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**ARAŞTIRMA MAKALESİ** **RESEARCH PAPER**

# Effect of Natural Diatomite Different Sizes on Ammonia Adsorption in Aquarium Water

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**Abstract:** In this study, it was aimed to examine the effects of four different sizes of diatomite on the retention of ammonium in water. The trial was planned into 5 groups of 3 replicated without fish and aeration. In the plastic aquariums where the trial was conducted, 500 ml of tap water, 0.5 g (47.5% crude protein, 6.5% crude oil, 2% cellulose, 6% moisture) and 3 g of diatomites of different sizes (excluding the control group) were placed in each replicate.When the mean water parameter values at the end of the trial were examined, there was no statistical difference in water temperature, dissolved oxygen and pH values (P>0.05). However, in NH4 and TAN values, it was found that the statistically determined difference between the groups was significant (P<0.05). When the ammonium values were compared between the diatomite groups and the control group, it was found that 25.27%, 28.62%, 31.82% and 34.45% lower in D1, D2, D3 and D4 groups, respectively.. As a result, diatomites of different sizes; It has been established that it does not have a negative effect on important water parameters such as pH and dissolved oxygen. According the results of this study, in which the effects of four different sizes of diatomite on water parameters were investigated, show that it can contribute positively to keeping ammonia values, which is extremely important especially for fish farming, at lower values.

**Keywords:** Diatomite sizes, ammonia, adsorption, aquaculture.

# Farklı Boyutlardaki Doğal Diyatomitin Akvaryum Suyunda Amonyak Adsorpsiyonu Üzerine Etkisi

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**Öz:** Bu araştırmada, dört farklı boyuttaki diatomitin sudaki amonyumun tutulması üzerine olan etkilerinin incelenmesi amaçlanmıştır.
Deneme, balık ve havalandırma olmayan 3 tekerrürlü 5 grup olarak düzenlenmiştir. Denemenin yürütüldüğü plastik akvaryumlarda her bir tekerrüre 500 ml çeşme suyu, 0.5 g (%47,5 ham protein, %6,5 ham yağ, %2 selüloz, %6 nem) ve 3'er g farklı boyutlardaki diatomitlerden (kontrol grubu hariç) konulmuştur. Deneme sonunda, akvaryumlardan alınan su örneklerinde su kalite parametreleri olarak ortlama su sıcaklığı, çözünmüş oksijen ve pH değerlerinde istatistiki olarak bir fark tespit edilmemiştir (P>0.05). Ancak, NH4 ve TAN değerlerinde ise gruplar arasında istatistiki olarak belirlenen farkın önemli olduğu bulunmuştur (P<0.05). Amonyum değerleri, diatomitli gruplar ile kontrol grubu arasında karşılaştırıldığında sırasıyla D1, D2, D3 ve D4 gruplarında %25.27, %28.62, %31.82 ve %34.45 oranında daha düşük değerlerde olduğu görülmüştür. Sonuç olarak farklı boyutlardaki diatomitler pH ve çözünmüş oksijen gibi önemli su parametrelerine olumsuz bir etki yapmadığı tespit edilmiştir. Dört farklı boyuttaki diatomitin su parametreleri üzerine olan etkilerinin araştırıldığı bu çalışmada elde edilen sonuçlar özellikle balık yetiştiriciliği açısından son derece öneme sahip olan amonyak değerlerinin daha düşük değerlerde tutulmasına olumlu katkı sağlayabileceğini göstermektedir

**Anahtar kelimeler:** Diyatomit boyutu, amonyak, adsorbsiyon, su ürünleri yetiştiriciliği.

## INTRODUCTION

Providing optimum water conditions and healthy nourishment is essential for sustainable aquaculture practices. Natural additives are being employed to enhance both water parameters and nutritional quality. Zeolite, leonardite, and diatomite, which are among the natural raw materials of our country, are minerals that can be used in many fields (agriculture, aquaculture, wastewater treatment, etc.) and are referred to as the mines of the century. High organic matter content in the effluents of aquaculture facilities can promote or increase eutrophication and algal bloom and therefore pose serious problems for the aquatic ecosystem. It is usually characterized by the increase in dissolved nitrogen and phosphorus content resulting from unconsumed feed residues and metabolic wastes of fish. Ammonia is the main nitrogenous waste produced by fish through metabolism (Cao et al., 2007). More than 90% of wastes in aquaculture pass into the water through unconsumed nutrients and fish excrement (Hlordzi et al., 2020). Ornamental fish culture, which constitutes an important place in the aquaculture industry and is a million-dollar sector, can benefit from these raw materials as filtration, decoration, and feed additive materials for the regulation of aquariums.

