of human life, much more wastewater is producing nowadays. On the other hand, people are concerned about environmental protection more than ever and relevant legislations. The ammonia sources, which are municipal, agricultural and industrial, contribute to accelerated eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving water [1]. $\text{NH}_4\text{-N}$ is becoming more important in the alleviation of environmental problems including eutrophication, corrosion and fouling. $\text{NH}_4\text{-N}$ removal is one of the fundamental aims in wastewater treatment. It can be carried out by biological, physical, chemical or a combination of these methods like adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological-nitrification and denitrification. Ammoniacal Nitrogen contamination is highly toxic and it would adversely affect aquatic life if it is discharged above sustainable limit. $\text{NH}_4\text{-N}$ is the toxicant that causes the death of tilapia fish [2]. The high content of ammoniacal nitrogen is the major factor that affects the toxicity of wastewater.

1) Sources of $\text{NH}_4\text{-N}$

The removal of dyes from industrial effluents is an area of research receiving increasing attention as government legislation surrounding the release of contaminated effluent is becoming increasingly stringent. The presence of very low concentrations of dyes in effluent is highly visible and undesirable. The effluents from the dyes industry containing high concentration of $\text{NH}_4\text{-N}$ contribute majorly to the wastewater pollutants. There are more than 100,000 dyes available commercially, most of which are difficult to decolorize due to their complex structure and synthetic origin. These systems depended on biological activity and were mostly found inefficient in the removal of the more resistant synthetic dyes. Most wastewater treatment plants do not accept dye-containing effluent due to its adverse effects on microbial populations that would affect the biological treatment i.e. aeration tank, secondary clarifier. Majorly fertilizer and dyes manufacturing industries have high $\text{NH}_4\text{-N}$ content in their effluent. The main pollutant in nitrogenous fertilizer manufacture is ammoniacal nitrogen [3]. Therefore the treatment of effluent for removal/recovery/recycle for ammoniacal nitrogen is essential [4].

2) Alternates for the removal of $\text{NH}_4\text{-N}$

Many processes have been studied for exploring the treatment of wastewater containing ammoniacal nitrogen. Of these few processes are of commercial importance and may be opted for treatment. The available processes of practical importance can be broadly divided into two main categories: physico-chemical processes which involve stripping of ammonia from effluent by air or steam and ion exchange [5]. It also includes the MAP process which satisfies technical-economic feasibility. Other category is the biological processes which include nitrification followed by denitrification of ammonia and algal uptake of ammoniacal nitrogen [6]. Some other methods of treatment which have less practical importance are chlorination, electrodialysis, reverse osmosis, distillation etc [7]. Stripping of ammonia in wastewater is transferred to surrounding atmosphere, whereas ion exchange capital and operating cost is very high.

1.Reduction By MAP Process

I. EXPERIMENTAL STUDY

It is carried to remove metal compounds from waste water. It is a two step process. In the first step precipitants are mixed with wastewater allowing the formation of insoluble metal precipitants [8].

1) Experiment

The experiment is carried out in a 2L of beaker with moderate speed agitator. If the sample is acidic, it has to be neutralized using 10% lime slurry. The sample considered here is highly alkaline hence direct treatment can be done. Once all the parameters are estimated, calculative amount of precipitating reagents can be added. Other than the chemical other important thing in chemical precipitation is pH. Metal hydroxides are amphoteric in nature and can react chemically as acids or bases and their solubility increases towards higher or lower pH. Thus, there is an optimum pH for hydroxide precipitation for each metal. Here pH should be maintained at about 8.5 for struvite precipitation. The sequential addition of reagent should be magnesium source followed by phosphate and then allowing the mixture to agitate for about 30 minutes at moderate speed and estimated the results. Similarly, duplicated the procedure for reaction time of 60, 90 and 120 minutes of reaction time and estimated the result. Degree of agitation along with pH plays an important role in efficient formation of struvite. After two hours of continuous stirring, precipitant is allowed to

settle down the container. For rapid settling, flocculent like poly electrolyte can be used. The supernatant is collected and again all the parameters are estimated to find out the parentage reduction in $\text{NH}_4\text{-N}$ [9].

