

# *In vitro* Comparison of Zeolite (Clinoptilolite) and Activated Carbon as Ammonia Absorbants in Fish Culture

H. Emadi, J.E. Nezhad and H. Pourbagher

## Abstract

Conditioned activated carbon was compared with zeolite (clinoptilolite) at different salinities, Total Ammonia Nitrogen (TAN) and times. The dosages of both materials were the same i.e. 10 ppt. Different salinities from 0 to 30 ppt were prepared in 24 three-liter plastic buckets. One, 3 and 5 ppm TAN were added to the buckets. TAN absorption trend was monitored every 4 hours over 24 hours. It was clear that over time, removed TAN decreased for both materials. No change was observed in the buckets containing zeolite, after 8 hours. A similar trend was observed for activated carbon, but, despite the decreasing rate of absorption by activated carbon, ammonia (TAN) absorption by both materials decreased. The largest difference between these two materials was observed at 0 ppt salinity and difference was not significant at 30 ppt salinity. After 24 hours, concentration of TAN in buckets containing 1, 3 and 5 ppm TAN decreased by 80.8%, 65.4% and 58.8%, respectively.

At the conclusion of the study, a significant difference was observed between zeolite and activated carbon and the results obtained by zeolite were found to be more satisfactory than activated carbon.

## Introduction

Ammonia at relatively low concentration can have negative effects on fish tissues and physiological factors such as growth rate, oxygen consumption and disease resistance (Piper et al. 1984) and can restrict yields in intensive fish culture (Delistraty et al. 1977; Colt and Armstrong 1981).

The two principal methods of removing ammonia in water are: (1) nitrification, and (2) ion exchange. Nitrification is a two-step oxidation of ammonia to nitrate by autotrophic bacteria, and is an essential part of a recirculating fish culture system (Bower et al. 1981). For nitrification, materials such as oyster shell, rock, sand, activated carbon, etc. are used to prepare a substrate for bacteria.

Ion exchange is a process in which ions of an exchanger (synthetic or natural resin) are exchanged with certain ions in wastewater. Some natural resins, such as zeolite, are

used in removing ammonia from wastewater culture systems. One of the best zeolites in ammonia removal is clinoptilolite. Activated carbon needs to be conditioned before use. At 20-22 °C, 60 days of conditioning is needed; a longer time is needed at lower temperatures (Bower et al. 1981). Clinoptilolite does not need conditioning.

Bower and Turner (1982) showed that the use of clinoptilolite in sealed plastic bags for the transport of live fish can be effective in reducing ammonia. Turner and Bower (1982) examined the influence of bacterial nitrification during the transport of live fish and showed that addition of a substrate containing nitrifying bacteria to sealed plastic bags is a practical way for reducing ammonia.

No study has yet been carried out to compare carbon and zeolite simultaneously. This study was therefore undertaken to compare the response of activated carbon containing nitrifying bacteria and

zeolite (clinoptilolite) under similar conditions.

## Materials and Methods

To cultivate nitrifying bacteria, four all-glass aquariums were equipped with airstone and immersion heater, each aquarium was allocated a certain salinity, i.e. 0, 10, 20 and 30 ppt. The aquaria were filled with 0.5 l of water from a trout farm. Ammonium chloride was added to the water as a source of ammonia (Turner and Bower, 1982) until the bacteria was capable of oxidizing at a rate of 5 ppm per 24 hrs. Water temperature was maintained at 22-24°C. As the pH of water was maintained above 8.0 no buffer was added. To accelerate bacterial propagation, activated carbon was placed in the underwater aquarium pump (filter), through which the water passes (Landau, 1992).

The carbon used was of commercial grade and the utilized zeolite was a product of Afrand Tooska Co. Ltd., Iran. The average diameter of the grains for both materials was 1-2 mm.

In 24 three-liter plastic buckets, solutions of different salinities, i.e. 0, 10, 20 and 30 ppt were prepared. Total ammonia nitrogen (TAN) was added at 1, 3 and 5 ppm. Ten ppt (30 g) activated carbon was added to half the number of buckets and 10 ppt zeolite was added to the remainder.

Every 4 hrs, a 100 cc sample was taken and replaced with the same volume of water of same salinity. Samples were preserved with sulphuric acid and stored in a fridge for later analysis (Clesceri et al. 1989).

TAN was determined spectrophotometrically by the method of Indirect Nesslerisation (Clesceri et al., 1989).

The statistical significance of the differences between mean values for various treatments was determined with Duncan's multiple range test and student's t-test.

