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Application of Zeolite (Clinoptilolite) Combine with Leonardite for the Removal of Ammonia in Different Sizes Microparticulate Fish Feed

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Abstract

In this study, the effect of feed size on ammonium release from non-consumed feed in aquaculture systems were investigated. In the 11-day study, nine experimental groups were formed in triplicates. Three different sizes of microparticule feed (F1: 100-200 µm, F2: 200-300 µm and F3: 300-400 µm) with the same nutrient content were used in the experiment. The first three groups (CF1, CF2, CF3) were organized as control groups and no adsorbent mixture was added to these groups during the experiment. In the other three groups (ABF1, ABF2, ABF3), the adsorbent mixture was added at the beginning of the experiment together with 3 different sizes of feed used in the experiment. In the last three groups (AF1, AF2, AF3), the adsorbent mixture was added to the experimental environment after the 7th day together with 3 different sizes of feed. At the end of the 11-day experiment, the highest and lowest mean ammonium levels were identified in the CF1 (25.85 ± 2.93 mg L^{-1}) and ABF1 (4.47 ± 0.71 mg L^{-1}) groups, respectively. The study concluded that the size of the fish feed was correlated with the release of nitrogenous compounds from the feed. Consequently, it can be recommended that larger particles should be preferred in fry fish farming, provided that the feed size is suitable for the mouth opening. Furthermore, it was determined that the use of adsorbent mixtures, particularly at the outset of the experiment (when nutrient concentrations were low), was highly effective in reducing ammonia values.

Keywords: Zeolite, leonardite, ammonia, fish feed size, adsorption

Farklı Boyutlardaki Balık Yemlerinde Amonyağın Giderilmesinde Leonardit ile Zeolit (Klinoptilolit) Kombinasyonunun Uygulanması

Öz

Bu çalışmada, su ürünleri yetiştiriciliği sistemlerinde, tüketilmeyen yemden amonyum salınımına yem boyutunun etkisi incelenmiştir. 11 günlük çalışmada, üç tekerrürlü dokuz deneme grubu oluşturulmuştur. Aynı besin içeriğine sahip üç farklı mikropartikül boyutunda yem (Y1: 100-200 µm, Y2: 200-300 µm ve Y3: 300-400 µm) kullanılmıştır. İlk üç grup (KY1, KY2, KY3) kontrol grubu olarak düzenlenmiş ve bu gruplara deneme süresince hiçbir adsorban karışımı eklenmemiştir. Diğer üç grup (ABY1, ABY2, ABY3) deneyin başında adsorban karışımıyla birlikte kullanılan üç farklı yem boyutunun eklendiği gruplar olmuştur. Son üç grup (AY1, AY2, AY3) ise deneyin 7. gününden sonra adsorban karışımı ve üç farklı yem boyutunun eklendiği gruplardır. 11 günlük deneme sonunda, en yüksek ve en düşük ortalama amonyum seviyeleri sırasıyla KY1 (25,85 ± 2,93 mg L^{-1}) ve ABY1 (4,47 ± 0,71 mg L^{-1}) gruplarında tespit edilmiştir. Çalışma, balık yemi boyutunun, yemden salınan azotlu bileşiklerle ilişkili olduğunu ortaya koymuştur. Sonuç olarak, yem boyutunun ağız açıklığına uygun olması kaydıyla, daha büyük partiküllerin yavru balık yetiştiriciliğinde tercih edilmesi önerilebilir. Ayrıca, adsorban karışımlarının, özellikle deneme başında (besin yoğunluklarının düşük olduğu dönem) kullanıldığında, amonyum değerlerini düşürmede oldukça etkili olduğu tespit edilmiştir.

Anahtar Kelimeler: Zeolit, leonardit, amonyak, balık yemi boyutu, adsorpsiyon

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1. Introduction

In aquaculture, it is of the utmost importance to regulate water quality parameters and maintain these within reasonable limits. Physical, chemical, and biological processes can be employed to regulate the water quality parameters specific to the aquatic species being cultured (Cargnin and João, 2021; Basyuni et al., 2023; Verma et al., 2023; Farrag et al., 2024).

