ZEOLITE AMMONIA REMOVAL FROM CATFISH POND WATERS

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INTRODUCTION

Need For Research

The research reported herein addresses a problem concerning research priorities 3, 5, 12 and 13, and priority 1 among the list of Mississippi Water Research priorities.

The aquaculture and agriculture industries of Humphreys, Sunflower, Washington and Leflore counties of Mississippi have produced, from 1981 to 1983, a water table drawdown of 3 to 6 feet. The catfish growing industry has been a major contributor to this, using large amounts of water -- an average of 40 million gallons annually per typical 20 acre pond. Two facts point to an increasing demand on the water supply: (1) The demand for catfish continues to grow at over 10% per year and (2) current fish growing has reached the limit of production per acre. Thus, the only course open is to build more ponds at a cost of about \$3500 per acre and pumps more water. These economic and environmental driving forces point to the desirability of high fish density water recirculation systems (Weatherly, 1983). However, an increased fish density can lead not only to acute low oxygen, but to chronic ammonia and nitrite buildup as well as off-flavor. Maintenance of water quality is, therefore, the key issue for increasing aquacultural productivity of catfish as well as many other species. One approach to maintaining water quality is to treat the water in a recirculation system. In principle ammonia can be removed by ion exchange. The natural zeolite clinoptilolite has been shown to be very effective at removing dilute ammonia from water (Mumpton, 1975, and Piper and Smith, 1983). In this work we addressed design concerns for the use of clinoptilolite in a filtration system to remove ammonia from catfish pond An effective technology would allow waters. increased fish density and hence increased production.

Research Objectives

The research objectives included first determining the ammonia uptake characteristics of clinoptilolite using model solutions and pond waters. Samples of clinoptilolite were obtained from various localities within the United States including some in Mississippi. The primary and Alabama characteristics investigated included dynamic ion and exchange, total exchange capacity, The second objective included regeneration. gathering of various design control data. These included pressure drop, ammonia capacity, and the required frequency of regeneration for the components of a zeolite (clinoptilolite) ammonia removal system. The final objective was the integration of components into a small scale ammonia removal system and the testing of this system.

Project Plan

The project was carried out in three parts. In the first part we evaluated a variety of zeolites in the laboratory to identify a zeolite species for continued studies. We required a good wet mechanical strength and ammonia uptake capacity. Accordingly we focused on determining the slaking index and the cation exchange capacity. Based on the results, a clinoptilolite was selected for further study. Column studies further revealed ammonia removal efficiency and regeneration for a packed zeolite bed at various flow rates and concentrations (Semmens, et al., 1978). Results of the initial work provided valuable data for sizing of bed volume, flow rate, pumps, brine air stripping equipment, etc.

In the second phase of the project we tested small scale components under field conditions to determine operability requirements. The main objective here was to test fine mesh screens for the straining of algae. Water strained through a 37 micron screen was passed through beds of coarse sand and zeolite while pressure buildup was monitored. Subsequent backwashing removed the algae which had accumulated on the zeolite grains.

In the third phase of the project we determined the effects of competing ions on ammonia uptake capacity. We then integrated components into a small scale pilot plant (2 gpm), tested the unit at a catfish pond, and regenerated the zeolite.

EXPERIMENTAL PROCEDURES

A. Slaking Index

For ion-exchange processes the zeolite must have high ammonium ion capacity and wet mechanical strength, or resistance to dispersion in a dynamic (moving) water. This dispersion is referred to as slaking and is quantified by the slake-durability index. To measure the index the sample is subjected to two cycles of tumbling in water (in a basket) and subsequent drying. Weight loss indicates the extent of dispersion in water. The higher index indicates higher resistance to dispersion and hence higher wet mechanical strength (Reynolds and Williford, 1988).

B. Zeolite Pretreatment

We crushed and sieved all zeolite samples to 20 x 45 mesh. We then alternately soaked the zeolite samples for several 30 minute periods in solutions of 1 M sodium chloride, NaCl, and 1 M ammonium chloride, NH4CI. This method assured the removal of exchangeable ions such as potassium to leave a NH4+-form zeolite. After this pretreatment, the zeolite was converted to the sodium form by shaking with 1 M sodium chloride solution, pH 11.5-12.0, for 24 hours. We then rinsed with distilled water until no chloride or ammonium ions were eluted, as respectively determined by silver nitrate and phenate methods (Reynolds and Williford, 1988). The zeolite was then dried overnight at 105°C and stored in a desiccator.