## Results and Discussion

Over time, efficiencies of both materials declined. The highest amount of TAN was removed in the first 4-hour period (Fig.1). After 4 hrs, TAN decline was not significant ( $P>0.05$ ); after 8 hrs, TAN decline continued constantly and was not significant ( $P>0.05$ ). There was no change in TAN concentration after 8 hrs in the buckets containing zeolite. Zeolite is an ion exchanger and in the presence of a large amount of ammonia, ion exchange will take place quickly, after which it loses its ion exchange ability. In the case of activated carbon, nitrifying bacteria need oxygen to oxidize ammonia; therefore dissolved oxygen decreases over time. In other words,

oxygen depletion leads to a reduction in nitrification rate (Lawson, 1994). Nitrification is a process which produces acid and it was noted that there was a definite decrease in pH in the buckets containing activated carbon, sometimes falling below seven.

The effect of salinity on the two materials studied was highly significant ( $P<0.0001$ ). With increasing salinity, the capability of both materials was reduced. This could be due to the fact that other cations in seawater may be competing with ammonium ( $\text{NH}_4^+$ ). The decrease in activated carbon efficiency due to salinity may be related to two factors: (1) biomass of bacteria was low or (2) bacteria species were not suitable for saline water. For conditioning of activated carbon in freshwater, effluent of a trout raceway was added to the aquaria. By increasing salinity from 0 to 30 ppt, the difference between the two materials decreased and at 30 ppt, no significant difference was observed ( $P>0.05$ ). It seems that at salinities higher than 30 ppt, activated carbon can be more promising than zeolite (Fig. 2). With regard to the interaction of ambient ammonia and salinity (Fig. 3), at each concentration of ammonia and at salinities more

than 10 ppt, it is recommended that activated carbon be used.

With increasing initial ambient ammonia, after a certain period, residual ammonia was further decreased. After 24 hrs, TAN in containers containing 1, 3 and 5 ppm decreased by 80.8%, 65.4% and 58.8%, respectively.

Although this study showed that zeolite generally acts better than activated carbon, it does not indicate that it is incapable of nitrification. Conditioning qualifications of activated carbon have effects on the results of this process; especially the material used for seeding of bacteria is very important. Environmental history of bacteria in seed media may be the primary determinant of the effectiveness of seeding (Bower and Turner 1981). As mentioned earlier, lack of access to a material as a suitable seed, especially for saline waters may be the main reason for the lack of effectiveness of activated carbon observed in this study. Zeolite has great potential for removing ammonia from water, especially at salinities lower than 10 ppt but the main obstacle in using zeolite is its uselessness after a few hours. This does not mean that it should not be used in fish culture as it is easy to regenerate.

Hours	0	4	8	12	16	20	24
Activated carbon	3	1.114	1.001	0.919	0.856	0.747	0.63
Zeolite	3	0.877	0.673	0.635	0.633	0.626	0.624

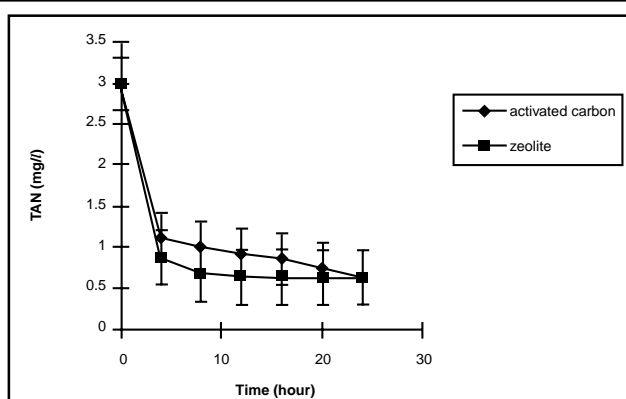


Fig. 1. TAN declining trend with time.

Zeolite is cheaper than activated carbon and does not need conditioning before use. This makes use of zeolite in fish culture facilities a better option for reducing ammonia concentration.

## References

Allen, G. L., G. B. Maguire and S. J. Hopkins. 1990. Acute and chronic toxicity of ammonia to juvenile *Metapenaeus macleayi* and *Penaeus monodon* and influence of flow dissolved-oxygen levels. *Aquaculture*. 91:265-280.

Bower, C.E. and D.T. Turner. 1981. Accelerated nitrification in new seawater

culture systems: effectiveness of commercial additives and seed media from established systems. *Aquaculture*. 24:1-9.

