Removal of NH_4-N by struvite precipitation: A review and study on MAP process at laboratory scale

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ABSTRACT

This study was conducted on the MAP process to improve struvite precipitation and more efficient removal of NH_4-N from the wastewater. MAP process is one of the innovative Physico-chemical process which can majorly contribute for the removal of NH_4-N by forming the struvite complex under required condition. In order to meet stringent discharge standards for NH_4-N, an experimental work was carried out focusing the general problem of effluent discharge for the industries of India containing high NH_4-N stream. For this we evaluated the effort of feeding sequence of precipitating reagent (lime, flocculent, magnesium and phosphate) for NH_4-N removal by forming MAP i.e. struvite deposit keeping calcium interference in mind. Various studies reviewed which effectively precipitate struvite by an addition of excess magnesium and phosphate sources with different stoichiometric ratios. The stoichiometric calculation for the optimized dosage of reagent makes the precipitation more efficient. Different stoichiometric ratio were tested to determine the required Mg^{2+} and PO_4^{3+} concentration for maximum NH_4-N removal by keeping NH_4^+ constant for the effluent.

Key words: Ammoniacal Nitrogen (NH_4-N), struvite precipitation, MAP (magnesium ammonium phosphate)

INTRODUCTION

Large scale urbanization, a consequence of economic development is leading to production of huge quantities of waste water in India and posing serious environmental problems for their disposal. It is evident that the protection of our water resources is of major importance on a global scale. The treatment and disposal of sludge produced during waste treatment is one of the most critical environmental issues of today. Sludge produced is large in volume and hazardous.

Another issue of concern is that the sewage sludge produced and effluents are frequently disposed off on agricultural lands as fertilizer and irrigation purpose, respectively, due to their nutrient contents, especially N and P without any treatments, but they may induce plant and soil toxicity Nitrogen contamination is highly toxic and it would adversely affect aquatic life if is discharged above sustainable limit. NH_4-N is the toxicant that is causes the death of tilapia fish[4]. The high content of ammoniacal nitrogen is the major factor that affects the toxicity of wastewater.

and may have depressive effects on the metabolism of soil microorganisms[1,2]. Therefore, there is a need for ecologically sound technologies which are not only cost-effective, but also sustainable in terms of possible recovery of recyclable constituents from sewage sludge as they are rich in nutrients and have higher organic content. NH_4-N has been identified as one of the major toxicants to microorganisms in the treatment system, suggesting that pre treatment prior to the biological treatment system is required to reduce the concentration of NH_4-N[3]. Ammoniacal

Sources of NH_4-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 NH_4-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 NH_4-N content in their effluent. The main pollutant in nitrogenous fertilizer manufacture is ammonical nitrogen[5]. Therefore the treatment of effluent for removal/recovery/recycle for ammoniacal nitrogen is essential.

Alternates for the removal of NH_4-N

Many processes have been studied for exploring the treatment of wastewater containing ammonical 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 of effluent by air or stream and ion exchange[6]. 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 has less practical importance are chlorination, electrodialysis, reverse osmosis, distillation etc. Stripping of ammonia in wastewater is transferred to surrounding atmosphere, where as ion exchange capital and operating cost is very high.

Technical perspective of MAP process

Nitrogenous compound may be present in the wastewater effluent as ammoniacal nitrogen, organic nitrogen i.e. urea and oxidized nitrogen i.e. nitrate and nitrite. The total nitrogen consists of the inorganic forms of nitrogen (ammonium (NH_4-N) and nitrate (NO_3^--N) and organic nitrogen (N_{org}). The total kjeldahl nitrogen value provides combined values of ammoniacal nitrogen and organic nitrogen but not oxidized nitrogen. Most of the toxic effluent from dyes and fertilizer industries having high NH_4-N is acidic and this in general are neutralized using lime slurry which brings calcium interference in the picture.

As an alternative to eliminate high level of NH_4-N in leachate, the precipitation of NH_4-N by forming magnesium ammonium phosphate (Struvite, $MgNH_4PO_4{\cdot}6H_2O$) has been studied, demonstrating that struvite precipitation is an excellent pretreatment process[1]. Struvite crystallizes as a white orthorhombic crystalline structure, which is composed of magnesium, ammonium, and phosphate in equal molar concentrations[7]. Struvite precipitation is controlled by pH, supersaturation, temperature, and impurities such as calcium. Struvite solubility decreases with increasing pH, while above a pH of 9 its solubility begins to increase[8]. Struvite precipitation will not occur without a nucleation in itself. Struvite precipitation is principally based on the thermodynamic equilibrium of constituent ions in the solution, this study was conducted in the assumption that a performance of struvite precipitation might vary according to feeding sequence of chemicals of magnesium and phosphate source[9]. Considering the case of Indian industries Phosphate is limiting and hence being added last. MAP complex process is pH sensitive method. A complex becomes insoluble at pH above 8.5 and hence accurate control of pH has to be shown in operation. The modelling is complex because of the interference of various different possible magnesium and calcium mineral precipitations (ion competition and simultaneous precipitation). Dosing of Mg and P source depends on the Stoichiometric calculation. The molar ratio of Mg:N:P varies for different sample. The struvite process removes ammonia in a dewatered filtrate of a sludge treatment facility by struvite preparation reaction, and at the same time recovers the struvite prepared. According to the presented ionic reaction Stoichiometric,

