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Dr. Sachin Madhavrao Kanawade
 Dr. Vasantrodada Patil
 Shetkari Shikshan Mandal's
 Padmabhooshan
 Vasantrodada Patil Institute
 of Technology, Budhgaon, Tal-
 Miraj, Dist - Sangali,
 Maharashtra, India, Pin –
 416304.

Removal of Ammonium by use of Ion Exchange

Sachin Madhavrao Kanawade

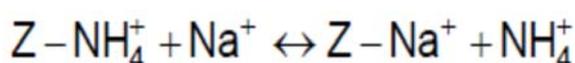
Abstract

Nitrogen in the Ammonia form can have deleterious effects in water resources. Ion Exchange by zeolite and biological Nitrification processes are two proposed methods for removing Nitrogen compounds from wastewater and effluents. The main objective of this research was to investigate the efficiency of nitrifying bacteria for regenerating Clinoptilolite zeolite. In this research, the Semnan Clinoptilolite zeolite was supplied in mesh 30. Then the capacity of zeolite in ammonium removal was determined in column system. To cultivate of nitrifying bacteria a sludge sample was taken from a domestic wastewater treatment plant and added to a 15 l aeration tank. Ammonium and other nutrients were added in the reactor daily over a month period and the effect of nitrate anion and MLVSS on nitrification process have been determined. After saturation of zeolite with ammonium, biological regeneration was done by contact of zeolite and nitrifying bacteria in column system. In this stage slurry of nitrifying bacteria is pumped up flow through the zeolite column and recycled to the aeration tank. The effluent containing the displaced ammonium is oxidized to nitrate by the nitrifying bacteria. Then the nitrified brine is clarified in a sedimentation tank and stored for reuses. The results showed that the cation exchange capacity was 10.06 (in breakthrough point) and 18.38 mg NH₄⁺ g⁻¹ zeolite as total capacity. The results indicated that nitrification accelerated by increasing in MLVSS concentration and concentration of nitrate remains in solution. The results obtained from bioregeneration tests of zeolite showed that the efficiency was 87.7 to 99.8% in period of 3.5 to 5.5 hours. Based on the results, since regeneration is achieved in high concentration of nitrate, the use of nitrifying sludge in several cycles is possible and the use of system can be appreciated to an alternative economical method for removing NH₄⁺ from effluent.

Keywords: Ammonium removal, Ion exchange, Zeolite, Nitrification, Biological regeneration

1. Introduction

Ammonia nitrogen compounds in the wastewaters and effluents have harmful effects on water resources [1]. The three most widely used methods for removal of ammonium from polluted water are air stripping, ion exchange with natural zeolite and biological nitrification denitrification [2]. Clinoptilolite is a natural zeolite that has been known for their ability to remove ammonium from polluted waters. The capacity of zeolite and chemical regeneration for ammonium removal was investigated in several studies [3-8]. Usually, the service cycle is a down flow packed bed column followed by chemical regeneration (usually by NaCl). The major drawback of this process is the high cost of the chemical regeneration stage and disposal of the concentrated ammonium-sodium brine produced [9]. During the last years several investigators have been studied the biological regeneration of ion exchange systems [9-13]. These researches supported that the mechanism of regeneration is ion exchange and nitrification of displaced ammonium respectively. The process are carried out in two separate phase [9, 11, 12]: 1) Ion exchange stage: A column filled with zeolite is used for ammonium ion exchange from secondary effluent. When NH₄ concentration breakthrough occurs, the bioregeneration stage after backwashing the bed started. 2) Bioregeneration stage: Biological regeneration has been done by contact of zeolite and nitrifying bacteria in column system. Thus the microorganisms can only oxidized ammonium released to solution, therefore, a cation containing solution is recirculated through the bed in order to desorb NH₄ to the solution (equation 1).



Correspondence

Dr. Sachin Madhavrao Kanawade
 Dr. Vasantrodada Patil
 Shetkari Shikshan Mandal's
 Padmabhooshan
 Vasantrodada Patil Institute
 of Technology, Budhgaon, Tal-
 Miraj, Dist - Sangali,
 Maharashtra, India, Pin –
 416304.

