A Review on Removal of Ammoniacal Nitrogen from Wastewater by Chemical Precipitation Method

Manali Desai[1] Prof. Mitali Shah[2]
[1]Student [2]Assistant Professor
[1]Department of Environmental Engineering [2]Department of Civil Engineering
[1,2]Sarvajanik College of Engineering & Technology, Gujarat, India

Abstract— Ammonium ions are the primary form of widespread nitrogen pollution in the hydrosphere and caused a remarkable increase of oxygen demand and biological eutrophication in local receiving water body. In recent years, various methods for ammonium ion removal from wastewater have been extensively studied. This paper reviews some alternate methods and briefly introduces the chemical precipitation method for the removal of Ammoniacal nitrogen from wastewater. Chemical precipitation is one of the innovative physico-chemical processes as it removes nutrients and produce precipitates which contain hardly any toxic substances and can be used as the fertilizer.

Key words: Ammoniacal Nitrogen, Chemical Precipitation

I. INTRODUCTION

Water is a precious natural resource, and due to this realization it has become a prevalent source of concern; more attention is placed on its maintenance and purification. The rapid development and industrialization coupled with an increased awareness about the need for a clean environment have forced industrialists, environmentalists and governments to look for cheap, efficient and long lasting solutions to waste water treatment and recycling of nitrogen and phosphorus. [18]

A wide range of organic compounds is detected in industrial and municipal wastewater. Some of these compounds (both synthetic organic chemicals and naturally occurring substances) pose severe problems in biological treatment systems due to their resistance to biodegradation or/and toxic effects on microbial processes.

Ammonia (NH_3), ammonium (NH_4^+), nitrite ion (NO_2), and nitrate ion (NO_3^-) are the important form of nitrogen components in aqueous solution and soil [15].

These kinds of pollutants can enter the environment from a variety of sources as contaminants, which have increased environmental problems in recent years. Therefore, effort to reduce emission and improve treatment methods for water and wastewater should be highlighted as a main public concern in the future [15].

Ammoniacal nitrogen (ammonia and ammonium) in agricultural wastewaters can promote eutrophication of receiving waters and be potentially toxic to fish and other aquatic life [9].

II. TOXICITY AND SOURCE OF AMMONIUM IONS

Molecular nitrogen (N_2) present in the earth atmosphere has to be reduced to ammonia (NH_3) by nitrogen-fixing bacteria living independently in the soil or in the root of leguminous plants before it is utilized by humans. Ammonia dissolves in water to form ammonium ions (NH_4+) and this form of reduced nitrogenise assimilated into amino acids and other nitrogen containing molecules. In aqueous solutions, ammonia is a base (any compound accepting hydrogen ions) forming a conjugated pair with the ammonium ion, according to the reversible reaction:

$$NH_3 + H^+ \; NH_4^+ \text{------ (1)}$$

Ammonia has a hazardous and toxic effect on human health and biotic resources also, only if the intake becomes higher than the capacity to detoxify and predefined permissible limits. If ammonia is administered in the form of its ammonium salts, the effects of the anion must also be taken into account. With ammonium chloride, the acidotic effects of the chloride ion seem to be of greater importance than those of the ammonium ion. At a dose of more than 100 mg/kg of body weight per day(33.7 mg of ammonium ion per kg of body weight per day), ammonium chloride influences metabolism by shifting the acid–base equilibrium, disturbing the glucose tolerance, and reducing the tissue sensitivity to insulin. So, Ammonium ion and various ammonium product based azo dyes compounds are toxic and hazardous to both the environment and human body, hence to remove these toxic pollutants and dyes several adsorbents are developed and these adsorbents has an excellent removal capacity [22].

III. EFFECT OF AMMONIUM ION ON RECEIVING WATER BODY

Ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-) are the most common ionic (reactive) forms of dissolved inorganic nitrogen in aquatic ecosystems. These ions can be present naturally as a result of atmospheric deposition, surface and groundwater runoff, dissolution of nitrogen-rich geological deposits, N2 fixation by certain prokaryotes and biological degradation of organic matter Ammonium tends to be oxidized to nitrate in a two-step process ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$) by aerobic chemoautotrophic bacteria (Nitrosomonas and Nitrobacter, primarily) The nitrification process can even occur if levels of dissolved oxygen decline to a value as low as 1.0 mg O2/L. Moreover, anthropogenic inputs of particulate nitrogen and organic nitrogen to the environment can also result in inorganic nitrogen pollution.

