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RESEARCH ARTICLE

Investigation of the use of zeolite (Clinoptilolite) as aquarium filtration material for electric blue hap (*Sciaenochromis ahli*)

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ABSTRACT

In this study, the effects of using zeolite, both inside and outside the filter, on water quality and the growth of electric blue hap (*Sciaenochromis ahli*) were investigated. The 3-month study consisted of 7 groups in triplicate. One of the groups was designated as the control, and zeolite was not used in this group. For the remaining 6 groups, zeolite was placed in tulle bags and used both inside and outside the filter in 3 various ratios (0.35, 0.70, 1.05 g l^{-1}). The statistical differences between groups for certain water quality parameters pH, NH_3) were significant ($P<0.05$), while the statistical differences between groups for other parameters (water temperature, dissolved oxygen) were found to be insignificant ($P>0.05$). Furthermore, the growth parameters, feed conversion ratio, and survival rate of the electric blue hap were determined. At the end of the study, the differences between weight gain, specific growth rate and feed conversion ratio were determined as statistically insignificant ($P>0.05$). At the end of the study, when the data were evaluated, no negative effects on the growth parameters and water parameters of the ahli cichlid fish were determined. Therefore, it is advisable to place zeolite in mesh bags at the bottom of the aquarium and in the aquarium filter to prevent ammonia from reaching high concentrations. Thus, when the findings on pH and NH_3 of the present study were evaluated, it can be suggested that low ratios as 0.35 g l^{-1} of zeolite may be used in tulle bags on floor or inside the filter to prevent ammonia rising to high concentrations.

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Introduction

Intensive aquaculture facilities frequently produce organic wastes such as feed residue and metabolic discharge. Ammonia, usually originating from organic waste, must be monitored and controlled in fish culture. Ammonia is difficult to detect as it is colorless and odorless in lower concentrations (Hagreaves & Tucker, 2004; Yıldırım & Korkut, 2004).

It has been reported that the toxicity of un-ionized ammonia (NH_3) begins at 0.05 mg l^{-1}, and causes mortality at 2 mg l^{-1} (Swann, 1992; Jorgersen, 2002; Deng, 2004; Hargreaves & Tucker, 2004; Floyd & Watson, 2005; Hekimoğlu, 2009).

In the physicochemical treatment process conducted with ion exchange, a type of zeolite; clinoptilolite, capable of keeping nitrogen compound away from aquatic habitats and maintaining ammonium (NH_4) adsorb around 90%, has caught attention as an environment-friendly, economical, and efficient material. Zeolites are hydrated crystalline aluminosilicates. The cage-like microporous structure of zeolite provides large internal and external surface areas for ion exchange (Uğurlu & Pınar, 2004; Surmeli (Sava) et al., 2019).

In the chemical treatment process, among nearly 40 natural zeolites, clinoptilolite is commonly used for this purpose due to its efficiency and low-cost (Emadi et al., 2001; Yörükoğulları, 2005; Deng, 2014). Ammonia concentrations in especially domestic and industrial wastewaters are much higher than those in aquaculture systems. It has been reported that while the ammonium concentration in aquaculture wastewaters should be as low as 1 mg l^{-1}, it may be 10 times higher in municipal wastewaters, and may exceed 100 mg l^{-1} in industrial wastewaters (Jorgersen & Weatherley, 2003). Furthermore, the ammonia adsorption efficiency of zeolites in aquaculture is affected by the chemical and physical properties of both the zeolite to be used, and the water to be treated (Şahin et al., 2018a; Şahin et al., 2019). It has been reported that the organic and suspended solids in the water may affect the charge density on the zeolite surface by providing cation exchange sites for NH_4^+ adsorption, or block the pores of zeolite and thus, block the NH_4 adsorption sites of the zeolite (Nguyen & Tanner, 1998). Therefore, increasing the number of studies regarding the use of zeolite in aquaculture systems is important for both the aquaculture industry and the utilization of zeolite. Zeolites can be used inside the filtration systems, as well as by placing at the bottom of aquariums (Öz et al., 2017; Skleničková et al., 2020). There are several studies conducted on the growth, reproduction, and water quality of the electric blue hap (*Sciaenochromis ahli*), a popular ornamental fish species (Trewavas, 1935) (Güllü et al., 2008; Erdoğan et al., 2012; Karslı et al., 2014). However, there is no research on the effect of zeolite on aquaculture conditions of the electric blue hap.