2) Precipitating reagent

MgO: The use of magnesium oxide as a reagent for struvite precipitation is liable to result in the presence of free ammonia, because its poor solubility reads to molar overdosing and thus to pH increases. For the source of magnesium, other compounds like $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and others can also be added but magnesium oxide is cheaper than other options [10]. Hence MgO for Mg source with phosphorus addition to cause struvite precipitation could be a viable solution for ammonium removal from sludge liquors. This would avoid the return of ammonium to the further stage, thus improving biological nutrient removal [11]. **Sodium Tripoly Phosphate (STPP):** It is easily soluble in water; it has got salient chelating capacity to ions of Ca and Mg etc. and can soften hard water to make suspension solution become into clear solution; it has got weak alkalinity but no corrosiveness. It is a surfactant, and has got outstanding emulsification to lubricants and fat [12].

3) Stoichiometric Calculation

It is necessary to optimize the dosage. The sample considered here has $\text{NH}_4\text{-N}$ of about 1800mg/l and the optimum ratio considered is 0.06:1:0.07. The calculation is shown in below Table [13].

CALCULATION OF PRECIPITATING REAGENT

$\text{NH}_4\text{-N}$ present in the sample	$1.8/14 = 0.128\text{gmole}$
Mg required to treat the sample,	$0.128 \times 0.06 = 7.71 \times 10^{-3}\text{gmole}$
Mg(24) content in $\text{MgO}(40)$	60%
70% MgO required,	$(7.71 \times 10^{-3} \times 25)/0.6 \times 0.7 = 0.4591\text{g/l}$
STPP required	$=(0.128 \times 0.07 \times 93) / 0.25 = 3.34\text{g/l}$

4) Analytical sampling of $\text{NH}_4\text{-N}$

The standard method for the detection of $\text{NH}_4\text{-N}$ is kjeldahl method though other method can be used like nessler's reagent method [14]. 100ml of water along with 10ml of sample are added in round bottom flask and pH is maintained by addition of caustic solution. pH should be about 10.25 as absorbion takes place at corresponding pH. Phenolphthalein as an indicator is added and the assembly is arranged for the simple distillation as shown in Figure-1. Distillate is collected in a beaker containing absorbent i.e. boric buffer and indicator. 100ml of distillate is collected and then titrated against 0.1N H_2SO_4 [15].

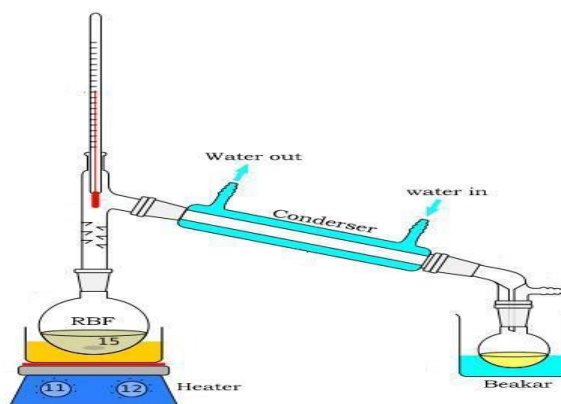


Fig.-1 Analytical Sampling of $\text{NH}_4\text{-N}$

II. RESULT AND DISCUSSION

No. of Samples.	Burette Reading (ml)	Initial NH ₄ -N (mg/l)	Concentration of Ammonical Nitrogen (ppm)
1	2.8	3870	313.6
2	2.4	2019	268.8
3	1.5	2800	168

The optimized ratio of Mg:N:P can be estimated by performing various experimental runs. The optimized ratio here is 0.06:1:0.07 as there is no prominent increase in the percentage reduction. For different influent sample, this ratio has to be optimized for better recovery [16]. If high ratios without optimization are used directly for ammoniacal nitrogen recovery, it would be waste of chemicals. If influents are segregated for separate treatment, the recovery would be higher [17].