Bower, C.E. and D.T. Turner. 1982. Ammonia removal by clinoptilolite in the transport of ornamental freshwater fishes. *Prog.Fish-Cult.* 4(1):19-23.

Clesceri, L.S., A.E. Greenberg and R.R. Trussell, Editors. 1989. Standards methods for the examination of water and wastewater, 17th edition. DHA-AWWA-WPCK. Washington D.C.

Colt, J.E. and D.A. Armstrong. 1981. Nitrification toxicity to crustaceans, fish and molluscs, p. 33-47. *In* L. J. Allen and E. C. Kinney (eds.) *Proceeding of*

the Bio-engineering Symposium for Fish Culture. Fish Culture Section of the American Society (FCS publ.1), Bethesda, Maryland.

Delistrarty, D.A., J.M. Carlberg, J.C. Van Olst and R. F. Ford. 1977. Ammonia toxicity in cultured larvae of the american lobster (*Homarus americanus*). *Proc.Annu.Meet.World Maricult.Soc.* 8:647-672.

Horsch, M.C. and J.E. Holway. 1984. Use of clinoptilolite for salmon rearing, p. 235-243. *In* W.G. Pond and F.A. Mumpton (eds.) *Zeo-agriculture, use of natural zeolites in agriculture and aquaculture*. Western Press.

Landau, M. 1992. *Introduction to aquaculture*. John Wiley & Sons, New York. p. 440.

Lawson, T.B. 1994. *Fundamentals of aquacultural engineering*. Chapman and Hall. p.355.

Piper, R.G. and C.E. Smith. 1984. Use of clinoptilolite for ammonia removal in fish culture systems, p. 224-234. *In* W.G. Pond and F.A. Mumpton (eds.) *Zeo-agriculture, use of natural zeolites in agriculture and aquaculture*. Western Press.

Turner, D.T. and C.E. Bower. 1982. Removal of ammonia by bacteriological nitrification during the simulated transport of marine fishes. *Aquaculture*. 29:347-357.

Wheaton, F.W. 1977. *Aquacultural engineering*. Wiley Interscience, New York.

Salinity (ppt)	0	10	20	30
Activated carbon	1.011	1.278	1.242	1.194
Zeolite	0.554	0.992	1.212	1.256

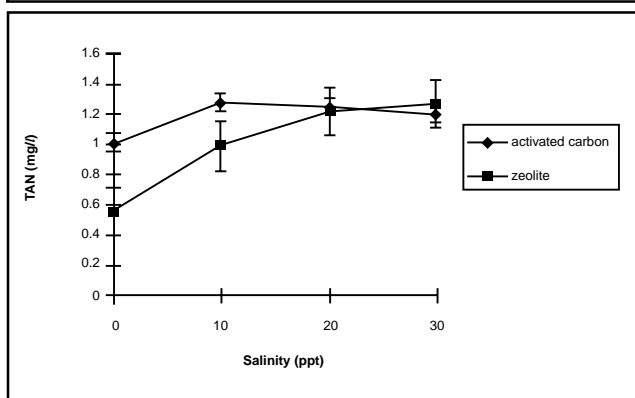


Fig. 2. Interaction of ammonia absorbant and salinity.

TAN	Salinity (ppt)			
	0	10	20	30
1	0.148	0.152	0.154	0.163
3	0.474	1.013	1.069	1.22
5	1.04	1.883	2.426	2.368

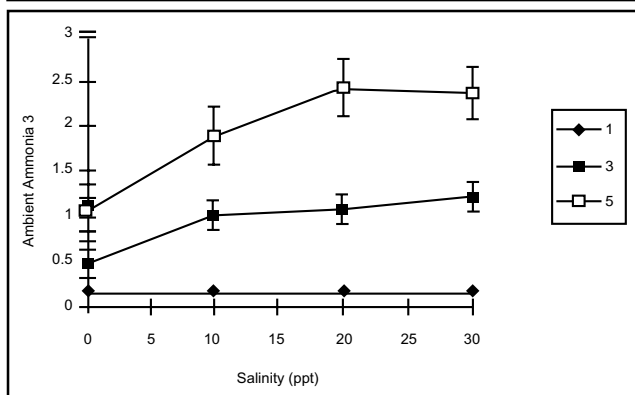


Fig. 3. Interaction of ambient ammonia absorbant and salinity.

**H. Emadi** is a visiting professor and **J.E. Nezhad** is a professor at the University of Tehran, Department of Science. **H. Pourbagher** graduated with an M.Sc from the University of Tehran.