Indian J. Fish., 49(3) : 229-233, Jul.-Sep., 2002

Effect of commercially available bioaugmentors on the removal of ammonia and sulphide from brackishwater

K.O. JOSEPH, M. MURALIDHAR, B.P. GUPTA AND K.K. KRISHNANI
*Central Institute of Brackishwater Aquaculture,
160, Mahalingapuram Main road, Nungambakkam, Chennai - 600 034, India*

ABSTRACT

The levels of amonnia and sulphide, when exceeded the critical limit became toxic to aquatic life in brackishwater systems. An experiment was conducted in laboratory to test the efficiency of commercially available materials *viz.* health stone, BN-10 and zeolite powder in removing ammonia and sulphide from brackishwater. Health stone + BN-10 combination was significantly ($P \leq 0.05$) superior over other treatments in decreasing ammonia (71.6%), whereas, other treatments including bioaugmentors were not effective when applied alone. Zeolite was not effective in brackishwater system for ammonia removal. Sulphide removal was 100% by 3rd day with zeolite alone and health stone + BN-10 combination.

Introduction

Ammonia is the principal end product of protein metabolism in crustaceans (Hartenstein, 1970; Kinne, 1976) and found in both ionised (NH_4^+) and unionised (NH_3) forms. The unionised form was usually toxic (Burkhalter and Kaya, 1977; Armstrong *et al.,* 1978). When the concentration of ammonia exceeded 2 or 3 mg/l, it became toxic to aquatic life (Mumpton, 1977). High concentrations of ammonia in intensive culture ponds caused poor growth and survival of fish and shrimp (Colt and Armstrong, 1981; Tucker and Robinson, 1990).

In intensive culture systems under anaerobic condition, certain heterotrophic bacteria can use sulphate and other oxidised sulphur compounds as terminal electron acceptors in metabolism and excrete sulphide (Boyd, 1982). The unionised form of hydrogen sulphide is toxic to aquatic organisms and the sulphide concentration of 0.01 to 0.05 mg/l is lethal to fish (Adelman and Smith, 1970; Smith and Oseid, 1975). Smith *et al.* (1976) suggested that any detectable concentration of hydrogen sulphide in pond water is considered undesirable. The build-up of hydrogen sulphide in the culture pond is considered highly toxic to shrimp and affects shrimp production (Gopakumar and Kuttyamma, 1997).

Fast ammonia removal by zeolites is a well known process in fresh water aquaculture (Sand and Mumpton, 1977). Zeolite treatment of shrimp ponds for ammonia control is a standard practice in south east Asia (Boyd, 1990). The literature available on the removal of ammonia and hydrogen sulphide from brackishwater systems is meagre. The present paper deals with the efficiency of commercially available materials tested under laboratory condition to remove metabolites from brackishwater.

Materials and methods

Health stone : This powder, imported from Taiwan comprised a mixture of inorganic salts containing SiO_2 (63.27%), Al_2O_3 (17.66%), Fe_2O_3 (3.93%), CaO (4.41%), MgO (2.68%), TiO_2 (0.32%), Na_2O (3.88%), K_2O (1.18) and LiO (1.16%). Health stone was applied @ 500 kg/ha.

BN-10 : A typical bacterial augmentation material imported from Taiwan contained nitrobacter, nitrosomonas, sulphobacteria and organic analytical microorganisms. The rate of application for BN-10 was 20 kg/ha.

Zeolite : Natural hydrous aluminium silicates with one or more alkaline metals easily exchanged for other cations. The processed zeolite mineral powder was used @ 500 kg/ha.

The experiment was conducted in 10 litre glass jars containing water with a salinity of 15 ± 0.5 ppt, temperature of 30.5 ± 0.5°C and pH 8.1. Standard ammonia (Ammonium sulphate) and sulphide (Sodium sulphide) solutions were added separately to the medium to make an initial concentration of 0.067 mg/l unionised ammonia and 1 mg/l sulphide. The test materials were applied to jars singly and in combination. The treatments were : (1) Health stone, (2) BN-10, (3) Health stone + BN-10, (4) Zeolite (5) Control (without any of test materials).