$$\mathbf{Mg^{+} + NH^{+} + H_2PO^{-}_4 + 6H_2O = MgNH_4PO_46H_2O + 2H^{+}}$$

It was previously reported that struvite crystals could be formed in the aerobic composting reaction provided that Mg and P salts are. The formation of struvite crystals significantly reduced gaseous loss of ammonia and resulted in substantial increase in the ammonia content in the compost, attaining 1.5%.[10] In this context, the present study was conducted to determine the optimal doses of Mg and P salts for struvite crystallization keeping calcium interference in mind. Various molar ratios are defined in different literature i.e. maximum of 88% ammonia removal at a pH of 9.5 with added magnesium and phosphate to achieve an ammonium: magnesium: phosphate molar ratio of 1:1.25:1[11]. Hence it becomes essential to optimize the dosage. Depending on the composition of the wastewater, struvite precipitation can be used to remove ammonia (NH_4^+), phosphate (PO_4^{3-}) or both. Regardless of the compound that is targeted for removal, all of the studies up to date have utilized the addition of Mg^{2+} ion, the usual limiting reactant in the formation of struvite, as the means for altering the solubility product equilibrium and initiating precipitation.

Table 1. Shows the data on the removal of ammoniacal nitrogen by struvite precipitation process for different wastewater along with optimized pH and molar ratios used for different studies.

Table 1. Data on the removal of NH_4^+ and PO_4 by struvite precipitation for different stoichiometric ratios

Type of effluent.	Removal	Molar ratios	pH	% removal	Ref
municipal landfill leachates	NH_4-N	(Mg:N:P) 1:1:1	9.0	85	Ozturk et al., 2003 [16]
Piggery wastewater	PO_4-P	(Mg:N) 2.5:1	8.5	96	Haiming H, 2011 [17]
municipal landfill leachate	NH_4-N	(Mg:N:P) 1:1.2:1.2	9.0	90	Daekeun Kim 2006 [8]
Anaerobically Treated wastes	NH_4-N	(Mg:N:P) 1:1.25:1	9.5	88	Ann Miles 1996 [11]
Anaerobically treated (UASB reactor) liquid	NH_4-N	(Mg:N:P) 1.2:1:1.4	9.8	92	Hipolito et al., 2004 [14]
semiconductor wastewater	NH_4-N	(Mg:N:P) 1.2:1:1	9.2	89	Hong-D R, 2008 [18]
anaerobic digester effluents	NH_4-N	(Mg:N:P) 1.2:1:1.2	8.5	77	Mustafa T, 2007 [19]
Combined wastewater from bovine and leather tanning factories	NH_4-N	(Mg:N:P) 1:1:1	9.0	82	Tunay O, 1997 [20]
Effluent from the biologically (UASBR) treated opium alkaloid wastewater	NH_4-N	(Mg:N:P) 1:1:1	9.2	65	Altinbas M, 2002 [21]
Effluent from the anaerobic treatment of domestic wastewater + 2% leachate	NH_4-N	(Mg:N:P) 1:1:1	9.2	77	Altinbas M, 2002 [22]

MATERIALS AND METHOD

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. Detention time depends on the wastewater being treated, chemical used and the desired effluent quality. In the second step precipitated metals are removed from wastewater through filtration or clarification and the resulting sludge must be properly treated, recycled or disposed. Initially all the parameters are estimated that are listed in table-2.

Table 2. Initial parameter

pH	10.25
TDS	1.75ppt
NH_4-N	1737mg/l
PO_4^{-3}	2.20mg/l

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 or above for struvite precipitation. The sequential addition of reagent should be magnesium source followed by phosphate and then allowing the mixture to agitate for about one hour at moderate speed. Degree of agitation along with pH plays an important role in efficient formation of struvite. After two hour 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 NH_4-N.

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 $MgSO_4.7H_2O$ and others can also be added but magnesium oxide is cheaper than other options. 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. 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.

