International Letters of Natural Sciences
ISSN: 2300-9675, Vol. 71, pp 34-42
doi:10.56431/p-f8l51a
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Submitted: 2018-05-28
Revised: 2018-07-12
Accepted: 2018-07-31
Online: 2018-09-25

Evaluation of Natural Minerals (Zeolite and Bentonite) for Nitrogen Compounds Adsorption in Different Water Temperatures Suitable for Aquaculture

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Keywords: Adsorption, Bentonite, Zeolite, Ammonium, Aquaculture

Abstract. In this study, it was aimed to determine the effects of zeolite and bentonite on the ammonium adsorption at different temperatures. In this research three trial groups with 3 repetitions were created for three different water temperatures (18±0.1°C, 24±0.0°C, 27±0.0°C). Experimental groups were prepared by adding NH_4^+ amount of 10.5 mg/l in 2 liters of water. After that, zeolite, zeolite+bentonite and bentonite were added into the bottles as 10 gram per liter. Water temperature, pH and TAN (Total Ammonium Nitrogen) values were determined during the trial period. At the end of trial TAN values at 27 °C were recorded as 10.103±0.11 mg/l, 9.227±0.13 mg/l and 7.933±0.17 mg/l in zeolite, zeolite+bentonite and bentonite groups, respectively. At the end of trial TAN values at 24 °C were recorded as 10.027±0.17 mg/l, 9.282±0.15 mg/l and 8.336±0.15 mg/l in zeolite, zeolite+bentonite and bentonite groups, respectively. At the end of trial TAN values at 18 °C were recorded as 9.012±0.28 mg/l, 7.702±0.14 mg/l and 6.594±0.14 mg/l in zeolite, zeolite+bentonite and bentonite groups, respectively. Maximum ammonium removal capacity, q_e, was found to be 0.50 mg/g in the bentonite (18 °C). The TAN values determined at 18 °C were statistically more significant ($p<0.05$) than the TAN values obtained at 24 °C and 27 °C.

Introduction

Nitrogen removal is important for both fish health and profitability of production [1]. Nitrogen exists in water in two forms (un-ionised ammonia NH_3, higly toxic to fish, ionised ammonium NH_4^+).

Adsorption is the period in which molecules from solution accumulate in the external or/and internal surface of the porous solid [2]. Adsorption and ion exchange participates of some basic characteristics. For this process different natural materials can be selected such as zeolite [3], bentonite [4], barbecue bamboo charcoal [5], kaolinite [6], fly ash and sepiolite [7], fruit waste [8] etc. In this study, we used zeolite and bentonite which are a kind of natural minerals because of their cheaper cost and higher selectivity for ammonium removal.

Zeolite and bentonite have large surface areas with a net negative charge, therefore, the cations (calcium, magnesium, sodium and potassium), anions (chloride, phosphate and sulfate) and organic acids (oxalic, citric and malic) can hold in the water [9-11]. The use of clay minerals is especially preferred for wastewater treatment in the removal of nutrients, organic compounds and heavy metals in the environment [12]. Bentonite is a phyllosilicate mineral formed by natural ways with high cation exchange and ion adsorption capacity, respectively [12]. There are two types of bentonite, sodium bentonite and calcium bentonite. Calcium bentonite is a low-swelling type, which evolves from volcanic ash deposited in freshwater environments, while sodium bentonite is usually a high-swelling type, derived from volcanic ash that is deposited in marine environments [13].

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Zeolites are crystallized hydrated alumina silicates with a framework comprising pores coated by water and alkali and alkaline earth cations [14]. Natural zeolites are cheap materials that are easily found in nature and have a high cation exchange ability, molecular sieve properties and a special design for adsorption and catalysis. [15].

In freshwater for ammonium adsorption process, pH and water temperature are two important parameters. For ammonia adsorption and sustainable aquaculture applications, optimum results are obtained between approximately 6-8.5 pH and 10-27°C values [16, 17]. In this study, it was aimed to determine the effects of zeolite and bentonite on the ammonium adsorption at different temperatures.

Materials and Methods

Experimental Materials

Natural zeolite (clinoptilolite) and bentonite (Ca-Bentonite) were taken from the Rota Mining Company in Manisa-Gördes in Western Anatolia and Samaş Industrial Materials in Tokat in Anatolia, respectively. Chemical composition of zeolite and bentonite were given in Table 1.