Water samples were collected for 5 days continuously after the application of test materials and analysed for ammonia on alternate days and sulphide every day. Ammonia nitrogen was estimated by Strickland and Parson method (1972), hydrogen sulphide concentration by iodometric method (A.P.H.A, 1989).

The experiment had a completely randomised design with three replicates. ANOVA and Duncan's multiple range tests were used to determine differences in treatment means (Gomez and Gomez, 1984).

Results and discussion

Ammonia removal

There was significant difference between different treatments in the removal of ammonia from the saline water. Health stone + BN-10 treatment combination was significantly superior (≤ 0.05) over the other treatments in reducing ammonia concentration from

TABLE 1. *Changes in ammonia concentration affected by treatments*

Days after treatment	Ammonia concentration (ppm)*				
	Health stone	BN - 10	Health stone + BN - 10	Zeolite	Control
1	0.060 (±0.002)^{d}	0.062 (±0.007)^{c}	0.055 (±0.004)^{f}	0.066 (±0.001)^{ab}	0.067 (±0.002)^{a}
2	0.058 (±0.01)^{e}	0.058 (±0.008)^{e}	0.044 (±0.006)^{g}	0.065 (±0.002)^{b}	0.066 (±0.001)^{ab}
3	0.039 (±0.005)^{i}	0.042 (±0.009)^{h}	0.019 (±0.01)^{j}	0.060 (±0.005)^{d}	0.065 (±0.005)^{b}

* - Average values of three replicates with standard deviation in parentheses. The values with similar superscript alphabets are not significant ($P \geq 0.05$).

0.067 to 0.019 ppm on the fifth day. Zeolite treatment was not effective when compared with control, as revealed by the decrease in unionised ammonia from an initial concentration of 0.067 to 0.060 ppm on fifth day after the treatment (Table 1). Two-way statistical analysis revealed that Health stone + BN-10 was able to decrease ammonia concentration upto 0.039 ppm (Fig. 1) whereas, on fifth day, the removal was 0.045 ppm from an initial value of 0.067 ppm.

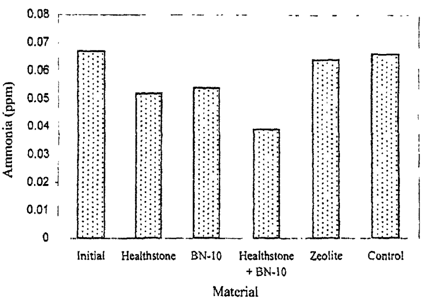

Fig.1. Effect of treatments and material on the removal of ammonia from brackishwater

Chiayavareesajja and Boyd (1993) reported that zeolite quickly reduced total ammonia nitrogen concentration in freshwater with little further removal. Zeolites function as ion exchange material. Zeolites shows a high preference for ammonium ions as it can be seen from the selectivity studies it exhibits for the following ions.

$Cs^+ > K^+ > NH_4^+ > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+}$

The present study showed that quick removal of ammonia by zeolite was not taking place in the tested saline water. The efficiency of zeolites was enormously reduced in seawater systems (Lopez-Ruiz and Fernandez del Barrio, 1987). In saltwater aquaculture systems, sodium in water competes with ammonia for binding sites on zeolite, making the latter less effective for removal of ammonia from saltwater than freshwater. The ion exchange capacity of zeolites is dependent on many factors such as size of exchanging ions, ion concentrations and presence of competitive ions, structure of zeolites etc. Papadopoulos *et al.* (1996) observed partial ion exchange capacity using natural zeolites and this was attributed to the blocked channels of the zeolite due to impurities and volume steric effect.

The mode of action of bacterial inoculate is claimed to be the enhancement of natural processes such as ammonia removal, organic matter degradation, denitrification and degradation of toxic pollutants. Bacteria augmentation with BN-10 alone reduced the ammonia concentration, but the decrease was more with health stone + BN-10 combination. The interaction effect (Treatments x Days of incubation - TXD) was significant in decreasing ammonia concentration.