IV. CONCLUSIONS

The process reduces NH₄⁺-N from high ammoniacal streams along with reduction in COD of around 18%. The precipitated struvite has shown to have relatively low heavy metal content, compatible with re-use as a fertilizer. Re-use routes are currently being developed as an organic horticultural fertilizer ingredient. The ongoing experiments showed the systematic pH controlled MAP process which is feeding an increasingly detailed data bank concerning struvite precipitation representative of waste water. Phosphate, magnesium, ammonium ions are maintained at optimized ratios for efficient precipitation. The ratio for different influent is different and has to be optimized for better recovery. And second order kinetic model was developed to predict the rate and extent of NH₄-N removal. This method converts the hazardous waste into non-hazardous useful nutritious resource. MAP process can stand tall for green revolution

2.Reduction by Stripping Tower

I. EXPERIMENTAL STUDY

The air stripping process can be simply defined as a unit process in which water and air are brought into contact with each other with the purpose of transferring volatile substances from water to air. This process has been effectively used in water and wastewater treatment to strip dissolved gases such as hydrogen sulphide, carbon dioxide and ammonia. In other applications, it has been successfully used to strip and reduce the concentration of taste and odour producing compounds and trace volatile organic [18].

In the case of ammonia stripping, it is feasible to achieve a high degree of removal. Once the ammonia is stripped, it's recovered from the airflow by absorption in a sulphuric acid solution, yielding ammonium sulphate, which can be obtained in an appropriate concentration. And it has some advantages over other similar processes such as [19]:

- The operation is relatively simple and not affected by wastewater fluctuation if pH and air temperature remain stable.
- Ammonia stripping is a mechanical procedure and creates no backwash or regeneration.
- Ammonia stripping is unaffected by toxic compounds that could disrupt the performance of a biological system.
- Ammonia stripping is a controlled process for selected ammonia removals.

The physico-chemical process of ammonia stripping consists in raising the wastewater pH to about 11, so the equilibrium during stripping will be favourable for ammonia desorption in air. High temperatures (60 °C) improve the equilibrium conditions for the stripping which makes the treatment more compact (more kg of water can be treated per kg of air)

Stripping towers may be classified as packed towers or spray towers. In packed towers, packing is used to provide large surface area per volume of packing. Both crossflow and counterflow packed towers have been extensively used for ammonia stripping, although counterflow gives better efficiencies. In spray towers, water is sprayed into the tower from a series of nozzles normally located at the top of the chamber, while air is blown upwards through the tower. Other methods occasionally used for ammonia stripping are holding ponds and diffused aeration systems. [20]

1) Design of stripping Tower

A pilot study was performed by us using a pilot tower with the following specification.

Data:

Diameter = 200 mm
 = 0.2 m
 = 0.65 ft.

Packed Height = 1200 mm
 = 1.2 m
 ≈ 4 ft.

Gas flow rate = 2.8 m³/min
 = 2800 liter/ min

Liquid flow rate = 5.4 liter/min

Temperature of Effluent = 40° C

Packing Material = Pall ring

Dimension of Packing material: Diameter = 38 mm
 Height = 38 mm

1) Calculating Gas to water ratio:

$$\frac{G}{L} = \frac{\text{Gas flow rate}}{\text{Liquid flow rate}}$$

$$= \frac{2800}{5.4}$$

$$\frac{G}{L} = 518 : 1$$

During the Pilot study the influent concentration the Ammonical Nitrogen is 2625 ppm was reduced to 1120 ppm in the effluent.