Materials that have gained commercial product characteristics as a substrate material in aquariums can be listed as sand, gravel, coral fragments, shellfish fragments, lava stone, quartz, etc. In addition to their use in aquatic plant cultivation, ground materials are also used for balancing the water (nitrogen and phosphorus cycles). In this sense, features such as inexpensiveness, processability, having no hazardous release into the water, and physical and chemical compatibility are very important. Diatomite also possesses features that can be functional in this regard. However, there is not sufficient research on the use of diatomite in aquaculture.

Diatomite is a biochemical sedimentary rock composed mainly of skeletons of diatoms, a very common type of marine plankton. Diatoms are small plants that float near the ocean surface. Their skeletons are composed of silica (silicon dioxide), a very durable substance. Since diatom skeletons are highly porous, diatomite is extremely light and their pure samples constitute excellent water filters (Yıldız, 2008; Medarevic et al. 2016; Qi et al. 2017). Diatomite is also a promising adsorbent substrate due to its natural porous or channel structure and low price (Ivanov and Belyakov, 2008; Zong et al. 2018).

Öz et al. (2022) reported in their study that diatomite retains ammonia in the water. In the present study, the effects of four different sizes of diatomite on ammonium retention in water and certain other water parameters were determined.

## MATERIAL AND METHOD

***Experimental materials and design:*** The diatomites used in the study were obtained from Nanotech Construction Chemistry Mining and Logistic Ind. & Trd. Inc. Diatomites in 4 different sizes (powder, 1-3 mm, 3-5 mm, 5-7 mm) were used in the experiment.

The experiment was designed to consist of 5 groups with 3 replications without fish and aeration. In the plastic aquariums where the experiment was conducted, each replication consisted of 500 ml of tap water, 0.5 g of feed (47.5% crude protein, 6.5% crude oil, 2% cellulose, 6% moisture), and 3 g of different-sized diatomites (except the control group). The 1st group (D1) received powder diatomite, 2nd group (D2) received 1-3 mm diatomite, 3rd group (D3) received 3-5 mm diatomite, 4th group (D4) received 5-7 mm diatomite, whereas diatomite was not used in the control group (C) (Figure 1). The feed used in the study was included as the waste material source in the environment (Kbria et al., 1997).

**Figure 1.** Diatomites used in the experiment

The chemical composition and characteristics of the diatomite tested in the study are presented in Table 1. Diatomite was also characterized by Scanning Electron Microscopy (SEM) (Figure 2). These analyses were carried out by the Kastamonu University Central Research Laboratory. The pH values were calculated according to Tokat (2019).

**Table 1.** Chemical composition and characteristics of diatomite.

| Diatomite | | | |
|---|---|---|---|
| | % | | |
| $SiO_2$ | 81.66 | $SiO_2/Al_2O_3$ | 8.149 |
| $Al_2O_3$ | 10.02 | BET Surface Area | 174.698 $m^2/g$ |
| MgO | 3.839 | pH | 7.06 |
| $K_2O$ | 0.99 | | |
| CaO | 2.041 | | |
| $Na_2O$ | 1.261 | | |
| $Fe_2O_3$ | 2.291 | | |
| $P_2O_5$ | 0.243 | | |

