

Comparison of the Zeolite Sodium Chabazite and Activated Charcoal for Ammonia Control in Sealed Containers

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Abstract

Zeolites are often used for water quality control in live fish transport. Activated charcoal has also been proposed for this purpose. In this experiment, the effects of the zeolite sodium chabazite and granular activated charcoal on water quality were studied in nine sealed 500 ml flasks held at 22°C. Three treatments were commercial grey zeolite (90% pure herschelite-sodium chabazite), commercial granular activated charcoal and control, each in triplicate. To each treatment was added 10 mg·l total ammonia-nitrogen (TAN) and for simulated stress control 9 g·l un-iodized salt (NaCl). Zeolite and activated charcoal were added at the rate of 20 g·l. In 96 h, total ammonia-nitrogen (TAN) means in the zeolite treatment and in the activated charcoal treatment both decreased significantly from 9.59 to 4.02 mg·l, and 9.40 to 7.91 mg·l, respectively. However, the mean pH of the zeolite treatment increased from 7.85 to 7.95, while the mean pH in the activated charcoal treatment increased from 8.12 to 9.13. Calculated un-ionized ammonia (UIA) levels of the zeolite treatment decreased from 0.35 to 0.16 mg·l, after 96 h, although not significantly. In the activated charcoal treatment, UIA increased significantly from 0.50 to 3.02 mg·l. Significant differences were observed in TAN, UIA and pH between the activated charcoal treatment and the zeolite treatment. Zeolite significantly controlled TAN and UIA, with stable pH. Activated charcoal slightly decreased TAN, but greatly increased pH and UIA. Therefore, this kind of activated charcoal reduced water quality and is judged to be not useful in fish transport. Commercial grey zeolite, even with salt addition, was effective in removing toxic ammonia for live fish transport.

Introduction

Ammonia is the principal nitrogenous waste product excreted by crustaceans and teleosts (Boyd and Tucker 1998). During live fish transport, total ammonia-nitrogen (TAN) can reach more than 14 mg·l as a result of fish metabolism, and to a lesser extent bacterial action on fish waste excreted into the water (Swann 1993). The TAN consists of two forms of nitrogen that exist

in a pH and temperature dependent equilibrium of un-ionized ammonia (NH_3 , UIA) and the ammonium ion (NH_4^+). While NH_3 is toxic to fish, NH_4^+ is not toxic to fish (Boyd and Tucker 1998). For a given concentration of TAN, the concentration of UIA increases with increasing pH, and to a lesser degree increasing temperature. The UIA form of ammonia is harmful at concentrations as low as 0.2 mg·l, and levels above 1.4 mg·l are lethal to some warm water fish (Collins 1990; Swann 1993). Two methods are commonly used to control the accumulation of ammonia in transport water: altering the metabolism of the fishes and removing ammonia from the water after it has been excreted. Ice, anaesthetics, salt, etc. have been applied to reduce metabolism in plastic bag transport (Martin 1980, 1981; Amend et al. 1982; Froese 1986; Teo et al. 1989; Swann 1993; Cole et al. 1999). Zeolite application is commonly used for controlling ammonia during live transport (Amend et al. 1982; Teo et al. 1989; Chiayvareesajja and Boyd 1993; Cole et al. 1999). Interest in activated charcoal has also been reported for shipping of ornamental tropical fish in Asia (Mike Freeze, Keo Fish Farm, AR, USA. Pers. Comm.), but published accounts are unavailable. Emadi et al. (2001) compared zeolite and nitrifying bacteria-colonized carbon for fish transport. The purpose of the present study was to compare the effects of zeolite and unconditioned activated charcoal on controlling ammonia in freshwater, with salt addition to simulate stress control requirements.