Zeolite reduced the ammonia concentration to a maximum of 10.5 percent only by fifth day, whereas, other treatments when applied singly, the percent reduction was up to 40. A maximum of 71.6 percent reduction in ammonia was observed with health stone + BN-10 combination.

Sulphide removal :

All the treatments except BN-10 recorded a significant decrease in sulphide as compared to control. Health stone + BN-10 combination was superior over other treatments followed by health stone alone, as revealed by the sulphide concentrations of 0.02 and 0.06 ppm respectively on 2nd day. Sulphide concentration was nil with zeolite and health stone + BN-10 treatments by third day, while it was nil with health stone alone by fourth day (Table 2). A decrease of 90 per cent and above was observed by second day with health stone and health stone + BN-10 treatments. BN-10 when applied alone was not effective as compared to control

TABLE 2. *Changes in sulphide concentration affected by treatments*

Days after treatment	Ammonia concentration (ppm)*				
	Health stone	BN - 10	Health stone + BN - 10	Zeolite	Control
1	0.98 (±0.02)[a]	0.99 (±0.01)[a]	0.99 (±0.01)[a]	1.0 (±0.01)[a]	1.0 (±0.01)[a]
2	0.06 (±0.03)[g]	0.62 (±0.08)[c]	0.02 (±0.02)[gh]	0.97 (±0.02)[a]	0.76 (±0.02)[b]
3	0.04 (±0.02)[gh]	0.36 (±0.05)[e]	Nil[h]	Nil[h]	0.52 (±0.07)[d]
4	Nil[h]	0.32 (±0.06)[e]	Nil[h]	Nil[h]	0.32 (±0.04)[e]
5	Nil[h]	0.14 (±0.05)[f]	Nil[h]	Nil[h]	0.16 (±0.03)[f]

Average values of three replicates with standard deviation in parentheses. The values with similar superscript alphabets are not significant (P≥0.05).

(84%), though the decrease in sulphide concentration was 86 per cent at the end of experiment.

Zeolite is an alumino silicate mineral that possesses unique properties due to its crystalline structure and resulting molecular-sized cavities. These cavities serve as a molecular sieve that absorbs hydrogen sulphide gas. BN-10 contains sulpho bacteria which may be responsible in decreasing sulphide concentration. Health stone is a mixture of inorganic salts containing ferrous compounds which might have replaced sulphide from the system.

The interaction effect of T X D was significant in decreasing sulphide concentration. Health stone + BN-10 combination followed by health stone alone and zeolite were effective as compared to control in decreasing sulphide concentration from an initial value of 1 ppm to 0.202, 0.216, 0.393 and 0.551 ppm, respectively (Fig. 2). The sulphide concentration on fifth day after treatment was 0.06 ppm as compared to 0.991 ppm on the first day.

Zeolite was not effective in decreasing ammonia concentrations, but effective in reducing sulphide. Bacterial augmentation with BN-10 and combination with health stone was more effective in reducing ammonia and sulphide concentrations as compared to their application alone.

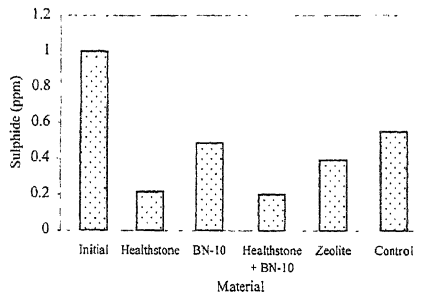

Fig.2. Effect of treatments and material on the removal of sulphide from brackishwater

Acknowledgements

The authors are grateful to Dr. G.R.M. Rao and Dr. K. Alagarswami, present and former Directors of Central Institute of Brackishwater Aquaculture for their keen interest and encouragement during the course of study.

References

Aldelman, I.R. and L.L. Smith, Jr. 1970. Effect of hydrogen sulphide on northern pike eggs and sac fry. *Trans. Amer. Fish Soc.*, **99**: 501-509.