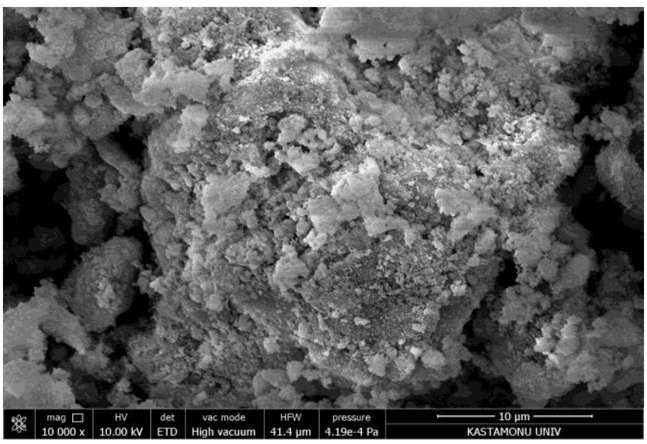

**Figure 2.** SEM analysis of the diatomite.

***Data Analysis:*** Ammonium nitrogen ($NH_4^+$-N), temperature, and pH values were measured using a multiparameter (YSI Professional Plus). Total ammonia nitrogen (TAN) and ammonia ($NH_3$) values were determined from the $NH_4^+$-N, temperature, and pH values (Chow et al. 1997; EPA, 1999; Emerson et al., 1975; Jorgensen, 2002; YSI, 2007). A previous investigation suggested that the results obtained from the Nessler method were similar and reliable to the results obtained from the traditional electrode method (Prajapati, 2014). The ammonia and TAN were computed as given below (Purwono et al., 2017):

$$\mathrm{pK}(NH_3) = \frac{2726.3}{273+℃} + 0.0963 \quad (1)$$

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

$$TAN = NH_3\text{-N} + NH_4^+\text{-N} \quad (3)$$

***Statistical Analysis:*** The initial water parameters were compared with the analysis of variance (ANOVA). ANOVA revealed that the differences between groups in terms of water parameters were not statistically significant (P>0.05).

Results obtained from the experiment were statistically tested with the "Minitab Release 15 for Windows" package program. When the prerequisites of the analysis of variance were met, parametric tests (ANOVA) were used. Non-parametric tests (Kruskal-Wallis) were employed when the prerequisites of the analysis of variance were not met. The results were presented as mean ± standard error (SE) and the confidence interval was set to 95%.

## RESULTS

Regarding the water parameter values in all aquariums; temperature, pH, dissolved oxygen, and $NH_4$ were determined as 19.8±0.01 ºC, 8.35±0.01, 0.30±0.01 mg/l, and 0.1±0.01 mg/l, respectively. The mean water temperature, pH, dissolved oxygen, $NH_4$, and TAN values measured in all groups at the end of the experiment are presented in Table 2.

**Table 2.** Water parameters at the end of the experiment (adsorption) (mean± SE)

| Experimental groups* | Temperature (°C) | Dissolved Oxygen (mg/l) | pH | $NH_4$ (mg/l) | TAN (mg/l) |
|---|---|---|---|---|---|
| D1 | 20.04 ±0.61 | 0.14±0.08 | 7.63±0.07 | 10.65±2.46 $^{ab}$ | 11.04±2.51 $^{ab}$ |
| D2 | 19.82±0.61 | 0.13±0.07 | 7.67±0.08 | 11.37±2.34 $^{ab}$ | 11.74±2.43 $^{ab}$ |
| D3 | 19.72±0.59 | 0.14±0.07 | 7.62±0.07 | 10.30±2.21 $^{ab}$ | 10.55 ±2.28 $^{ab}$ |
| D4 | 19.81±0.59 | 0.13±0.06 | 7.57±0.07 | 9.32±2.14 $^{b}$ | 9.51±2.20 $^{b}$ |
| C | 20.05±0.58 | 0.13±0.09 | 7.63±0.08 | 16.82±3.26 $^{a}$ | 17.30±3.30 $^{a}$ |

*Different superscript letters in the same column indicate significant differences (p<0.05) between groups. Means were tested by ANOVA and classified by Tukey's multiple range test.

When the average water parameter values at the end of the experiment were examined, no statistical difference was found for the water temperature, dissolved oxygen, and pH values (P>0.05). On the other hand, the statistical differences between the groups for $NH_4$ and TAN values were found to be significant (P<0.05). The ammonia amount resulting from the unconsumed feed in the aquariums was determined at the end of the 8-day study. When the $NH_3$ values were examined, it was observed to start increasing after the 5$^{th}$ day of the experiment (D1: 0.09 mg/l, D2: 0.14 mg/l; D3: 0.10 mg/l; D4: 0.06 mg/l; C: 0.22 mg/l) (Figure 3).