The chemical and physical characteristics of the feed used in fish feeding activities, along with the metabolic waste produced by the fish, directly affect the quality of the water. This is crucial for the successful implementation of aquaculture (Verma et al., 2023). In studies on fish feeding, it has been reported that physicochemical properties of are influenced by physical properties such as feed quantity and size, as well as chemical properties such as crude protein, fat, carbohydrate, and vitamin-mineral content (Kibria et al., 1997; Sirakov et al., 2015; Basyuni et al., 2023).

An increase in water temperature and pH can affect the balance of ammonia (NH_3) and ammonium (NH_4^+) in water, resulting in elevated levels of ammonia, which, in excess, can be toxic to aquatic organisms. Furthermore, the rise in water temperature accelerates the dissolution of unconsumed feed, resulting in an elevated NH_3 content and a diminished oxygen content of the water (Yadav et al., 2023). Nutrient quality, quantity and size of feed that remains unconsumed in the water have a direct influence on water quality parameters (especially NH_3/NH_4^+, pH and dissolved oxygen) (Mustapha and Akinshola, 2016; Ragab et al., 2022).

Previous studies on the effects of nutrient content, quantity and size of feed on water quality parameters have highlighted the importance of the study (Ogbonna and Chinomso, 2010; Sirakov et al., 2015; Kong et al., 2020; Godoy-Olmost et al., 2022; Şahin et al., 2023). For instance, Sahin (2023), examined the impact of varying quantities of feed on ammonia release. Kong et al. (2020) explored the effects of different nutrient compositions in feeds. Kibria et al. (1997) analyzed the influence of varying protein content, water temperature, and pH on nitrogen compound release. Öz, (2024a) investigated the removal of ammonium compounds released from feeds with varying protein content using natural adsorbents. A limited number of studies have examined the impact of feed size on water parameters. These include studies by Li et al. (2009), Wu et al. (2012), Yi et al. (2023) and Öz, (2024b). Unlike the above-mentioned studies, the effects of the smallest size feeds (range of 100-400 micron) produced as starter feed for fish larvae on ammonia release were investigated in this study. During the larval fish farming stage, feeding with mouth opening and sufficient nutrient content are two major factors. In this sense, it provides an important advantage to balance ammonia values with natural adsorbent mixtures.

In aquaculture, ammonia values should be below 1 mg L^{-1}, dissolved oxygen values should be above 5 mg L^{-1}, pH should be approximately 6.5-8.5 and temperature should be between 17-38°C (Datta, 2012). Balanced feeding and optimum water conditions are essential for sustainable aquaculture practices. Removing ammonium (NH_4^+) from the environment is necessary since its excessive amount is toxic to aquatic life. For example, the ammonium nitrogen concentration should not exceed 0.05-1 mg L^{-1} of NH_4^+ ions for most fish species (Alshameri et al., 2014). Therefore, preventing nitrogen pollution by removing NH_4^+ from wastewater is very important (Jorgensen and Weatherley, 2003). Various methods, such as aeration, biological processes, and adsorption, have been used for NH_4^+ removal (Gupta et al., 2011). Zeolite has been investigated in many studies in terms of protecting water quality and improving feed quality in filtration (physical, chemical, biological treatment) systems for aquaculture and in live fish transportation. Clinoptilolite type zeolite has been used for a long time to improve feed and water quality in aquaculture (Danabas and Altun, 2011; Danabas and Dorucu, 2021; Tekeşoğlu and Ergün, 2021). Studies on ammonia removal of leonardite and zeolite mixtures in aquaculture are few in number (Şahin 2022, 2023; Öz 2024a, 2024b).

Zeolites are microporous crystalline hydrated aluminosilicates and are used in various applications due to their many qualities such as ion exchange and adsorption-desorption properties (Moreno et al., 2017; Ghasemi et al., 2018; Shalaby et al., 2021; Tantalu et al., 2024). Zeolites are used for various applications, for example, as natural toxin binders in industry, agriculture, veterinary medicine and environmental protection (Demirel et al., 2018). Clinoptilolite can be used as an additive in fish feed at concentrations of 1% to 10% (Sava et al., 2020). In many studies conducted to date, it has been examined as a feed additive for different fish species in terms of properties such as growth, water parameters, feed binding and mycotoxin content (Demir and Aybal, 2004; Danabas and Altun, 2011; Zahran et al., 2020). Leonardite, a concentrated form of humic and fulvic acids used in agricultural production, is an oxidized lignite product and occurs in shallow places with its coal-like structure. In addition, leonardite is a natural organic material formed by a decomposition process lasting billions of years (Ratanaprommanee et al., 2016; Moreno et al., 2017; Terdputtakun et al., 2017).