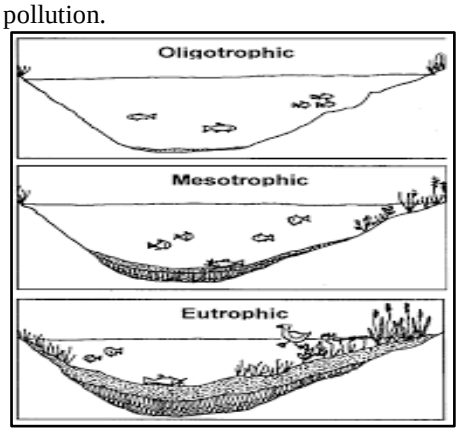

Fig. 1: eutrophication of water body

All rights reserved by www.ijsrd.com

Concentrations of inorganic nitrogenous compounds (NH_4^+, NO_2^-, NO_3^-) in ground and surface waters are hence increasing around the world, causing significant effects on many aquatic organisms and, ultimately, contributing to the degradation of freshwater, estuarine, and coastal marine ecosystems.

Major environmental problem due to dissolved inorganic nitrogen are as follows:

1) Inorganic nitrogen pollution can increase the concentration of hydrogen ions in freshwater ecosystems without much acid-neutralizing capacity, resulting in acidification of those ecological systems;
2) Inorganic nitrogen pollution can stimulate or enhance the development, maintenance and proliferation of primary producers, resulting in eutrophication of freshwater, estuarine, and coastal marine ecosystems. In some cases, inorganic nitrogen pollution can also induce the occurrence of toxic algae;
3) Inorganic nitrogen pollution can impair the ability of aquatic animals to survive, grow and reproduce as a result of direct toxicity of inorganic nitrogenous compounds.

In addition, inorganic nitrogen pollution of ground and surface waters can induce adverse effects on human health and economy. [10]

IV. Alternatives for Removal of Ammoniacal Nitrogen

NH_4-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. Available technologies include adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological nitrification and denitrification.

A. Adsorption:

Adsorption is a process in which a substance (adsorbate), in gas or liquid phase, accumulates on a solid surface (adsorbent). It is based on the capability of porous materials with large surfaces to selectively retain compounds on the surface of the solid (adsorbent). The adsorption process of the adsorbate molecules from the bulk liquid phase into the adsorbent surface is presumed to involve the following stages:

1) Mass transfer of the adsorbate molecules across the external boundary layer towards the solid particle.
2) Adsorbate molecules transport from the particle surface into the active sites by diffusion within the pore–filled liquid and migrate along the solid surface of the pore.
3) Solute molecules adsorption on the active sites on the interior surfaces of the pores.
4) Once the molecule adsorbed, it may migrate on the pore surface trough surface diffusion [7].

Azhar Abdul Halim,et al studied on, "Ammonia Removal from Aqueous Solution Using Organic Acid Modified Activated Carbon". The optimum conditions for adsorption in the batch study occurred at pH range of 8 to 9 and contact time of 30 min. The Langmuir isotherms corresponded slightly better than Freundlich isotherm for both organic acid modified activated carbon (AC-RCOONa) and pristine activated carbon (AC) [4].

B. Biological treatment:

Conventional biological nitrogenous compounds removals obtained by a two-step process involving nitrification, which is the aerobic oxidation of ammonia to nitrite(NO_2^-) and nitrate, and denitrification, which is the dissimilatory reduction of nitrate to nitrogen gas (2). The two-step nitrification–denitrification by ammonia and nitrite oxidizing biomass is preformed via conversion of ammonium (NH_4^+) to nitrite (NO_2) and nitrate (NO_3^-); finally, and according to the following reactions [13]:

$$NH4^+ + 3/2O_2 \rightarrow NO_2^- + 2H + H_2O \quad \text{——} (2)$$

$$NO_2^- + 3/2O_2 \rightarrow NO_3^- \quad \text{——} (3)$$

Sheela. B et al studied on, "Simultaneous Nitrification and Denitrification of Ammonical Wastewaters Using Bacillus SpeciesSB1 Isolated from Domestic Sewage". The study was attempted to develop a process for ammonia bioremediation in a single stage aerobic nitrification and denitrification of ammonia. The results reveal that the optimum pH for the isolated Bacillus species strain was 8 and optimum temperature was 300C. At optimum pH and temperature this organism was able to remove 72.7% of ammonia in flask cultures supplemented with 860 mg l-1 of ammonia. The study on ammonia toxicity revealed that toxicity was due to increase in hydrogen ion concentration and osmosis [17].

C. Ion-exchange:

Ion exchange can be used for the removal of undesirable anions and cations from a wastewater. Cations are exchanged for hydrogen or sodium and anions for hydroxyl ions. Ion exchange resins consist of an organic or inorganic network structure with attached functional groups. Most ion exchange resins used in wastewater treatment are synthetic resins made by the polymerisation of organic compounds into a porous three-dimensional structure.

T.C. Jorgensen et al studied on, "Ammonia removal from wastewater by ion exchange in the presence of organic contaminants". The ion exchangers included a natural zeolite clinoptilolite, and two polymeric exchangers, Dowex 50w-x8, and Purolite MN500. The organic compounds studied included citric acid and a number of proteins. The traditional method for removal of ammonium and organic pollutants from wastewater is biological treatment, but ion exchange offers a number of advantages including the ability to handle shock loadings and the ability to operate over a wider range of temperatures. The results show that in most of the cases studied, the presence of organic compounds enhances the uptake of ammonium ion onto the ion exchangers [19].

D. Chemical Precipitation Method:

Chemical precipitation of ammonium nitrogen removal by adding magnesium salt and phosphate to form magnesium ammonium phosphate hexa hydrate (MAP) is a useful method. MAP is a white crystal substance consisting of equal molar concentrations of magnesium, ammonium and phosphorus.

All rights reserved by www.ijsrd.com

V. CHEMICAL PRECIPITATION (STRUVITE) METHOD

Struvite precipitation is one the innovative physico-chemical processes which can majorly contribute for the removal of NH_4^+-N or phosphorous forming complex under required conditions. It is also an ecologically sound technology which is not only cost –effective, but also sustainable in terms of possible recovery of recyclable constituents from industrial effluent rich in nutrients [16].

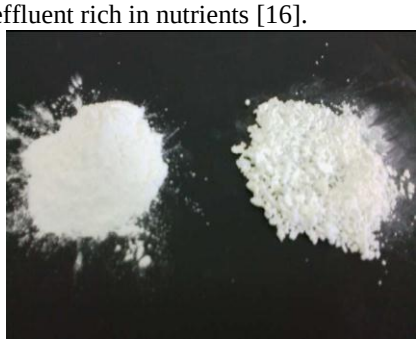

Fig. 2: Struvite picture in powder and granulated forms [16]

Struvite crystallizes as a white orthorhombic crystalline structure, which is composed of magnesium, ammonium, and phosphate in equal molar concentrations. Struvite precipitation is controlled by pH, super saturation, temperature, and impurities such as calcium. Struvite solubility decreases with increasing pH, while above a pH of 9 its solubility begins to increase [8].The chemical reaction is expressed in Eq.4. [20]

$$Mg^{+2}+NH_4^{+}+PO_4^{-3}+6H_2O \leftrightarrow MgNH_4PO_4+6H_2O\downarrow \quad (4)$$

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 precipitation Operating conditions. Doses of Mg and P depend on the stoichiometric calculations. The recovered struvite contains hardly any toxic substance, and can be sold to fertilizer companies as a fertilizer raw material [16].