Materials and Methods

The experiments were conducted in nine 500-ml flasks. Commercial grey zeolite (5 mm X 3 mm chips) and granular activated charcoal (5 to 15 mm pellets, 4 mm diameter) were obtained from Southern Aquaculture Supply, Lake Village, AR. The zeolite was a hydrous sodium aluminosilicate highly rated for use in aquaculture and 90% pure natural harschelite-sodium chabazite (CABSORB, #ZS-500H, GSA Resources Inc., Tucson, AZ), with a 0.2 micron crystalline structure and CEC of between 2.5 and 3.0 meq×g. Treatments of zeolite, activated charcoal and a control were designed. Each treatment had 3 replicates. A stock solution of 500 mg·l NH_4Cl standard solution was prepared and diluted with dechlorinated Pine Bluff tap water (Sparta aquifer source-26 mg·l hardness, 30 mg·l alkalinity) to provide 500 ml of approximately 10 mg·l TAN solution in each flask. Uniodized salt was applied to all flasks at 9 g·l, as recommended for stress reduction (Cole et al. 1999). The zeolite and activated charcoal were added at 20 g·l at the beginning of the experiment and the flasks were sealed by stretched parafilm. The experiments lasted for 96 h, during which time the TAN, pH and water temperature in each flask were monitored at 0.25, 3, 6, 12, 24, 48, 72 (76.5 h for TAN), and 96 h. Temperature during the trial was 22.0 ± 0.1°C. The Nessler method and colorimeter were used to determine TAN; pH was monitored by Orion Model 420 A pH meter. UIA (Un-ionized ammonia) concentrations were calculated by UIA formula according to the corresponding pH, temperature and salinity (Boyd and Tucker 1998).

Statistical significance of the differences in means of pH (following negative log transformation), TAN and UIA among the control, activated charcoal, and zeolite treatments were determined using ANOVA with GLM procedure by SAS software (SAS Institute Inc., Cary, NC, USA 1989). When the F-ratio for the ANOVA was statistically significant ($P < 0.05$), Least Square Means and Duncan's Multiple Range Test were conducted to evaluate all pair-wise comparisons of means. Simple linear regressions between pH, TAN or UIA and time were performed and best fit chosen.

Results

The TAN decreased in all three treatments (Fig. 1). After 96 h, TAN in control treatment decreased by 1.05 mg·l (from 9.91 to 8.86 mg·l), or 10.6%. In the activated charcoal treatment TAN decreased by 1.49 mg·l (from 9.40 to 7.91 mg·l), or 15.9%, and TAN in zeolite treatment decreased by 5.57 mg·l (from 9.59 to 4.02 mg·l), or 58.1%. The regression equations of TAN in control, activated charcoal, and zeolite treatments with time (h) are: $y = -0.0042x + 9.42$ ($r = 0.6448$); $y = -0.0098x + 8.94$ ($r = 0.8526$); $y = -1.338\ln(x) + 10.29$ ($r = 0.9959$), respectively. Mean TAN at 96 h of both activated charcoal and zeolite treatments were significantly different from that of the control ($P < 0.01$). Zeolite treatment's effects on TAN were also significantly better than that of activated charcoal ($P < 0.01$).

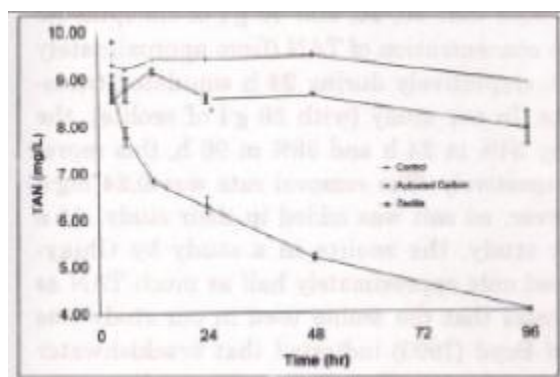


Fig. 1. Change in mean TAN over 96 h in each treatment.

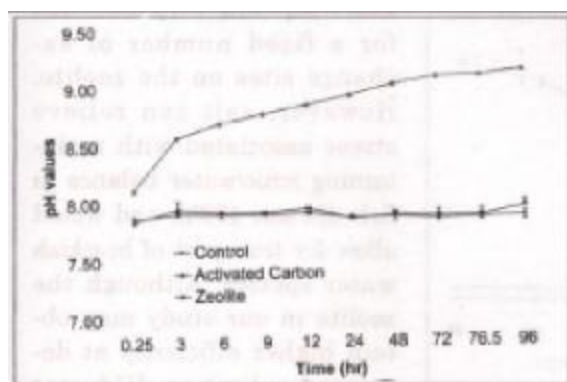


Fig. 2. Change in mean pH over 96 h in each treatment.

lite treatments were significantly different from that of the control ($P < 0.01$). Zeolite treatment's effects on TAN were also significantly better than that of activated charcoal ($P < 0.01$).