Research on the use of natural additives for environmental applications is expanding due to various beneficial properties of these additives, such as non-toxicity, low cost, wide application area, etc. (Karadağ et al., 2006; Şahin, 2022).

In fry fish farming, where the water quality of the rearing environment is carefully controlled, it is also of great importance to feed the fish regularly and at short intervals with nutrient-rich feeds of an appropriate size for the mouth opening (Qur'ania and Verananda, 2017; Yanuhar et al., 2022).

In aquaculture, uneaten feed, feces and other organic and inorganic compounds constitute waste, which pose a risk to the environment. Since aquaculture largely depends on a good water environment, the success of aquaculture development should be mainly related to it (Cretu et al., 2016).

Depending on the amount and composition of the fish feed, the amount of nitrogen compounds released from the feed into the water can vary, and the sensitivity of fish to compounds such as NH_3 increases, especially at the juvenile stage. Because of all these factors, it is very important to study species-specific water conditions and feeding practices, especially for juvenile fish culture.

In aquaculture, it is necessary to remove certain compounds from the environment before they reach harmful levels. The adsorption process, which can be used for this purpose, employs the use of natural, economical, processable, and reusable natural materials (Terdputtakun et al., 2017; Cargnin and Joao, 2021; Runtti et al., 2023; Yadav et al., 2023). These natural materials have been the subject of numerous studies on the identification, diversification, and enhancement of their utilization properties; Prashanthakumara and Venkateshwarlu, (2016); Şahin et al., (2018); Setiadi et al., (2019); Maharani et al., (2020); Öz et al., (2021); Öz et al., (2022) etc. To regulate and maintain water parameters with natural adsorbents, further research is required, as the aquatic species targeted for cultivation, their feed properties and the adsorbent properties create unique conditions.

The zeolite and leonardite utilized in this research are natural raw materials that have a beneficial impact on the protection of water quality parameters, without exerting any deleterious effects on aquatic organisms (Şahin, 2022, 2023; Runtti et al., 2023; Öz, 2024c). The objective of this study was to investigate the ammonia levels released from feeds produced in microparticle sizes and the effects of natural adsorbent mixtures on the reduction of these ammonia levels during the fry rearing period, when water quality parameters should be carefully regulated.

2. Materials and Methods

2.1. Materials

Three different sized commercial micro-particle feeds (F1: 100-200 microns, F2: 200-300 microns and F3: 300-400 microns) with the same nutritional content were used in the experiment. The feed used in the experiment was a commercial aquarium fish feed and crude protein of the feed was reported as 57%, crude fat as 14%, inorganic substance content as 7% and moisture content as 7%.

In the present study, clinoptilolite type zeolite was used. The general formula of clinoptilolite is as follows: $(K, Na, Ca)_6[(Si, Al)_{36}O_{72}]\ nH_2O$ (n=20-24 Pabiś-Mazgaj et al., 2020). Leonardite is an oxidized form of lignite with brown and coal-like appearance and often found at shallow depths overlying more compact coal in a coal mine (Qian et al., 2016). Zeledón-Toruño et al. (2007) reported that leonardite contains 60-70% humic acid (HA), 55.2% C, 3.4% H, 0.8% N, 2.4% S, 38.1% O, 2.87 meq g^{-1} of CEC, 3.12 meq g^{-1} of -COOH groups and 2.07 meq g^{-1} of -OH groups.

Powder clinoptilolite and powder leonardite are used in their raw form. The clinoptilolite samples were procured from Rota Mining Corporation (Manisa, Türkiye). The Leonardite samples were provided by Kütahya Kimya (Kütahya, Türkiye).