Stoichiometric Calculation

It is necessary to optimize the dosage. The sample considered here has NH_4-N of about 1800mg/l and the optimum ratio considered is 0.06:1:0.07. The calculation is shown in table-3

Table-3 Calculation of precipitating reagent

NH_4-N present in wastewater sample	1.8/14 = 0.128gmole
Mg required to treat the sample,	=0.128 x 0.06 = 7.71 x 10^{-3} gmole
Mg(24) content in MgO(40)	60%
70% MgO required,	= (7.71 x 10^{-3} x 25)/0.6 x 0.7 = 0.4591g/l
Similarly, calculating STPP required	(0.128 x 0.07 x 93)/0.25
	= 3.34g/l

Analytical sampling of NH_4-N

The standard method for the detection of NH_4-N is kjeldahl method though other method can be used like nessler's reagent method. 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 absorbsion takes place at corresponding pH. Phenolphthalein as an indicator is added and the assembly is arranged for the simple distillation as shown in fig-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

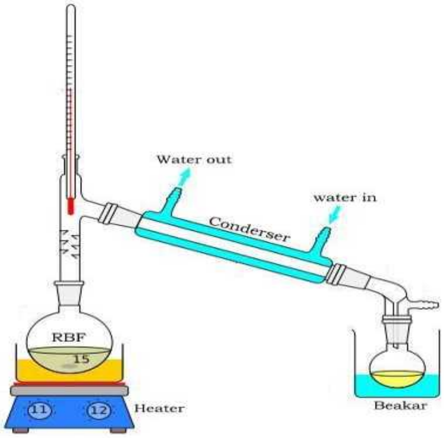

Fig-1 Analytical Sampling of NH_4-N

RESULT AND DISCUSSION

Models are important tools for process control. In the case of struvite, the modelling is complex because of the interference of various different possible magnesium and calcium mineral precipitations (ion competition and simultaneous precipitation). The recovered struvite contains hardly any toxic substance, and can be sold to fertilizer companies as a fertilizer raw material[14]. Ammonium nitrogen is absorbed by soils but is largely converted to the nitrate form in a matter of one to three weeks in many soils. The result of various experimental runs is listed in table-4

Table-4 Result showing percentage reduction

Initial NH_4-N (mg/l)	NH_4-N after treatment(mg/l)	% reduction
1768	772	56.33
1792	784	56.25
1686	752	55.39
1736	764	56.00
1698	756	55.47
Avg 1736	765	55.88

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. Fig-2 shows the comparision between different stoichiometric ratios. The increase in the ratio would be the wastage of excess chemicals and would just add into the sludge . formation, may even spoil the basic chemistry

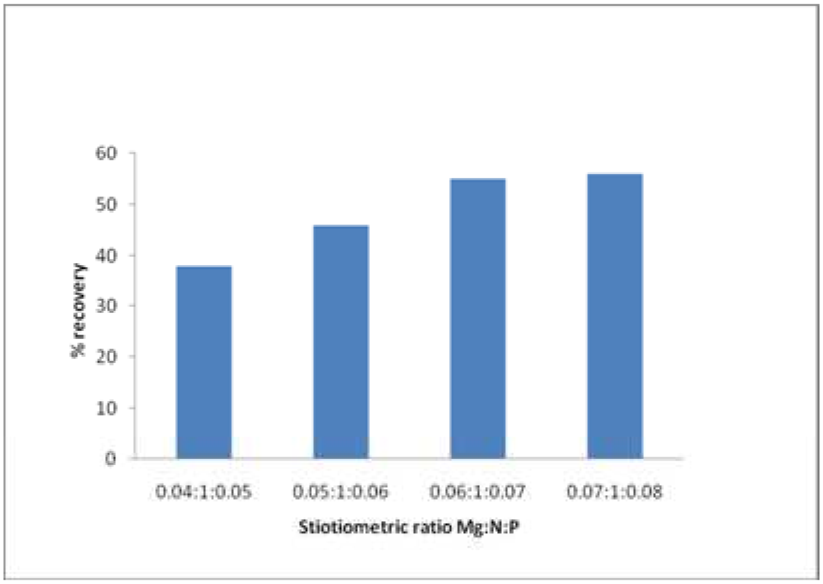

Fig. 2 Comparision of various ratio

If the sample is acidic, it becomes essential to neutralize the sample which would aid into interference of calcium The comparision between acidic and the basic samples after treatment is shown in fig-3. The acidic sample shows less reduction because of calcium interference.

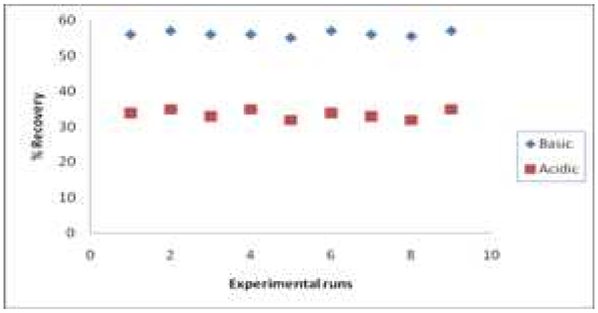

Fig-3 Comparision between acidic and basic samples after treatment

For the molar ratio Ca:Mg above 1:1, calcium ions compete with magnesium to form an amorphous calcium phosphate changing the basic chemistry needed for MAP complex process and inhibiting struvite formation. This is the general problem with acidic wastewater samples which have to be neutralized for the treatment.

CONCLUSION

The process reduces NH_4^+-N from high ammoniacal streams along with reduction in COD of around18%. 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. This method converts the hazardous waste into non-hazardous useful nutritious resource. MAP process can stand tall for green revolution.

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