The pH in the control and zeolite treatment remained relatively stable during the 96 h experiment (Fig.2). The pH means in the control ranged from 7.85 to 7.91 and those in zeolite treatment ranged from 7.85 to 7.95. However, the pH means in activated charcoal treatment increased with time from 8.12 to 9.13. The regression equation between pH and time (h) in activated charcoal treatment is: $y = 0.412\ln(x) + 8.20$ ($r = 0.9959$). Mean pH in zeolite treatment was not significantly different from that of control ($P = 0.0765$), however, there were significant

differences between activated charcoal treatment and control, and between activated charcoal treatment and zeolite treatment ($P < 0.01$).

The UIA in the control group remained relatively stable during the experiment (Fig. 3). The UIA in the activated charcoal treatment increased with time from 0.50 to 3.02 mg·l (+ 504%); and UIA in the zeolite treatment decreased with time from 0.35 to 0.16 mg·l (-54.3%). The linear regression equations of UIA in control, activated charcoal, zeolite treatment with time (h) are: $y = -0.0080x + 0.35$ ($r=0.8523$); $y = 0.4967x + 0.29$ ($r=0.9632$); $y = -0.0379x + 0.37$ ($r=0.9784$), respectively. The 96 h mean UIA in the activated charcoal treatment was significantly higher than that of control and that of zeolite treatment ($P < 0.01$). The 96 h mean UIA in the zeolite treatment was lower than, but not significantly different, from that of the control ($P > 0.05$).

Discussion

The increase in pH values in the activated charcoal treatment is attributed to absorption of hydrogen ions by the activated charcoal. Thus, UIA was at toxic levels in the activated charcoal treatment throughout the 96 h. By contrast, in the zeolite treatment, pH increased only 0.1 unit, TAN decreased almost 58.1%, and UIA decreased by 54.3% to a relatively safe level.

Bower and Turner (1982) reported that 10, 20, and 40 g·l of clinoptilolite (zeolite) consistently decreased the concentration of TAN (from approximately 10 mg·l) by about 73, 87, and 93% respectively during 24 h simulated transport in polyethylene shipping bags. In our study (with 20 g·l of zeolite), the zeolite treatment decreased TAN by 34% in 24 h and 58% in 96 h, this represents 0.09 mg·g and 0.15 mg·g, respectively. The removal rate was 0.24 mg·g in Bower and Turner's study however, no salt was added in their study. At a similar salinity condition to our study, the zeolite in a study by Chiayvareesajja and Boyd's (1993) removed only approximately half as much TAN as the zeolite in our study. This indicates that the zeolite used in our study was very efficient. Chiayvareesajja and Boyd (1993) indicated that brackishwater drastically decreased the effectiveness of zeolite for ammonia removal, as compared to freshwater. When the salinity of water increases, there are more cations competing with ammonia

for a fixed number of exchange sites on the zeolite. However, salt can relieve stress associated with maintaining ionic/water balance in fish (Swann 1993), and would allow for transport of brackish water species. Although the zeolite in our study may obtain higher efficiency at decreased salinities, UIA was lowered to a nontoxic level

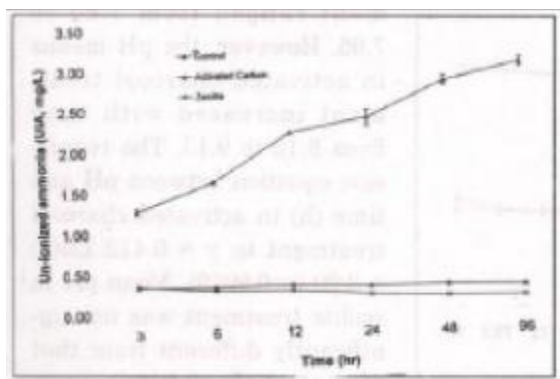


Fig. 3. Change in mean UIA over 96 h in each treatment.

without a pH buffer and with 9 g·l salinity. In contrast, activated charcoal increased UA to toxic levels. Therefore, without adding pH buffer or when using low buffer capacity water, this study indicated that the kind of activated charcoal used is not useful in controlling toxic ammonia during live fish transport.

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