2.2. Experiment Plan

The research consists of 9 groups with three replications. The research was terminated when the time required for the adsorbents used in the experiment to reach saturation was determined. The experiment was conducted over a period of 11 days. The experimental feeds were added at a rate of 500 mg per 500 ml of tap water in all experimental groups. The first three groups (CF1, CF2, CF3) were designated as control groups and no adsorbent mixture was added to these groups during the experiment. In the other three groups (ABF1, ABF2, ABF3), the powder adsorbent mixture (2 g leonardite:1 g zeolite) was added at the beginning of the experiment together with 3 different sizes (F1: 100-200 microns, F2: 200-300 microns and F3: 300-400 microns) of the feed used in the experiment. In the last three groups (AF1, AF2, AF3), 3 different sizes of feed were added at the beginning of the experiment, but the adsorbent mixture was added after day 7 (Kibria et al., 1997; Şahin, 2022; Öz, 2024a).

2.3. Data and Statistical Analysis

Water parameters (water temperature, pH and ammonium) were measured using a YSI professional plus instrument. All data obtained during the study were statistically analyzed. The statistical analyses were conducted using Minitab Release 17 for Windows software at a significant level of 0.05. All data are presented as mean ± standard error (SE). The resulting data were subjected to one-way analysis of variance (ANOVA) and Tukey HSD post hoc for multiple comparisons. Conversely, non-parametric tests (Kruskal-Wallis) were employed when the prerequisites were not met.

Total Ammonia Nitrogen (TAN) and NH_3 values were calculated from NH_4^+, water temperature and pH values. Ammonia and TAN values were calculated according to Purwono et al., 2017.

$$\mathrm{pK}(NH_3) = 2726.3273 + {}^\circ\mathrm{C} + 0.0963 \quad (1)$$

$$NH_3\text{-}N = 10(pH - \mathrm{pK}(NH_3)) \times NH_4\text{+-}N \quad (2)$$

$$TAN = NH_3\text{-}N + NH4\text{+-}N \quad (3)$$

The removal efficiency (%) for the three trial groups was calculated using the following equation (Alshameri et al. 2014):

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} * 100 \quad (4)$$

Where, C_0 represents the initial ammonium concentration (mg L^{-1}), C_e represents the equilibrium ammonium concentration (mg L^{-1}).

The pH of zeolite and leonardite was measured in accordance with the methodology outlined by Tokat (2019). The SiO_2/Al_2O_3 ratio of zeolite and leonardite was calculated according to Liu (2000).

2.4. Characterization studies

BET (Brunauer-Emmett-Teller), XRF (X-ray Fluorescence) and SEM-EDS (Scanning Electron Microscope) analyses of clinoptilolite and leonardite used in the study were carried out at the Kastamonu University Central Research Laboratory using Quantachrome brand Nova Touch LX4, Spectro brand Xepos II and FEI brand Quanta FEG 250 model devices, respectively.

3. Results

3.1. XRF analysis

The results of XRF analysis, one of the techniques used to determine the elements in a solid sample, are presented in Table 1.

Table 1. The characteristics of leonardite and zeolite determined by XRF analysis

Characteristics of the adsorbents (%)	Leonardite	Zeolite
SiO_2	13.68	78.41
Al_2O_3	7.07	13.83
Fe_2O_3	1.24	1.41
TiO_2	1.25	1.05
CaO	0.32	3.88
MgO	0.11	1.65
MnO	0.027	0.29
P_2O_5	0.054	0.58
K_2O	0.045	2.37
Na_2O	<0.014	1.04
SiO_2/Al_2O_3	1.93	5.67
Na	0.773	0.0101
Mg	0.9927	0.0643
Al	7.32	3.742
Si	36.65	6.396
K	0.1969	0.3765
Ca	2.777	0.2306
Mn	0.02223	0.00211
Fe	0.9889	0.8662
P	0.0254	0.0237
Se	$4.0x10^{-5}$	0.00035

3.2. SEM-EDS, BET, FTIR and XRF analysis

Surface morphology, functional groups, and structure are determined for zeolite and leonardite via SEM-EDS, BET, FTIR and XRF studies, respectively. The BET was employed to ascertain the material's surface area and specific surface area (BET, $m^2\ g^{-1}$) were found as 12.253 and 34.3162 for leonardite and zeolite, respectively (Figure 1).

The pH values of zeolite and leonardite were determined to be 8.81 ± 0.02 and 4.31 ± 0.01, respectively.