Type of effluent	Removal	Molar ratios	pH	% removal	Ref
municipal landfill leachates	NH_4N	(Mg:N:P) 1:1:1	9.0	85	[12]
Piggery wastewater	PO_4-P	(Mg:N) 2.5:1	8.5	96	[6]
municipal landfill leachate	NH_4-N	(Mg:N:P) 1:1.2:1.2	9.0	90	[5]
Anaerobically Treated wastes	NH_4-N	(Mg:N:P) 1:1.25:1	9.5	88	[11]
Anaerobically treated (UASB reactor) liquid	NH_4-N	(Mg:N:P) 1.2:1:1.4	9.8	92	[1]
semiconductor wastewater	NH_4-N	(Mg:N:P) 1.2:1:1	9.2	89	[14]
anaerobic digester effluents	NH_4-N	(Mg:N:P) 1.2:1:1.2	8.5	77	[21]
Effluent from the biologically (UASBR) treated opium alkaloid wastewater	NH_4-N	(Mg:N:P) 1:1:1	9.2	65	[2]
Effluent from the anaerobic treatment of domestic wastewater + 2% leachate	NH_4-N	(Mg:N:P) 1:1:1	9.2	77	[3]

Table 1: The summary of reports on ammonium ions removal by Chemical precipitation method

VI. INFLUENCING PARAMETERS

A. Molor Ratio:

Magnesium is another important constituent ion for struvite precipitation. Hence, it also affects the super saturation level and the progress of precipitation process. The addition of magnesium from an external source is necessary as struvite forms in a theoretical Mg:N:P molar ratio of 1:1:1.Although unwanted struvite can be formed at any Mg:P molar ratio, for intentional struvite crystallization the Mg:P ratio should be at least unity. Higher magnesium can increase the P-removal from reaction solutions. At a given pH, any increase in the Mg: P ratio would increase the degree of saturation with respect to struvite formation, which, in turn, would enhance the phosphorus removal. [9]

It is found that a wide range of PO_4 and Mg ratio was applied for struvite precipitation, but in most cases, the effective ratio was 1:1 or 1:1.2 (Rahman et al., 2011). The addition of chemicals to the wastewaters would be needed to provide an equimolecular condition of PO4and Mg [10].

B. pH:

The pH plays an important role during the struvite precipitation process. Struvite or MAP can be precipitated at a wide range of pH (7.0–11.5). The rate of pH decrease reflects the speed of crystal growth rate and also influences the quality of precipitated crystals. So, pH might be used as an indicator of struvite nucleation. It is established through several researches that a comparative higher pH reduces the struvite crystal size within the same reaction time. Struvite precipitation potential significantly increases due to its solubility and decreases with the increasing of pH. Increase in pH produces higher nuclei population densities that might be the cause of producing smaller crystals. Higher pH in the crystallizer is not only responsible for smaller particles, but also higher size diversity. On the other hand, prolonged contact time of crystal suspension with supersaturated condition increased the struvite crystal size significantly [10].

VII. CONCLUSION

The presence of ammonium ions in wastewater is a major concern for environment conservation and human health. Until now, the process of removal of these ions has not reached the optimum conditions. To increase stringent environmental regulations more and more, a wide range of treatment technologies such as ion-exchange, adsorption, bio sorption, wet air oxidation, bio filtration, diffused aeration, nitrification and denitrification methods have been developed for ammonium ions removal from wastewater.

All rights reserved by *www.ijsrd.com*

Struvite crystallization process is an effective eco-friendly process that removes and recovers P and N from wastewaters. The hazardous elements in wastewaters (mainly NH_4 and PO_4) might be converted to a valuable resource through this process. So, the optimization of Mg molar ratio, pH level, aeration rate, reaction time and temperature would enhance the quality as well as production.