According to Zain et al. (2018), even though there were many research conducted on the application of zeolite in fish culture, there is no specific dosage for specific fish culture. On top of that, it is considered to be an obstacle in application of zeolite for large-scale aquaculture (Ghasemi et al., 2016). The specific dose of zeolite is impossible to be recommended especially in fish rearing system. The dose of zeolite is depending on such factors as the stocking density of fish, protein content in feed, feed stability and definitely the quality of water (Abdel-Rahim, 2017).

In this study, the effects of using zeolite, inside and outside the filter, on water quality and the growth of the electric blue hap were investigated.

Material and Methods

The study was conducted at Sinop University Fisheries Faculty Aquarium Fish Culture Unit. The trial consisted of 7 groups in triplicate, and zeolite was not used in the control (C) group. 1-3 mm sized zeolites were placed in tulle bags for the other 6 groups in 3 varying ratios (0.35, 0.70, 1.05 g l^{-1}). After zeolite into net bags were placed on the bottom of the aquarium and into aquarium filter. 3 of the bags were placed inside the filter (IF) and the other 3 at the bottom of the aquaria (OF). In the study, internal (canister) filters were used, which are appropriate for physical and biological filtration, functioning in 50 cm at 500 l $hour^{-1}$ capacity (Skleničková et al., 2020). Electric blue hap, an interesting species among aquarium fish, was used in the experiment. Fish were obtained from Akdeniz Fisheries Research, Production, and Education Institute (Kepez, Antalya, Turkey). In this study, a total of 273 fish were used, with 13 fish in each aquarium randomly for each repetition. The aquarium used in the study were 30×45×50 cm sized glass tanks with 20 l capacity. The uneaten feed and feces were removed by a siphon method and, 10% volume of water in each aquarium was changed twice a month.

The filtration material (commercially known as Filter-Clino) was obtained from Enli Mining as 1-3 mm sized granules. Zeolites, prior to being placed in tulle bags, were washed until clear and dried at 105°C (Nguyen & Tanner, 1998, Öz et al., 2017). The study was conducted for 3 months, and the water quality parameters were regularly monitored at 3-day intervals. Dissolved oxygen, pH, ammonium, and temperature were measured with the YSI Professional Plus multiparameter. Daylight photoperiod (10 hours light – 14 hours dark) was applied in the experiment.

The fish weight was measured monthly, and they were starved on the measuring day. The fish were fed twice a day *ad-*

libitum. The trial feed was commercial cichlid feed containing 40.3% crude protein, 6.1% crude fat, 2.2% cellulose, and 9.9% ash.

Data Evaluation

The following variables were calculated as:

$$Weight\ Gain\ (g) = Final\ weight\ (g) - Initial\ weight\ (g) \quad (1)$$

$$\mathrm{SGR} = \frac{\ln W_2 - \ln W_1}{\text{Number of experiment days}} \times 100 \quad (2)$$

SGR: Specific growth rate (%day^{-1})

W_2: Final weight (g)

W_1: Initial weight (g)

$$\mathrm{FCR} = \frac{\text{Total weight of given dry feed (g)}}{\text{Total weight gain by fish (g)}} \quad (3)$$

FCR: Feed conversion ratio

$$\mathrm{SR} = \frac{\text{Final number of fish}}{\text{Initial number of fish}} \times 100 \quad (4)$$

SR: Survival rate (%)

During the study, NH_3 and TAN levels were calculated from NH_4^+, water temperature and pH values (Emerson et al., 1975; Chow et al., 1997; EPA, 1999). The calculation of the ammonium concentration was given below:

The dissociation constant, K_a, of ammonium ion was expressed as:

$$K_a = [NH_3][H^+][NH_4{}^+] \quad (5)$$

Eq (5) can be further arranged as:

$$[NH_3][H^+] = K[H^+] \quad (6)$$

Thus, the relationship between ammonia and ammonium concentrations may be described by:

$$\log 10\,[NH_3][NH_4{}^+] = pH - pK_a \quad (7)$$

pK_a varies with solution temperature. This temperature dependence is given by Emerson et al. (1975) as follows:

$$pK_a = 0.09018 + 2729.22(273.2 + T) \quad (8)$$

Where T is the solution temperature in °C. Also;

$$[NH_4{}^+] = [NH_3]T - [NH_3] \quad (9)$$

$[NH_3]T$ being the total concentration of ammonia forms. Rearrangement of this equation yields can be explained as follows:

$$\log 10\,[NH_3][NH_3]T - [NH_3] = pH - [0.09018 + 2729.92(273.2 + T)] \quad (10)$$

Statistical Analysis

The results obtained from the study were statistically analyzed using *Minitab Release 17 for Windows* software at 5% level of significance. To data meeting the prior conditions of variant analysis, parametric (ANOVA), to those that did not, non-parametric tests (Kruskal-Wallis) were used. All data on growth, FCR and survival of fish are expressed as mean ± standard error (SE).

Results

At the beginning of the study, water temperature, dissolved oxygen, pH and ammonium were arranged as 26.5°C, 6.69 mg l^{-1}, 8.7 and 0.2 mg l^{-1}, respectively suitably for ahli cichlid culture and were same for all groups (P>0.05). Throughout the ninety-day experiment period, measurements were made periodically, and certain water quality parameters were determined. The water quality parameters determined at the end of the experiment are shown in Table 1.

Table 1. Water quality parameters in the 3-month experiment (mean±SE)*

Experimental Groups	Water Quality Parameters			
	Water Temperature (°C)	pH	Oxygen (mg l^{-1})	NH_3 (mg l^{-1})
0.35 OF	24.9±0.13	8.79±0.02^b	7.09±0.07	0.28±0.015^b
0.70 OF	24.9±0.13	8.78±0.02^b	7.18±0.09	0.29±0.015^b
1.05 OF	24.8±0.12	8.91±0.02^a	7.13±0.08	0.43±0.023^a
0.35 IF	24.8±0.12	8.81±0.02^b	7.05±0.08	0.30±0.015^b
0.70 IF	24.8±0.12	8.90±0.02^a	7.20±0.07	0.39±0.020^a
1.05 IF	24.8±0.15	8.89±0.02^a	7.16±0.11	0.42±0.026^a
Control	24.8±0.12	8.80±0.02^b	7.12±0.09	0.29±0.016^b
P	**0.99**	**0.00**	**0.76**	**0.00**

Note: SE: Standard error; *Different letters in the same column indicate significant differences between experimental groups (P<0.05). OF: Outside the filter; IF: Inside the filter

Table 2. Growth parameters, feed conversion ratio (FCR), and survival rate of the electric blue hap in the 3-month trial (mean±SE)*

Experimental Groups	Growth Parameters*					
	W_1 (g)	W_2 (g)	WG (g)	SGR (% day^{-1})	FCR	SR (%)
0.35 OF	1.35±0.07	3.98±0.22	2.64±0.01	1.49±0.00	1.29±0.01	100±0.00
0.70 OF	1.35±0.07	3.74±0.27	2.39±0.24	1.40±0.05	1.42±0.01	100±0.00
1.05 OF	1.33±0.07	3.84±0.27	2.51±0.21	1.45±0.04	1.37±0.01	100±0.00
0.35 IF	1.35±0.06	3.79±0.25	2.44±0.14	1.41±0.03	1.40±0.00	100±0.00
0.70 IF	1.34±0.06	3.79±0.24	2.44±0.14	1.42±0.02	1.38±0.00	100±0.00
1.05 IF	1.36±0.06	3.90±0.29	2.54±0.07	1.44±0.01	1.32±0.00	96.16±3.84
Control	1.34±0.06	3.98±0.24	2.64±0.22	1.49±0.04	1.28±0.01	94.87±2.56
P	**1**	**0.99**	**0.47**	**0.38**	**0.33**	**0.07**

Note: SE: Standard error; W1: Initial weight; W2: Final weight; WG: Weight gain; SGR: Specific growth rate; FCR: Feed conversion rate; SR: survival rate; OF: Outside the filter; IF: Inside the filter

It was determined that the pH and NH_3 values given in Table 1 were statistically different ($P<0.05$), and the water temperature and dissolved oxygen values were insignificant ($P>0.05$).