C. Cation Exchange Capacity (CEC) Determination

The method for CEC determination generally involved three different steps (Reynolds and Williford, 1988): (1) preparation of the sample (outlined in the preceding section); (2) saturation of the sample with ammonium ions (ammonium chloride in this case); (3) and displacement and measurement of the ammonium ions. For step 2 we saturated a 5 gram sample (from step 1) for 2 hours with 200 ml of a 1 M NH₄Cl solution at 80°C. The elevated temperature, and frequent stirring assured equilibrium conversion to the ammonium ion form. The sample was rinsed with distilled water until no chloride ions are eluted, dried overnight at 105°C, and stored in a desiccator (Reynolds and Williford, 1988).

D. Ammonia Uptake Kinetics

We first circulated an ammonia solution, 1 mg $NH_4^{+}-N/I$, through 0.04 gram zeolite samples at 400 ml/min. We then removed the samples after contact times of 2, 4, 6, and 12 hours, rinsed with distilled water as above to eliminate free ions, dried at 105°C overnight and stored in a desiccator. The zeolite was then soaked in NaCl solution for several days to displace the NH_4^{+} ions which were then measured by the phenate method.

E. Column Studies

1. Equipment. Figure 1 shows the arrangement of the equipment used in the column study.

The column consisted of a clear plexi-glass tube 2.54 cm ID x 100 cm long. It contained 30 grams (38 ml) or 125 grams (152 ml) of clinoptilolite supported by glass beads and a 80 mesh stainless steel screen. Solutions were pumped by Cole-Parmer Dual Head Chemical Feed, model C-17125LP.



Figure 1. Flow diagram for column studies

2. Procedure.

a. Monoionic Solutions: We pumped ammonia solutions (1 - 6mg NH4+-N/I) downflow through the column at 15 - 316 bed volumes/hr. When the effluent concentration reached 0.2 mg NH₄+-N/I, we stopped the service cycle and prepared the column for regeneration. We first rinsed the zeolite with 6 liters of deionized water pumped upflow to remove excess ammonium ions. We then pumped the sodium chloride solution (0.2 - 0.5 M and pH 11.5) upflow through the column at 15 BV/hr. We stopped the regeneration cycle when the effluent contained no measurable ammonium ions and then pumped an acid solution upflow at 15 BV/hr to adjust column ph from 11.5 to 7-7.5. Finally we pumped deionized water upflow through the bed prior to the next service cycle. During this procedure we observed that using this final wash to expand the bed about 50% moves finer particles upward in the bed and improves column efficiency.

b. Competing Cations Solutions: We pumped solutions with the competing cations Ca^{+2} and Mg^{+2} , 1 and 6 meq/l total, and Na^{+} , 1 meq/l, downflow through a 30 gram (38 ml) zeolite bed at 39,79, and 158 BV/hr. The ammonium cation concentration was 1 mg NH₄+-N/l. The operation of the column is the same as for monoionic solutions.

F. Pilot Unit Studies

Equipment. Figure 2 shows the schematic 1. diagram of the system. It consisted of two multimedia filters and one clinoptilolite tank, each 30 cm ID x 100 cm long steel tanks. Each filter contained three layers of filter media - from the top down six inches of 0.5 mm sand, six inches of 30x40 mesh garnet, and six inches of No. 2 gravel. The pump was a Sears 1 HP swimming pool pump, and the blower, a Dayton high-pressure, direct-drive. The stripping column, a 6" ID x 10' long PVC pipe was packed with Koch 5/8" plastic FLEXIRING. All system tubing was 1/2" plastic with PVC or plastic fittings.



Figure 2. Schematic diagram for the pilot unit system

Procedure. We divided Pilot Unit operation into 2. two cycles: The service cycle, where the ammonia is removed from the water by the zeolite, and the regeneration cycle, where the zeolite is regenerated by a high pH brine solution.

The service cycle was designed to continuously treat 2 gal/min of catfish pond water for a period of one day. Pond water was pumped downflow through the first of the multi-media filters to remove solids and algae. After the filter, the water was passed downflow through the zeolite bed and then back into the pond. Ammonia analysis samples were collected periodically at the inlet and outlet of the zeolite tank. When pressure drop through the filter reached approximately 20 psi, the second filter was put into operation and the first one shut down. Clean water from the second filter was used to back flush (upflow) the first one and get it ready for the next filtration period. The same treatment was applied to the second filter when it reached a high pressure drop.

We terminated the service cycle when the effluent from the zeolite bed reached 0.2 mg NH4+-N/I. The zeolite bed was then moved to the laboratory for regeneration.