2) Calculating the HTU from the pilot test data:

$$\text{Stripping Factor, } S = \frac{G}{L} * H_c$$

$$= 518 * 1.940$$

$$= 1004.92$$

Where,

S = stripping factor
 H_c = Henry's constant

$$HTU = \frac{Z}{NTU}$$

$$NTU = \left(\frac{S}{S-1} \right) \ln \left[\frac{C_{inf}(S-1)}{C_{eff}} + \frac{1}{S} \right]$$

$$= \left(\frac{1004.92}{1004.92-1} \right) \ln \left[\frac{2625(1004.92-1)}{1120} + \frac{1}{1004.92} \right]$$

$$= 1.000 * \ln (2352.93)$$

$$= 1.000 * 7.7634$$

$$NTU = 7.7634$$

Where,

NTU = Number of Transfer Unit
 C_{inf} = Influent Concentration
 C_{eff} = Effluent Concentration
 S = Stripping Factor

Now,

$$HTU = \left(\frac{Z}{NTU} \right)$$

$$= \left(\frac{1.2}{7.7634} \right)$$

$$HTU = 0.154 \text{ m}$$

Where,

HTU = Height of Transfer Unit
 Z = Packed Height

$$\begin{aligned} Z &= NTU * HTU \\ &= 7.7634 * 0.154 \\ Z &= 1.2 \text{ m} \end{aligned}$$

3) Calculating Gas to water ratio:

$$\begin{aligned} \frac{G}{L} &= \frac{\text{Gas flow rate}}{\text{Liquid flow rate}} \\ &= \frac{8400}{16.2} \\ \frac{G}{L} &= 518 : 1 \end{aligned}$$

Checking the efficiency of stripping tower at influent
 Ammonical Nitrogen concentration is 3000 ppm.

4) Calculating the HTU from the pilot test data:

$$\begin{aligned} \text{Stripping Factor, } S &= \frac{G}{L} * H_c \\ &= 518 * 1.940 \\ &= 1004.92 \end{aligned}$$

Where,

S = stripping factor
 H_c = Henry's constant

$$HTU = \frac{Z}{NTU}$$

$$\begin{aligned} NTU &= \frac{Z}{HTU} \\ &= \frac{3.6}{0.154} \\ &= 23.37 \end{aligned}$$

$$\begin{aligned} NTU &= \left(\frac{s}{s-1} \right) \ln \left[\frac{C_{inf}(s-1)}{C_{eff}} + \frac{1}{s} \right] \\ 23.37 &= \left(\frac{1004.92}{1004.92-1} \right) \ln \left[\frac{3000(1004.92-1)}{C_{eff}} + \frac{1}{1004.92} \right] \\ C_{eff} &= 0.0002 \text{ ppm} \\ NTU &= 7.7634 \end{aligned}$$

Where,

NTU = Number of Transfer Unit
 C_{inf} = Influent Concentration
 C_{eff} = Effluent Concentration
 S = Stripping Factor

So we get,

$$\begin{aligned} \% \text{ Removal} &= \frac{3000 - 0.0002}{3000} * 100 \\ &= 99.99 \% \end{aligned}$$

So, at industrial level we can get around 99.99 % of efficiency or removal of Ammonical Nitrogen.



Fig 7: Reduction by Stripping Tower at Pilot scale.

2) Procedure:

- First assemble the stripping tower as shown in above figure
- Then Spray the effluent which is contain Ammonical Nitrogen from top of the tower with the help of motor or pump.
- Then pass the air from bottom of the tower by using blower.

Then after collect the effluent from bottom of the tower then recirculate the effluent based on the concentration of Ammonical Nitrogen. Means if we have higher concentration of Ammonical Nitrogen then recirculate it 2 or 3 times. Finally reduction is done.

I. RESULT

No. of Samples.	Initial NH ₄ -N (mg/l)	Concentration of Ammonical Nitrogen (ppm)
1	3870	810
		475
		80
2	3019	670
		515
		65
3	2800	610
		475
		50

II. CONCLUSIONS

When the water entering an air stripper contains inorganic substances near the limits of their solubility, precipitation of these metals or minerals within the air stripper may occur. At the aeration nozzle, ferrous iron in solution oxidizes and precipitates as insoluble ferric oxides. Manganese may also be oxidized to an insoluble form within the air stripper. Air stripping removes VOCs (volatile organic compounds) from water by facilitating their transfer to the gaseous phase where presumably by dilution they become less hazardous.

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