The biological regeneration process will therefore result in the accumulation of brine. This nitrate brine is easy to dispose of. It may be mixed with raw wastewater and denitrified to harmless nitrogen gas. The purpose of this study was removal of ammonium from secondary effluent by clinoptilolite followed by bioregeneration.

2. Materials and Methods

The system is composed of the following items: a column made of Plexiglas was 120 cm long with an internal diameter of 2.5 cm; 1 feed pump; 1 centrifugal recirculation pump; pH meter; 15 liter container as aeration tank and air compressor. The clinoptilolite was obtained from Semnan mines at the north part of Iran. The samples were grounded and sieved based on U.S. standard mesh number 30 and conditioned by 0.25 M ammonia sulfate and 1 M sodium chloride respectively [6]. The column filled with 30 g clinoptilolite and the bed volume obtained 36 ml. An ammonium chloride solution with 100 mg/l ammonium was applied to the column by gravity feed constant head device with 12 bed volume per hour. The ammonium content of the column effluent was measured with time. Service cycle was stopped when the ammonium concentration increased to 2 mg/l. The breakthrough curve so obtained was used to calculate the capacity of the zeolite for ammonium exchange. A schematic of pilot is shown in Fig. 1.

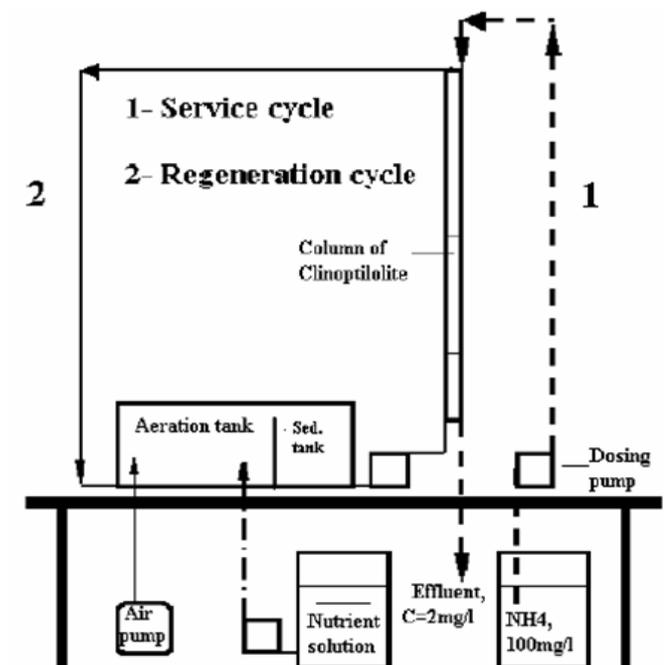


Figure 1. Schematic of designed pilot

2.1. Culturing nitrifying bacteria and nitrification test

The sludge sample from a wastewater treatment plant was used as a source of nitrifying bacteria. The volume of reactor for culturing of nitrifying bacteria was 15 liters. Nutrient solution was provided by dechlorinated water and following materials, carbonate and bicarbonate as source of C, K_2HPO_4 as source of K and P, NaCl as source of cation in regeneration period, other materials were $CaCO_3$, $MgSO_4$ and Ammonium-molibdate [11]. The source of nitrogen was Ammonium sulfate (10 to 120 mg/l). Initially, low concentration of ammonium was added to the reactor and over a five-week period the concentration of ammonium was increased to 120 mg/l. as N. The pH of reactor was

controlled at 8.0 by addition of 1M Na_2CO_3 . The temperature of reactor was controlled at 29 ± 2 °C with an immersion heater. The oxygen of reactor was supplied with an air compressor at 2 to 3 mg / l. concentrations. The rate of nitrification was determined by measured of ammonium concentration and volatile suspended solids content (MLVSS) of the aeration tank with time [11].