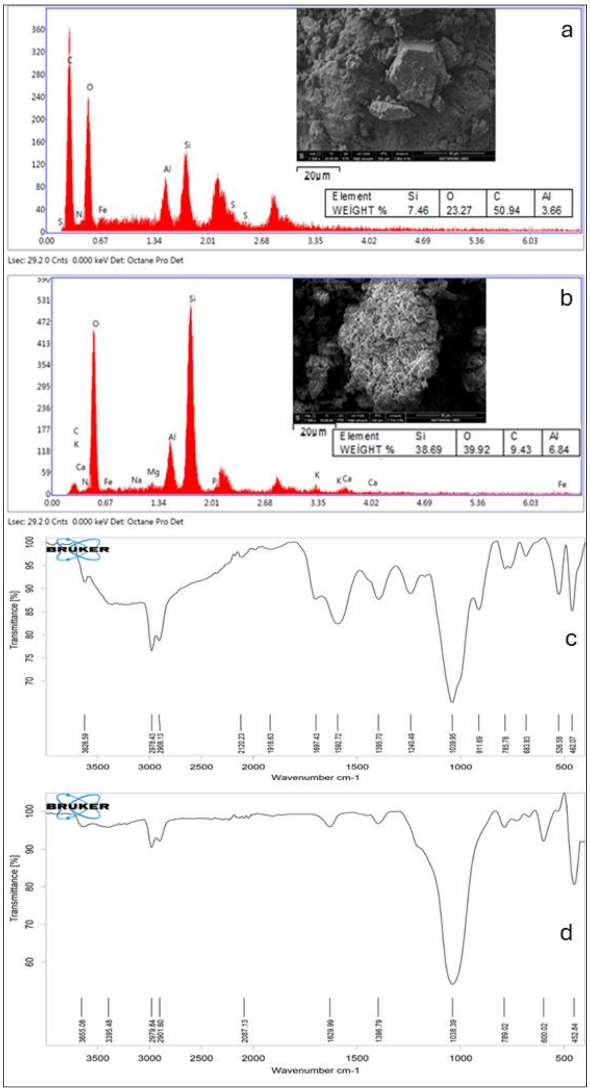

Figure 1. SEM images and EDS analyses of leonardite (a) and zeolite (b); FTIR spectra of leonardite (c) and zeolite (d)

When the EDS analyzes in Figure 1 were examined, it was determined that zeolite contained more silicon than leonardite, and leonardite contained more carbon than zeolite. The Fourier transform infrared (FTIR) spectra of clinoptilolite and leonardite are shown in Figure 1 and the intensity of adsorbent peaks is in the band range of 452-4000 cm^{-1}.

600–1200 cm^{-1} Band: The stretching mode observed in FTIR spectroscopy is sensitive to the Si/Al ratio of the framework in clinoptilolite (Zengin, 2013). The Si/Al bands for clinoptilolite were observed in the range of 600.02 to 789.02 cm^{-1}, whereas leonardite exhibited three Si/Al bands at 683.83 and 785.78 cm^{-1}. The characteristic band in the 1038–1039 cm^{-1} range was attributed to the Si–O vibrations of silicates, confirming the presence of the mineral phase and silicate molecules in both clinoptilolite and leonardite structures.

1200–1800 cm^{-1} Band: The FTIR band for clinoptilolite at 1629.99 cm^{-1} corresponds to the O–H deformation of water. The FTIR spectrum presented in Figure 1 clearly represents a typical spectrum for clinoptilolite (Erdogan and Ulku, 2013). For leonardite, the –COOH groups, O–H deformation, and the stretching frequency of the carboxyl group (–COOH) were observed in the 1700–1400 cm^{-1} range, at 1395.7 cm^{-1} and1592.72 cm^{-1}, respectively. The results obtained are similar to Olivella et al. (2002).

1800–4000 cm^{-1} Band: A broad absorption band in the 3200–3700 cm^{-1} range is attributed to hydrogen-bonded hydroxyl or amino groups. The band at 3696 cm^{-1} represents the stretching ν(O–H) vibration of OH groups in leonardite. The band at 3616 cm^{-1} corresponds to the stretching ν(O–H) vibrations of inner –OH groups for all adsorbents. The band at 3400 cm^{-1} is assigned to the stretching and bending vibrations of hydroxyl functional groups. For clinoptilolite, the band at 3385 cm^{-1} is attributed to the stretching and bending vibrations of the hydroxyl functional groups (Figure 1). The results obtained are similar to Zengin (2013).