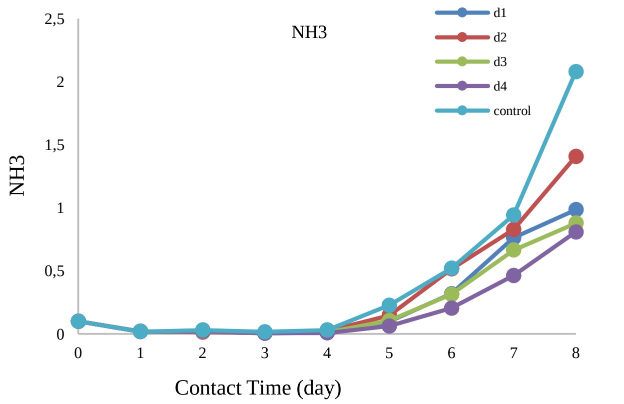


**Figure 3.** $NH_3$ exchange during the 8 days.

## DISCUSSION

As a result of the study, where the effects of four different sizes of diatomite on water parameters were examined, it was determined that when the obtained findings were evaluated, it contributed positively to the optimum limits of ammonia values, which are extremely important, especially for aquaculture. Nitrogenous compounds are essential for the continuity of living beings because nitrogen is one of the basic building blocks of living beings (Şahin et al., 2019). Ammonia exists in water in two forms (non-ionized ammonia $NH_3$ and ionized ammonium $NH_4^+$) and especially ammonia ($NH_3$) is highly toxic to fish (Ortiz et al., 2022). The typical $NH_4^+$ concentration in aquaculture is 1 to 5 mg/l (Jorgensen, 2002). When the average $NH_3$ values obtained in this study were examined, it was observed that the ammonia values resulting from the feed were lower in the diatomite groups compared to the control group until the 4$^{th}$ day, and when the diatomite groups were evaluated within themselves, the ammonia values in the powder diatomite group were found to be lower than those of others. In the following days (5$^{th}$, 6$^{th}$, 7$^{th}$, and 8$^{th}$), when the diatomite groups were evaluated within themselves, it was determined that $NH_3$ values in the D4 group were lower than the other groups, especially in the last measurements. The reason for this may be that the powder diatomite adsorbs ammonia faster and therefore reaches saturation rapidly. On the other hand, as the size of the diatomite increased, the time to reach saturation was prolonged, which allowed longer use. When this result is evaluated for a freshwater aquarium environment, size preference can be made based on these determined characteristics. Moreover, reusing opportunities can be applied by taking the different saturation times of different sizes into account. Noferesti et al. (2018) examined the effect of different-sized diatomites on the soil in their study. Similar to our study, Because the diatomite is a highly porous material, crushing the diatomite is likely to destroy part of its porosity that the diatomite was more effective as the size increased. Hu et al. (2022), on the other hand, ground the diatomite at various times (10, 30, 60, 90, and 120 min) in their study and examined the level of ammonium adsorbing under certain pressure. They found that the diatomite that was ground for a longer time (120 min) adsorbs the ammonium more than the ones ground for a shorter period of time. However, they also reported that the adsorption time takes longer for the ones that were ground for 10, 30, 60, and 90 min, in a way to be inversely proportional to the grinding time. The nitrogen adsorption capacity of the diatomite samples was small at low relative pressure ($p/p0 < 0.1$), indicating that no microporous structure existed in the diatomite. The ammonium adsorption of natural adsorbents varies based on the conditioning, amount of minerals, pore size, surface area, mining area, initial concentration, pH, temperature, and presence of other cations in the solution (Huang et al., 2017). In this study, the effects of different sizes of diatomites on ammonia and other water parameters were investigated.

Only a few studies have investigated the use of diatomite in aquaculture. Similar to this study, Öz et al. (2022) reported that diatomite and clinoptilolite displayed a positive effect in their study where they examined the removal of ammonia in water.

Moreover, it was determined that there was no statistical difference ($p>0.05$) between the water temperature, pH, and dissolved oxygen values examined in the present study. These findings were similar to the study of Öz et al. (2022).

At the end of the study; ammonium values resulting from the feed, which contains 47.5% protein, increased to an average of 40.63 mg/l in the control group maintained at an average temperature of 19.9 ºC for 8 days. When the ammonium values of the diatomite groups were compared with the control group, it was found that D1, D2, D3, and D4 groups displayed 25.27%, 28.62%, 31.82%, and 34.45% lower values, respectively. In conclusion, diatomites of different sizes did not have an adverse effect on important water quality parameters such as pH and dissolved oxygen but showed a positive effect on water parameters, of which excess amounts can be toxic, such as ammonia. This study serves as the first study to determine the use characteristics of diatomite in aquaculture. Investigation of different adsorbent amounts and yield-enhancing conditioning processes in further studies will contribute to aquaculture.

***Ethics approval and consent to participate:*** This article does not contain any studies with animals performed by any of the authors**.**

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