2.2. Bioregeneration of zeolite

In the beginning of bioregeneration mode, the column was backwash with water for 5 minutes at approximately 30 percent expansion and the feed of nutrient solution to aeration tank was stopped. The clinoptilolite was regenerated by recirculating a slurry through the column. The slurry was drawn from sedimentation tank, pumped upflow through the column and then recirculated to the aeration tank. A variable speed pump recirculated the effluent of 5 l/hr. and fluidized the bed to 20% expansion. The slurry on contact with spent clinoptilolite the solution eluted ammonium ions which were transported to the aeration tank for the oxidation. The pH of the solution was regulated at 8 ± 0.2 with manual addition of 1M Na_2CO_3 . The ammonium content of the aeration tank was monitored with time after the start of regeneration. Regeneration was stopped when the ammonium concentration fell below 0.5 mg / l. In certain interval time, The NH_4^+ content of the reactor and the amount of base added for the maintenance of pH were measured. Then the column was backwash for 5 minutes at 30% expansion to ensure that all the slurry was removed from the column. After backwash the column was replaced in service. For determination of biological regeneration efficiency of zeolite for each test, the amount of ammonium removed from the zeolite was estimated by subtracting the amount of ammonium eluted from the total ammonium content of the saturated then by dividing the amount of ammonium removed from the Clinoptilolite by the total original ammonium content of the Clinoptilolite. All analysis were made according to the standard methods [14].

3. Results and Discussion

3.1. Characterization of Clinoptilolite

The cation exchange capacity of the Semnan Clinoptilolite for ammonium was determined. The tests results on conditioned zeolite showed that the cation exchange capacity was 10.06 (in breakthrough point) and 18.38 mg $NH_4^+ g^{-1}$ zeolite as total capacity (6, 8). The results indicated that high level of regeneration (95-98%) might be achieved with solution of ClNa (table 1).

Ammonium con., C_0 , mg l ⁻¹	101
Breakthrough Capacity, mg $NH_4^+ g^{-1}$ zeolite	10.06
Total capacity, mg $NH_4^+ g^{-1}$ zeolite	18.38
Total ammonium adsorbed in column, mg	551.4
Total ammonium realized in regeneration, mg	558.37

In culturing nitrifying bacteria and nitrification test the MLVSS concentration slowly rose from approximately 190 near to 630 mg / l. The generated sludge was very flocculent and settled well. The NH_4^+ ion concentration fed to the reactor (120 mg/l.) was depleted to near zero within a matter of 4 to 6 hr. For determination of NH_4^+ stripping under the test condition prior to any nitrification test, 1 l. of distilled

water content of 120 mg / l. NH_4^+ as N was held at pH=8 and 30 °C and aerated. Long aeration time indicated an hourly NH_4 loss of 0.95 to 1.12 mg N l⁻¹ hr⁻¹ [10]. Since the rates of nitrification in this study were very much greater

than the rate of NH_4^+ stripping were negligible [13]. The activity of the nitrifying sludge were measured as mg N oxidized l⁻¹ hr⁻¹ mg MLVSS-1 (Fig. 2).