We carried out the regeneration cycle with a brine solution of 0.35 M NaCl at a pH of 11.5. The solution was pumped upflow through the zeolite at 1 gal/min. The effluent from the zeolite tank passed downflow through the stripping tower in contact with up flow air at about 80-100 ft3/min.

RESULTS AND DISCUSSION

A. Slake-Index and Cation Exchange Capacity

Table 1 lists first and second cycle slake-durability indices, differences, natural water contents, and CEC's for clinoptilolite bearing materials from twelve localities in the United States. These results indicate that the clinoptilolites from Mississippi and Alabama had the poorest CEC's in comparison with those from other states. The best clinoptilolites were from Death Valley Junction, California and Castle Creek, Idaho, with CEC's over 200 meg/100 grams zeolite. Other test results, not reported here (Reynolds and Williford, 1988), show that the lowest CEC zeolite type was the Analcime, and the highest was Phillipsite with average CEC's of 6 and 251.8 meg/100 grams respectively.

Table 1. Cation exchange capacity, slake durability index, and natural water content for clintilolites

Locality	W (\$)	Id ₁ (*)	Id ₂ .(%)	Id 1-2	CEC*
Fish Creek Mountains, NV	4.19	99.08	98.48	0.60	136.28
Mountain Green, UT	4.02	98.14	96.00	2.14	110.82
Barstow, CA	4.38	99.48	98.45	1.03	116.58
Wellton, AZ	4.26	98.72	98.49	0.46	125.63
Bector, CA	4.44	98.75	98.49	0.26	171.31
Death Valley Junction, CA	5.26	98.46	97.42	1.04	218.48
Ft. LaClede, WY	5.38	97.84	95.59	2.25	188.13
Sand Draw, WY	5.96	98.30	95.59	1.60	155.20
Horseshoe Dam, AZ	5.92	98.84	96.70	1.37	171.84
Little Humbolt, NV	3.62	97.94	96.65	1.29	150.01
Land, AL	27.19	90.46	82.08	7.38	65.85
	77 77	72.24	53.59	13.65	60.75

* CEC in meg NH4 +/100 gram

= natural water content W

m = natural water content Id₁ = first cycle slake-durability index Id₂ = second cycle slake-durability index

** Lower values of Id indicate higher resistance to slaking

Other zeolite species were also determined to have substantialammonia CEC's. Phillipsite from Pine Valley, Nevada has a CEC of 236.7 meq/100 grams, but is too soft, with an I_{d1} of only 93.8 and an I_{d2} of 88.8. The I_{d1} - I_{d2} difference indicates a very low durability to wetting and drying much lower than most clinoptilolites. Phillipsite from Shoshone, California also has a high CEC of 266.8 meq/100 grams, but a maximum slake-durability of 95.9% and an I_{d1} - I_{d2} of 5.48. Most chabazites tested had promising CEC's ranging from 120 to 160 meq/100 grams. However, the slake durability indices were considerably lower than for most clinoptilolites. Mordenite CEC's ranged from 15 to 130 meq/100 grams.

B. Ammonia Uptake Kinetics

We determined the rate of ammonia uptake of three zeolites: Castle Creek, Spring Creek, and Death Valley Junction. The three show similar uptake rates. During the first 4-5 hours most of the ammonia exchange takes place at a high rate of about 15 meq NH₄+-N/100 grams zeolite/hr. The zeolites then slowly approach equilibrium over another 7-10 hours. Castle Creek reached equilibrium first, but the Death Valley Junction material reached a slightly higher equilibrium uptake of 85 meq NH₄+-N/100g.

C. Batch Regeneration With NaCl

Regeneration of Castle Creek, Spring Creek and Death Valley Junction zeolites required 1 to 1.5 hours for completion. This demonstrated batch regeneration rates of 150 meq NH₄+-N/100 g zeolite/hr. This high rate indicates dynamic regeneration in a packed bed can be carried out in just a few hours, depending on the concentration of the regenerating solution. The Castle Creek and Spring Creek samples had slightly higher regeneration rates.

D. Column Studies

1. Zeolite. We selected the Death Valley Junction clinoptilolite for these studies. Based on the results of the above sections it has the best combination of ammonia uptake and resistance to slaking. The material is mined by East-West Minerals, Inc.

2. Column Performance.

Ammonia removal from monoionic solution: We have evaluated ammonia uptake in a packed bed as a function of influent ammonia concentration and flow rate. Results appear as column effluent ammonia concentration versus bed volumes. In this work we defined breakthrough at an effluent concentration of 0.2 mg NH_4 +-N/I.