REFERENCES

[1] "Struvite its role in phosphorus recovery and recycling", Summery report, International conference, Scope Newsletter no. 57, 2004.
[2] Altinbas M, Ozturk I, Aydin AF, "Ammonia recovery from high strength agro-industry effluents" Water Sci Tech..45, pp. 189–96, 2002.
[3] Altinbas M, Yangin C, Ozturk I. "Struvite precipitation from anaerobically treated municipal and landfill wastewaters" Water Sci Tech. 46, pp. 271–278, 2002.
[4] Azhar Abdul Halim, MohdTalibLatif and 2Anuar Ithnin, Ammonia Removal from Aqueous Solution UsingOrganic Acid Modified Activated Carbon , 24 (1): 01-06, 2013 ISSN 1818-4952.
[5] Daekeun K, Ryu H.D, Kim M.S, Kim J., Lee S., "Enhancing struvite precipitation potential for ammonia nitrogen removal in municipal landfill leachate", Jr. of Env. Quality 30, pp 1548-1563, 1996.
[6] Huang H, Xu C and Zhang W, "Removal of nutrients from piggery wastewater using struvite precipitation and pyrogenation technology", Bio. Tech., Volume 102, Issue 3, pp.2523-2528, 2011.
[7] I. A. Bello, M. A. Oladipo, A. A. Giwa, D. O. Adeoye, Adsorptive Removal of Phenolics from Wastewater; A Review, E-ISSN:2301-4458, P-ISSN:2301-8038.
[8] K J Suthar, N P Chokshi,Study On Map Process At Laboratory Scale For The Removal Of Nh4-N, Institute Of Technology, Nirma University, Ahmedabad-382 481, 08-10 December 2011.
[9] M. L. NGUYEN, C. C. TANNER, Ammonium removal from wastewaters using natural New Zealand zeolites, New Zealand Journal of Agricultural Research, 1998, Vol. 41: 427-446.
[10] Md. MukhlesurRahman, MohamadAmranMohd. Salleh , Umer Rashid, AmimulAhsan, Mohammad MujaffarHossain, Chang Six Ra , Production of slow release crystal fertilizer from wastewaters through struvite crystallization – A review,Arabian Journal of Chemistry (2014) 7, 139–155.
[11] Miles A, Ellis T.G, "Struvite Precipitation potential for nutrient recovery from anaerobically treated wastes". Ames, IA, pp. 50011-3232, 1996.
[12] Ozturk J, Altinbas M, Koyuncu I, Arikan O and Gomec I.Y, "Advanced physico-chemical treatment experiences on young municipal landfill leachates", waste management. 23, pp 441-446, 2003.
[13] Reza BaratiRoshvanlo, AbassRezaee, HooshyarHossini, MohamadShiri, Ammonium Removal by Nitrification and Denitrification in an Integrated Fixed Film Activated Sludge Process, Health Scope. 2014 November; 3(4): e18347.
[14] Ryu H.D, Kim D, Lee S, "Application of struvite precipitation in treating ammonium nitrogen from semiconductor wastewater", Jr. of Haz. Mat. 156, page 163–169, 2008.
[15] S.A.R. Mousavi, S. Ibrahim, M.K. Aroua, S. Ghafari, Bio-electrochemical denitrification -A review, International Journal of Chemical and Environmental Engineering, April 2011, Volume 2, No.2.
[16] Sh. El Rafie, S. Hawash and M. S. Shalaby ,Evaluation of struvite precipitated from chemical fertilizer industrial effluents , Advances in Applied Science Research, 2013, 4(1):113-123.
[17] Sheela. B, KhasimBeebi, and YellajiRao.O, Simultaneous Nitrification and Denitrification ofAmmonical Wastewaters Using Bacillus SpeciesSB1 Isolated from Domestic Sewage , International Journal of Life Sciences Biotechnology and Pharma Research Vol. 4, No. 1, January 2015.
[18] Sudarsan.J.S, Renganathan.K, Ann Christy, Cost effective method for ammoniacal Nitrogen removal using SBR coupled photobioreactor, ISSN 0976 – 4402, Volume 2, No 1, 2011.
[19] T.C. Jorgensen, L.R. Weatherley, Ammonia removal from wastewater by ion exchange in thepresence of organic contaminants, Water Research 37 (2003) 1723–1728.
[20] Tao Zhang a, Lili Ding a, HongqiangRen a,*, Xiang Xiong, Ammonium nitrogen removal from coking wastewater bychemical precipitation recycle technology, water research 43 (2009) 5209 – 5215.
[21] Turker M, Celen I, "Removal of ammonia as struvite from anaerobic digester effluents and recycling of magnesium and phosphate", Bio. Tech. 98 pp. 1529–1534, 2007.
[22] V.K. Gupta, H. Sadegh M. Yari, R. ShahryariGhoshekandi, B. Maazinejad, M. Chahardori, Removal of Ammonium Ions from Wastewater A Short Review in Development of Efficient Methods, 1(2): 149-158, Spring 2015, ISSN 2383 – 3572.

All rights reserved by *www.ijsrd.com*