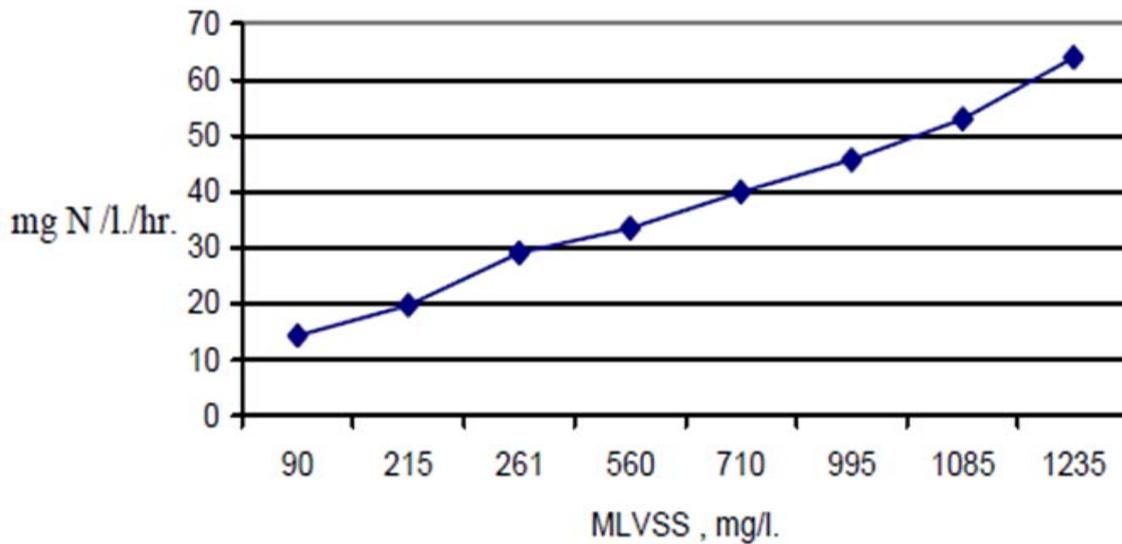


Figure 2. Influence of sludge concentration on rate of nitrification

The amount of base to control the pH in nitrification test was determined "1.47 to 1.86" meq meq⁻¹ of ammonium oxidized. The amount of base added per meq of ammonium oxidized in stoichiometric equilibrium is 2 meq meq⁻¹ NH_4^+ oxidized. It is probable that the stripping of CO_2 during aeration may account for the remaining differences between the measured and stoichiometric base requirements. Since

there was no relationship between the amounts of base added to the amount of NH_4^+ oxidized, the rate of base addition could not be used to monitor the rate of nitrification with any accuracy^[11]. The results of biological regeneration efficiency of zeolite showed 87.7 to 99.8% regeneration level achieved in a range of 3 to 5.5 hr. depending upon the MLVSS concentration (table 2).

Table 2. The results of biological regeneration test of Clinoptilolite

Test No.	MLVSS, (mg l ⁻¹)	Regeneration time (hr)	Eluted NH_4 (mg)	Nitrate produce (mg)	Oxidized N (mg N l ⁻¹ hr ⁻¹)	Efficiency (%)
1	817	3.75	531.32	1830	9.18	96.36
2	654	5	510.65	1759	6.59	92.61
3	712	4.25	536.95	1849	8.19	97.38
4	519	5.5	494.17	1702	5.82	89.62
5	649	4.75	527.47	1817	7.2	95.66
6	878	3.5	544	1874	10.07	98.66
7	545	5.5	514.13	1771	6.06	93.24
8	935	3.25	547.65	1886	10.92	99.32
9	723	4.25	483.96	1667	7.38	87.77
10	955	3	550.3	1895	11.89	99.8

In figure 3 that plotted from data in table 2 the rate of nitrification measured as mg N oxidized $L^{-1} hr^{-1}$ is plotted vs. the concentration of MLVSS.

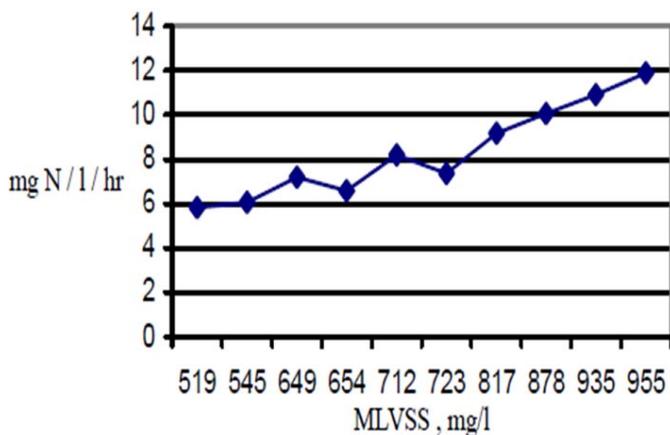


Fig 3: Influence of sludge concentration rate on bioregeneration

The results obtained from bioregeneration studies have clearly shown that the regeneration of saturated Clinoptilolite with ammonium through the use of nitrifying bacteria is possible [7, 9, 10]. This process is rapid and time required for regeneration depends very much upon the nitrifying activity of the sludge used. Fig 3 shown the amount of ammonium oxidized per hour vs. MLVSS in regeneration period. This figure is analogous to figure 2 calculated for the nitrification tests. From figures 2 and 3 the rate of nitrification is much slower during regeneration than it is when the ammonium is present in free solution. In the bioregeneration the ammonium ions within the crystalline cages of the zeolites are not accessible to nitrifying bacteria. For the oxidation of NH_4^+ ion, it must first diffuse to the particle surface or into solution where it becomes accessible to the bacteria. The relation between ammonium ion concentration in solution and variation for MLVSS concentration indicated that, the use of higher sludge concentration resulted in the displacement of higher ammonium concentration from the zeolite [11]. The higher MLVSS concentrations content the higher ambient salt concentration and thus encouraged the exchange displacement of ammonium ions and resulted in the higher solution concentration observed. So the result obtained from the influence of salt concentration in nitrification period indicated that the rate of regeneration increased with salt concentration [9].