Table 2 summarizes the effect of changing flow rate (15 to 316 BV/hr) and influent ammonia

concentrations (1-6 mg NH₄+-N/I). Results include total bed volumes treated, ammonia uptake, average effluent concentration, and time required for breakthrough to an effluent with 0.2 mg NH₄+-N/I. Throughput volume to breakthrough appears inversely related to flow rate, although the results were a little different. The same pattern appears with respect to the ammonia exchanged onto the zeolite. In contrast, the value of the effluent average concentration increases with flow rate. In other words, increasing the flow rate decreases the efficiency of water treatment. For example, with 1 mg NH₄+-N/I influent, doubling the flow rate from 158 to 316 BV/hr reduces the ammonia uptake cycle from 4.5 to 2.14 days approximately and bed volumes treated from 17236.84 to 16250.00. The average effluent concentration increased from 0.0206 to 0.0314 mg NH4+-N/I.

Table 2. Column study results-monoionic solutions

Conditions: Influent Concentration mg NH ₄ ⁺ -N/1 (flow rate,BV/hr)	Bed volumes* treated	Ammonia absorbed mg NH4 ⁺ -N	Average effluent concentration mg NH ₄ ⁺ -N/1	Time days
6,3112 (63)	2203.77	2108.34	0.0177	1.45
6.0405 (32)	2384.68	2186.00	0.0101	3.15
5.0000 (15)	2305.74	1705.31	0.0062	6.41
4.2006 (59)	2124.83	1351.60	0.0161	1.50
3.1082 (24)	4868.03	2295.72	0.0059	8.56
3.2137 (118)	4078.95	1974.21	0.0295	1.44
1.0133 (158)	17236.84	2600.95	0.0206	4.55
0.9932 (316)	16250.00	2375.56	0.0314	2.14

 $1 \text{ BV} = 152 \text{ cm}^3 = 0.152 \text{ l.}$

Regeneration with brine: Following the above service cycles we regenerated the zeolite with brine. Sodium exchanged onto the zeolite displacing ammonium ions into the effluent stream. To regenerate the zeolite 90 to 95% required approximately 2 to 3 hours with a brine concentration of 0.35 M NaCl. Time increased to about 5 to 6 hours with concentration of 0.2 M NaCl. Increasing the brine concentration to 0.5 M NaCl did not reduce required regeneration time. The optimum concentration appears to be about 0.35 M NaCl. The results in this study agree well with those from the batch regeneration study.

Ammonia removal from solution with competing ions: We also passed solutions containing competing ions, Ca⁺⁺, Mg⁺⁺, and Na⁺, in addition to ammonia through zeolite. The presence

of competing ions reduces capacity for ammonia removal as expected. We further examined the effect of changing flow rate and ionic concentrations on the ammonia exchange capacity. Table 3 shows the number of bed volumes treated, ammonia absorbed, and the average effluent concentration for the different flow rates used. Flow rate significantly affects breakthrough saturation time. The flow rates used in these studies are considered high (Koon and Kaufman, 1971). The results show that there could be an optimum flow rate to get a maximum volume of water treated by the ion exchange process when other competing cations are present. Lowering the concentration of Ca+2 and Mg+2 to 1.0 meg/l without the presence of Na+ increased the ammonia ion exchange capacity to 0.21 meq/g. With only 0.5 meq/I Na+ present ammonia ion exchange capacity increased to 1.13 meg/g. The Na+ cation does not affect the zeolite performance as much as the Ca+2 and Mg+2 cations do. Subsequent regeneration proceeded essentially as with zeolite saturated with monoionic solution.

Table 3. Column Study Results - Competing Cations.

Cation(s) (meq/l)	Flow Rate BV/hr	Bed Volumes* Treated	Ammonia Absorbed mg NH ₄ +-N	Average Effluent Concentration mg NH ₄ +-N/I
Ca-Mg(6)	39	967	35.29	0.0396
Na(1)	79	1042	37.87	0.0435
	158	568	24.49	0.0561
Ca-Mg(1)	158	2289	87.00	0.0510
Na(1)	79	5210	159.00	0.0259
Na(0.5)	79	10989	476.00	0.0282

* 1 BV = 38 cm³ = 0.038 l.

Ammonia influent = 1 mg NH4+-N/I.

E. Pilot Unit Studies

Table 4 shows the analysis of the pond water used. High concentrations of Ca^{+2} , Mg^{+2} , and Na^{+} were present.