A.P.H.A., 1989. *Standard methods for the examination of water and wastewater.* 16th ed., A.P.H.A., Washington, DC, 874 pp.

Armstrong, D.A., D. Chippendale, A.W. Knight and J.E. Colt 1978. Interaction of ionised and unionised ammonia on short term survival and growth of the Malaysian prawn, *Macrobrachium rosenbergii. Biol. Bull.,* **154**(1): 15-31.

Boyd, C.E. 1982. *Water quality management for pond fish culture,* 319 pp. Elsevier Sci. Publ. Co., Amsterdam.

Boyd, C.E. 1990. *Water quality in ponds for aquaculture.* 482 pp. Ala. Agric. Exp. Sta., Auburn University, Al, USA

Burkhalter, D.E. and C.M. Kaya 1977. Effects of prolonged exposure to ammonia on fertilised eggs and sac fry of rainbow trout *(Salmo gairdneri). Trans. Amer. Fish. Soc.,* **106**: 470-475.

Chiayvareesajja, S. and C.E. Boyd 1993. Effects of zeolite, formalin, bacterial augmentation and aeration on total ammonia nitrogen concentrations. *Aquaculture,* **116**: 33-46.

Colt, J.E. and D.A. Armstrong 1981. Nitrogen toxicity to crustaceans, fish and molluscs. In: *Bio Engineering Symp. Fish Culture,* American Fisheries Society, North East Society of Conservation Engineers, Bethesda, MD, p. 34-37.

Gomez, K.A. and A.A. Gomez 1984. *Statistical Procedures for Agricultural Research,* 2nd ed. 680 pp. An International Rice Research Institute Book. Wiley, New York.

Gopakumar, G. and V.J. Kuttyamma 1997. Effect of hydrogen sulphide on the substratum selectivity of shrimp *Penaeus indicus* (Crustacea/Decapoda). *Indian J. Mar. Sci.,* **26**: 104-106.

Hartenstein, R., 1970. Nitrogen metabolism in non-insect arthropods. In : *Comparative biochemistry of nitrogen metabolism Vol. 1,* Academic Press, New York, p. 299-372.

Kinne, O. 1976. Cultivation of marine organisms: Water quality management and technology. In: *Marine Ecology,* O. Kinne (Ed.), Wiley Interscience, New York, p. 79-300.

Lopez-Ruiz, J. and M.T. Fernandez del Barrio 1987. Elimination of ammonium by zeolites. 1 Congreso Nacional de Acuicultura, El Grove. Cuadernos Marisqueros. Publ. Technica no. 9, 209-213.

Mumpton, F.A., 1977. Natural Zeolites, In : *Natural Zeolites.* L.B. Sand and F.A. Mumpton (Eds.), Perganon Press, New York, 463 pp.

Papadopoulos A., E.G. Kapetanios and M. Loizidou 1996. Studies on the use of clinoptilolite for ammonia removal from leachates. *J. Environ. Sci. Health,* **31**:1:211-220.

Sand, L.B. and F.A. Mumpton 1977. *Natural Zeolites,* 463 pp. Perganon Press, New York, USA.

Smith, L.L. Jr. and D.M. Oseid. Chronic effects of low levels of hydrogen sulphide on freshwater fish. *Progress in Water Technology,* **7**:599-605.

Smith L.L. Jr., D.M. Oseid, G.L. Kimball and S.M. El-kandelgy 1976. Toxicity of hydrogen sulphide to various life history stages of bluegill *(Lepomis macrochirus). Trans. Amer. Fish Soc.,* **105**: 442-449.

Strickland, J.D.H. and T.R. Parson 1972. *A practical handbook of seawater analysis.* 310 pp. Fish Res. Bd. Can., Ottawa, No. 167.

Tucker, C.S. and E.H. Robinson 1990. *Channel Catfish Farming handbook,* 454 pp. Van Nostrand Reinhold, New York.