3.3. Results of water parameters

At the beginning of the experiment, tap water with the same characteristics was used for all groups and initial water parameter values were measured as water temperature 19 ºC, pH 8.8 and ammonium 0.2 mg/L. The water parameter values obtained at the end of the study are presented in Table 2.

Table 2. Water temperature (ºC), pH and ammonium (mg L^{-1}) mean values determined at the end of the eleven-days study

Experiment groups	Water temperature (ºC)	pH	NH_4^+ (mg/L)
CF1	19.69±0.18	8.04±0.07^{a}	25.85±2.93^{a}
CF2	19.66±0.18	8.07±0.06^{a}	24.32±2.91^{ab}
CF3	19.66±0.18	8.02±0.07^{a}	23.20±2.70^{b}
ABF1	19.74±0.17	7.45±0.04^{c}	4.47±0.71^{d}
ABF2	19.73±0.17	7.49±0.04^{c}	4.86±0.82^{d}
ABF3	19.73±0.17	7.49±0.04^{c}	5.55±0.78^{d}
AF1	19.69±0.18	7.82±0.05^{b}	20.71±2.11^{ab}
AF2	19.66±0.18	7.79±0.05^{b}	17.80±1.97^{b}
AF3	19.66±0.17	7.80±0.05^{b}	11.66±1.31^{c}

Different superscript letters in a column indicate significant differences between groups ($p<0.05$). CF1:Control Feed1100-200 micron; CF2:Control Feed2 200-300 micron; CF3: Control Feed3 300-400 micron; ABF1: Adsorbent in the Beginning of experiment: 100-200 micron; ABF2: Adsorbent in the Beginning of experiment 200-300 micron; ABF3: Adsorbent in the Beginning of experiment 300-400 micron; AF1: Adsorbent in the 7th day of experiment 100-200 micron; AF2: Adsorbent in the 7th day of experiment 200-300 micron; AF3 : Adsorbent in the 7th day of experiment 300-400 micron.

pH values were found to be 8.02-8.07 in the control group, 7.45-7.49 and 7.79-7.82 in the ABF and AF groups, respectively. Water temperature values were not statistically ($p>0.05$) different in all groups. Upon examination of the results of the eleven-day water parameter measurement, it was determined that the lowest NH_4^+ values were found in the experimental groups with adsorbent mixture from the beginning. While the ABF1, ABF2, and ABF3 groups exhibited no statistically significant differences (p>0.05) among themselves, they were statistically distinct (p<0.05) from all other experimental groups.

On the 7th day of the study, adsorbent mix was added to AF1, AF2 and AF3 groups. Ammonium values were measured before adding adsorbent mix to these three groups and were determined as 37.15±1.44 mg L^{-1}, 32.81±0.99 mg L^{-1} and 20.60±1.11 mg L^{-1} for AF1, AF2 and AF3 groups, respectively. The NH_3 (mg L^{-1}) values obtained at the end of the eleven-day experiment are presented in Figure 2. NH_3 values reached 0.6 mg L^{-1} on the 5th day and 5.9-7.43 mg L^{-1} on the 11th day in the groups without adsorbents. From the beginning, NH_3 values remained at 0.3-0.4 mg L^{-1} even on the 11th day in the groups with adsorbents (ABF1, ABF2 and ABF3).

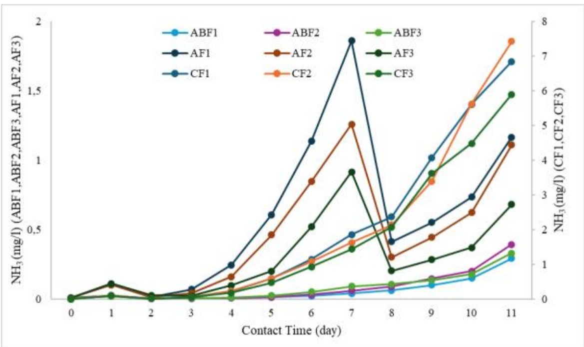

Figure 2. Change of ammonia concentration with time

4. Discussion

In aquaculture, it is necessary to remove certain compounds from the environment before they reach harmful levels. The adsorption process, which can be used for this purpose, employs the use of natural, economical, processable, and reusable natural materials (Terdputtakun et al., 2017; Cargnin and Joao, 2021; Runtti et al., 2023; Yadav et al. 2023). These natural materials have been the subject of numerous studies on the identification, diversification, and enhancement of their utilization properties; Prashanthakumara and Venkateshwarlu, 2016; Şahin, et al. 2018; Setiadi et al., 2019; Maharani et al., 2020; Öz et al., 2021; Öz et al., 2022 etc. To regulate and maintain water parameters with natural adsorbents, further research is required, as the aquatic species targeted for cultivation, their feed properties and the adsorbent properties create unique conditions.