We prepared two batches of zeolite for this study. The amount of zeolite was calculated with basis on preliminary studies of ammonia removal with the presence of competing cations. Both of the two batches performed well only for approximately 6 hrs. instead of the 24 hrs. for which they were calculated to obtain the breakthrough effluent concentration. The process of ion exchange onto zeolites is also a surface area dependent process. Table 4. Pond water specifications

Parameter	Concentration, mg/1		
Ca ⁺²	64		
Mg ⁺²	17		
c1-	9		
Na ⁺	20		
K+	Negligible		
Bicarbonate	284		
Sulfate	30		
Total hardness	230		
Alkalinity	233		
pH, morning	8.21		
afternoon	8.67		

Because of the filters not working efficiently, much algae went to the zeolite bed, therefore, it was possible that this algae blocked macro and micro pores in the zeolite reducing the access to available area for the ion exchange process to occur. Moreover, a study performed by Watten and English (1985) showed a significant, 20%, reduction in the performance of zeolite when relatively high concentrations of organic matter was found in the water.

Although the filters can be operated for periods of almost 3 hrs, much algae, perhaps the majority passed through the filter. This was observed in earlier field work in which 90% of the algae passed through a 3 inch bed. In this work we used a flow rate of 2.55 gal/min/ft². The initial pressure drop through the system was 3 psi, and during the first hour of operation it climbed at a rate of 2 psi/hr. Then, the rate increased to 8 psi/hr. The filtration process was terminated when the pressure drop reached 20 psi because the pump would not deliver the expected flow rate.

The pilot unit's stripper design was done by scaling down other units used for similar purposes, and by considering the operating conditions needed in our research. The regeneration of the zeolite was carried out at 30 BV/hr, twice the flow rate recommended by earlier studies. We found effluent concentrations of 6 mg NH4+-N/I in contrast with concentrations of 30 mg NH4+-N/I obtained with the competing cations study. This low concentration could have caused the poor performance of the stripper. Only 1 mg NH4+-N/I was removed out of the regenerant solution, and after about 3 hr this performance was minimum. Obviously, the optimum operation of the stripping tower would be found after several runs, and optimum performance was not obtained here. However, our results compared well with those of Piper and Smith (1983).

CONCLUSIONS

1. The zeolite mineral clinoptilolite demonstrates ion exchange and wet mechanical strength suitable for ammonia removal from low concentration solutions.

2. Ammonia removal from dilute monoionic, 1 ppm NH_4^+ , solution is excellent with a typical capacity of 1.48 meq/g zeolite.

3. The zeolite can be effectively regenerated over a three hour period with a flow of 15 BV/hr of 0.35 molar NaCI.

4. Water hardness causes a significant reduction in ammonia uptake capacity. This chiefly results from competition of Ca⁺⁺ and Mg⁺⁺ ions with the NH_4^+ ions for exchange sites. Use of pond water causes further reduction possibly related to organics and algae present.

5. However, algae does not present a major problem with respect to filtration. Most passes through the filter. Backflushing effectively removes filtered algae.

6. The major obstacle to economic application of this technology is the cost of brine for the frequent regenerations required. The fact that flow can be maintained without severe plugging problems offers the possibility of applying somewhat different chemistry for ammonia removal.

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REFERENCES

- Koon, J. H. and W. J. Kaufman. "Optimization of ammonia removal by ion exchange using clinoptilolite". Sanitary Engineering Research Laboratory, College of Engineering and School of Public Health, University of California, Berkeley, Project # 17080 DAR, September 1971.
- Mumpton, F. A. "Commercial utilization of natural zeolites". <u>Industrial Rocks and Minerals</u>. Lefond, S. J., ed., A.I.M.E., Seeley Mudd Series, 4th Ed., 1975, 1262-1274.
- Piper, R. G. and C. E. Smith. "Use of clinoptilolite for ammonia removal in fish culture systems". <u>Zeo-Agriculture: Use of</u><u>Natural Zeolites in</u> <u>Agriculture and Aquaculture</u>. W. G. Pond and F. A. Mumpton. Westview Press, Boulder, Colorado, 1983, 223-228.
- Reynolds, W.R. and Williford, C.W., "Zeolite Ammonia Removal From Catfish Pond Waters," Technical Completion Report Project G1431-05, Water Resources Research Institute, Mississippi State University, 1988.
- Semmens, M. J., A. C. Booth, and G. W. Tauxe. "Clinoptilolite column ammonia removal model". Journal of the Environmental Engineering Division. April, 1978, 231-244.
- Watten, B. J. and M. J. English. "Effects of organic matter in aquacultural waste on the ammonium exchange capacity of clinoptilolite". Aquaculture. 46, 1985, 221-235.
- Weatherly, L. R. "Protein via fish farming". Chemtech. Oct., 1983, 231-244.