Growth parameters, FCR and survival rates obtained at the end of the study are presented in Table 2. At the end of the study, the difference between weight gain, specific growth rate, feed conversion ratio and survival rate were found to be statistically insignificant ($P>0.05$).

Discussion

The specific growth rate, feed conversion ratio and survival rate results obtained at the end of the study are similar to those of others conducted on blue electric hap (Güllü et al., 2008; Erdogan et al., 2012; Karslı et al., 2014).

When the results obtained at the end of the study were examined, it was determined that there were no differences among groups in terms of weight gain, water temperature, and dissolved oxygen. The results of this study are similar to a study conducted on rainbow trout (*Oncorhynchus mykiss* Walbaum, 1792), wherein effects of zeolite addition in different ratios (0, 1, 2, 3 mg l^{-1}) were examined on the growth rate of the fish and the water quality parameters (Danabaş & Altun, 2011). On the other hand, in the present study, pH and NH_3 values were found to be different between experimental groups. Moreover, pH and NH_3 values increased in parallel with the zeolite amount in all groups. This finding regarding pH is supported by another study in which the ammonium retention capacity of clinoptilolite in various concentrations was investigated (Zabochnicha and Malinska, 2010; Şahin et al., 2018a; Şahin et al., 2018b; Şahin et al., 2019). The pH increases in zeolite treated groups are considered to be caused by the hydrolysis of the calcium and magnesium carbonates ($CaCO_3$ and $MgCO_3$) in the zeolite (Mazeikiene et al., 2008).

Although the pH values of all experimental groups were affected by zeolite addition, they were determined to be within the acceptable limits (6.5-9.0) specified for aquaculture (Swann, 1992).

Since zeolite can only adsorb NH_4, the efficiency of zeolite decreases in high pH levels (Deng, 2014). In this study, likewise, pH levels increased in parallel with the zeolite amount resulting the increase in the amount of ammonia (NH_3) compared to the amount of ammonium (NH_4) thus, the ammonium adsorption capacity of the zeolite decreased. Although the NH_3 values increased in parallel with the zeolite amount, they were determined to be within the acceptable limits for aquaculture in all groups. In the further studies, ammonia adsorbing of zeolite (clinoptilolite) will can be modified using by different natural adsorbent besides zeolite for lower pH.

The ammonium adsorption capacity of zeolite decreases in lower concentrations of ammonia. Booker et al. (1996) investigated the effect of natural zeolite on ammonium adsorption and reported that the ammonium adsorption capacity decreased in values lower than 1 mg NH_4-N l^{-1}. In the present study, the ammonia values varied between 0.29 and 0.43 mg l^{-1}. Thus, the NH_4^+ concentration did not increase to a level at which the zeolite is effective. It can be suggested that it would be beneficial to conduct further studies to increase the ammonium adsorption capacity of zeolite in lower concentrations of ammonia, by also considering the necessity of low levels of ammonia presence (below 1 mg l^{-1}) in aquaculture systems.

Conclusion

Ammonia is among the potential risk factors in aquaculture as its concentrations can unexpectedly rise and it does not display indications available to sensory perception such as odor, color, etc. Thus, when the findings of the present study were evaluated, it can be suggested that low levels of zeolite may be provided in tulle bags or inside the filter to prevent ammonia rising to high concentrations.

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Compliance with Ethical Standards

Authors' Contributions

MÖ planned the experiments, performed the statistical analyses and managed the project. DŞ collected data, contributed to the writing and preparation of the manuscript. ZK collected data, performed the aquarium laboratory work. OA checked the results. MB performed the aquarium laboratory work.

Conflict of Interest

The authors declare that they have no conflict of interest.

Ethical Approval

The study protocol was approved by ethics committee of Sinop University (Protocol No: 2014/08) and experiments were carried out in accordance with the ethical guidelines and regulations declared by the Sinop University and the international principles of laboratory animal use and care.

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