The ion exchange process has the advantages such as high reaction rate, good control of effluent quality and no sensitivity to fluctuation in NH_4^+ in effluent concentration. Also regeneration is achieved in high concentration of nitrate. Thus the use of system can be appreciated to an alternative economical removal of NH_4^+ from effluent.

4. Conclusions

The results showed that the cation exchange capacity was 10.06 (in breakthrough point) and 18.38 mg $NH_4^+ g^{-1}$ zeolite as total capacity. The results indicated that nitrification accelerated by increasing in MLVSS concentration and concentration of nitrate remains in solution. The results obtained from bioregeneration tests of zeolite showed that the efficiency was 87.7 to 99.8% in period of 3.5 to 5.5 hours.

Based on the results, since regeneration is achieved in high concentration of nitrate, the use of nitrifying sludge in

several cycles is possible and the use of system can be appreciated to an alternative economical method for removing NH_4^+ from effluent.

5. Acknowledgment

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Author's Biography:

Dr. Sachin Madhavrao Kanawade was born in 11 March 1978 at Nashik, Maharashtra, India. His native place is Nimgaonpaga, Tal-Sangamneer, Dist-A'Nagar, Maharashtra, India. He received his Bachelor's Degree in Chemical Engineering from Pravara Rural Education Society's Pravara Rural Engineering College, Pravaranagar (Loni) which is affiliated to Pune University in India in Nov.2001. Then he worked as a Production Officer in different Multinational Chemical Industries in India (2001 to 2008) like M/S Watson Pharma Ltd, Ambarnath, MIDC, Mumbai, MS, M/S Glenmark Pharmaceuticals Ltd, Mohol, Dist. Solapur, MS, M/S Sun Pharmaceutical Industries Ltd, A. Nagar, MIDC, MS for 7 years.

Then he changes his field. He joined K. K. Wagh College, Nasik, MS, India in 2008 & worked as Lecturer for 2 years. At the same time he received his Master of Engineering in Environmental Engineering from Pravara Rural Education Society's Pravara Rural Engineering College, Loni in Dec.2010. Then he joined Pravara Rural Education Society's Sir Visvesvaraya Institute of Technology, Chincholi, Tal-Sinnar, Dist-Nasik, M.S. India in 2010 & worked as Assistant Professor in Chemical Engineering Department for 5 years. In the same period he completed his PhD Degree in Chemical Engineering in session 2011 – 2014 from Kumar Bhaskar Varma Sanskrit and Ancient Studies University Nalbari, Assam, India.

Presently he is Associate Professor at Dr.Vasatraodada Patil Shetkari Shikshan Mandal's Padmabhooshan Vasatraodada Patil Institute of Technology, Budhgaon, Tal-Miraj, Dist-Sangali, Maharashtra, India in Chemical Engineering Department. Presently he is Reviewer/Editorial Board Member/Advisory Board Member of 64 different International Journals of different fields. He having 21 International Professional Membership of different Organizations. He published 47 Technical Research Papers in different International Journals like International Journal of Wastewater Treatment & Green Chemistry, International Journal of Chemical Engineering, International Journal of Environmental Pollution Control & Management, International Journal of Multidisciplinary Approach & Studies, International Journal of Chemical Engineering & Applications, International Journal of Chemistry & Material Science & International Journal of Engineering Studies and Technical Approach etc. His research topic includes & interested in Chemical Engineering, Environmental Engineering, Wastewater Treatment by Adsorption, Advanced Separation Process, Chemical Engineering Design, Mass Transfer, Chemical Process Synthesis, Chemical Engineering Thermodynamics etc.