The zeolite and leonardite utilized in this research are natural raw materials that have a beneficial impact on the protection of water quality parameters, without exerting any deleterious effects on aquatic organisms (Şahin, 2022, 2023; Runtti et al., 2023; Öz, 2024c). The objective of this study was to investigate the ammonia levels released from feeds produced in microparticle sizes and the effects of natural adsorbent mixtures on the reduction of these ammonia levels during the fry rearing period, when water quality parameters should be carefully regulated.

As a result of examining the physico-chemical analysis values of the natural adsorbents used in the experiment for ABF1, ABF2, ABF3, AF1, AF2 and AF3 (0.3-1 mg L^{-1}), it was determined that they did not pose a threat to aquatic organisms, similar to Boyd, (2013) and Alshameri et al., (2014).

The high aluminium and silicon content of zeolite and the carbon and oxygen content of leonardite have been identified as contributing factors in the regulation of water parameters. The Si/Al ratio and cation content (e.g., Na, K, Ca, P, Mg) of natural adsorbents have been identified as key factors influencing ammonium adsorption and ion exchange (Terdputtakun et al., 2017; Liu et al., 2022). In addition, some of these minerals (e.g., calcium, phosphorus, and magnesium) must be supplied from water or feed for cultured fish (Öz, 2024). Upon examination of the FTIR spectra of zeolite and leonardite in our study, it was observed that the Si-O vibrations of silicate and the vibrations of OH groups exhibited similarities to the findings of Korkuna et al. (2006), Zengin (2013), and Kannan and Parameswaran (2021).

At the end of the experiment, it was determined that the ammonia values released from three different feed sizes decreased with increasing feed size (CF1, CF2, CF3, AF1, AF2 and AF3) ($p<0.05$). These results are similar to Yi et al. (2023) and Öz, (2024b), but different from the results of Li et al. (2009) and Wu et al. (2012). Microparticle feed is the most important factor affecting the success of the larval feeding period and this study determined that particle size has an effect on ammonia release.

It was determined that the ammonium values determined in the ABF1, ABF2, and ABF3 groups, in which the adsorbent mix was utilized from the outset (at a time when the nutrient values released from the feed to the water were relatively low), were at the lowest level and statistically distinct from the other groups ($p<0.05$). During the period in which the nutrient values released from the feed to the water increased (Day 7), it was determined that the ammonia values were lower than those observed in the CF1, CF2, and CF3 groups and higher than those observed in the ABF1, ABF2, and ABF3 groups in the groups to which the adsorbent mixture was added (AF1, AF2, and AF3). These results were consistent with those reported by Öz, (2024a). The observation that ammonia values remained lower in the groups in which adsorbent mixtures were used concurrently with the feed may be attributed to the presence of other nutrients, other than ammonium, released from the feed, the priority of release, or the priority of retention. The adsorption process is influenced by several factors, including the ion charge, ammonia concentration, temperature, and pH of the aquatic environment. The efficiency of natural adsorbents can also be affected by properties such as the presence of competing ions in the environment (Magalhaes et al., 2022; Yadav et al., 2023). In previous studies (Zengin, 2013, Şahin, 2022, 2023, Öz, 2024a), it has been reported that the mixture of leonardite and zeolite has a positive effect on adsorption. The aim of this study is to increase the adsorption efficiency of the zeolite and leonardite mixture by taking advantage of the low pH values of leonardite. Yan et al. (2024) reported that when the pH value is 6-8, the removal rate of ammonia nitrogen is significantly higher, especially when the pH value is 7, the removal rate reaches approximately 78%. They explained this as the reason for this being that when the pH value is low, the H^+ concentration in the solution is high and ammonia nitrogen is mostly in the form of NH_4^+, and the ionic radius of NH_4^+ is much larger than H^+, which is not easy to penetrate the zeolite. In addition, when the pH value is high, the H^+ concentration in the solution decreases, ammonia nitrogen is mostly in the form of $NH_3 \cdot H_2O$, and the exchange ability of zeolite with NH_4^+ is weakened, mostly by adsorption of $NH_3 \cdot H_2O$, which causes the overall adsorption efficiency to be low. Therefore, the optimum pH value of the ammonia nitrogen adsorption solution by zeolite should be controlled at 6–8. The findings of this research also supported the presented theory and NH_3 values were found to be lower in the adsorbent groups with lower pH values compared to the control group. The outcomes of removal studies conducted in the absence of competing ions may not be directly comparable to those observed in aquaculture systems, where numerous variables are involved. This study, which investigated the NH_4 removal properties of natural adsorbents, yielded data that can inform the use of natural adsorbent mixes in aquaculture conditions. The previously reported leonardite and zeolite mixtures used for adsorbates removal are presented in Table 3.

Table 3. Reported adsorption efficiency for leonardite and zeolite mixtures

Adsorbent amount (g)	Adsorbate	Removal efficiency	References
0.1	Zn	454.55 mg g^{-1}	Zengin, (2013)
3	NH_4^+	89 %	Şahin, (2022)
3	NH_4^+	30-40 %	Şahin, (2023)
3	NH_4^+	93-95 %	Öz, (2024a)
3	NH_4^+	71 %	*Present study*

Yadav et al. (2023) reported that about 50% of the ammonia adsorption occurred in the first 40 minutes and gradually increased to 67.92% after 2 hours. No further increase was detected after 120 minutes due to the complete loading of ammonia on the clinoptilolite surface. This change in the adsorption rate can be attributed to the fact that initially, all adsorbent sites were unoccupied, and the NH_4^+ concentration was high. Over time, as the number of vacant sites decreases, the NH_4^+ concentration also diminishes, resulting in a reduction in the NH_4^+ adsorption rate. In this study, it was determined that the decrease was very rapid in the first 45 minutes and the decrease in the following processes was similar to the study of Yadav et al. (2023).

NH_3 values are an important parameter for aquaculture. The harmful level for fish varies according to species, life stages and environmental conditions. Ammonia toxicity in water bodies is a global problem. Different approaches have been adopted to get the ammonia concentration in water back to permitted level (0.5 mg L^{-1} for aquaculture and 5 mg L^{-1} for environmental discharge) (Gogoi et al., 2021). In this study, NH_3 values reached 0.6 mg L^{-1} on the 5th day and 5.9-7.43 mg L^{-1} on the 11th day in the groups without adsorbents. From the beginning, NH_3 values remained at 0.3-0.4 mg L^{-1} even on the 11th day in the groups with adsorbents (ABF1, ABF2 and ABF3), similar to the results reported in Öz, (2024a).

5. Conclusion

In general, TAN values, which are the sum of NH_3 and NH_4^+ values, were found to be 49% to 71% less in concentration compared to the groups without adsorbents at the end of the experiment and it was determined that the natural adsorbent mixture had a positive effect on the effective reduction of ammonia values. The study concluded that the size of the fish feed was correlated with the release of nitrogenous compounds from the feed. It was observed that ammonium release generally increased with decreasing size. Moreover, the adsorbent mixture was demonstrated to be an effective means of reducing ammonium levels. Consequently, it can be recommended that larger particles should be preferred in fry fish farming, provided that the feed size is suitable for the mouth opening.

When these results are evaluated, the use of adsorbent mixture can be recommended for the removal of ammonia release from feed. In future research, the use of this mixture, which can also be used as a feed additive, in the feed may contribute to the research. Because the most ideal values were obtained in the groups in which the adsorbent mix was present in the environment at the same time with the feed.

Author contribution

Şahin, D: Conceptualization, Investigation, Formal analysis, Writing—review and editing; Öz, M: designing, performing the experiment and data analysis, data collection and writing; Öz, Ü: Investigation and data analysis. All authors read and approved of the final manuscript.

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Conflict of interest statement

The author(s) declares no actual, potential, or perceived conflict of interest for this article.

Ethical Standards

'No Ethics Committee Approval is required for this study'

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