Table 1. Chemical composition of zeolite and bentonite that are used in study from manufacturer label

Oxide component	% (persentage by weight) for zeolite	% (persentage by weight) for bentonite
SiO_2	61.28	71.00
Al_2O_3	17.79	11.80
Fe_2O_3	3.01	1.70
CaO	4.54	3.40
Na_2O	2.70	0.40
MgO	2.10	1.40
K_2O	1.24	2.40

Ammonium chloride stock solution (1000 mg/l) was prepared by dissolved NH_4Cl in deionized water. Initial solution (10.5 mg/l) was prepared by dilution from the concentrated ammonium solution for 2 liter tap water for trial groups [6]. In this research trial groups with 3 repetitions were created at three different temperatures (18 °C, 24 °C, 27 °C) during 225 minutes. The water temperature in the experimental groups was regulated at the desired values by using a heater. After that, zeolite (3-5 mm) (10 g/l), zeolite+bentonite (5 g/l+5 g/l) and bentonite (0.075 mm) (10 g/l) were added into the bottles (Fig. 1).

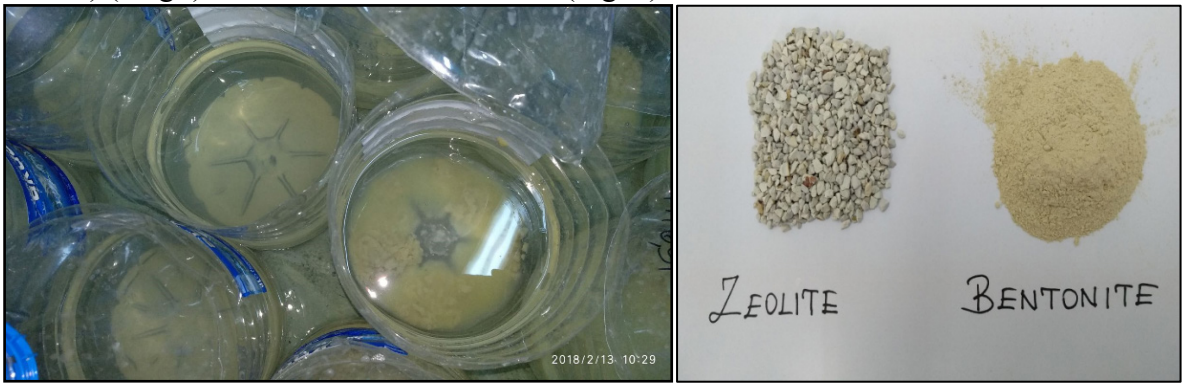

Figure 1. Experimental design and experimental materials

Aeration, lighting, agitation procedures were not applied during the trial period. Zeolite and bentonite were obtained from nature and then experimental materials were washed in tap water until the turbidity was removed and dried at 105 °C. Water temperature, pH, dissolved oxygen and TAN values were determined during the trial period. Water parameters were measured by YSI Professional Plus hand and field measurement units. This study was carried out with electrode method which is a serial and practical method and can also be used in the field and laboratory. [18] reported that, when Nessler method is compared to the conventional electrode method, the two measurement methods in the study gave very close values and were reliable. Electrode method was preferred in this study because it was easy, quick, reliable and various measurements could be obtained in a very short period of time in aquaculture.

Calculations of Data

The removal efficiency (%) for the three trial groups were calculated by using the following equations [19]:

Removal efficiency (%)=$\frac{C_0-C_e}{C_0} * 100$; C_0 is the initial ammonium concentration (mg/l), C_e is the equilibrium ammonium concentration (mg/l). The amount of ammonium ions adsorbed onto zeolite, zeolite+bentonite and bentonite, q_e (mg/g) was calculated according to following equation [20]:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

C_0 (mg/l), C_e (mg/l) are the initial and equilibrium concentrations of ammonium ion in solution, respectively. V (l) is the volume of the solution, and W (g) is the mass of the adsorbent used.

During the study NH_3 and TAN levels were calculated by using NH_4^+, water temperature and pH values. The calculation of the ammonium concentration is formulated below [21]:

The dissociation constant, K_a, of ammonium ion is expressed as

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} . \quad (1)$$

Eq. (1) can be further arranged as

$$\frac{[NH_3]}{[NH_4^+]} = \frac{K_a}{[H^+]} . \quad (2)$$

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

$$log_{10} \frac{[NH_3]}{[NH_4^+]} = pH - pK_a . \quad (3)$$

pK_a varies with solution temperature. This temperature dependence is given as follows:

$$pK_a = 0.09018 + \frac{2729.92}{(273.2+T)} . \quad (4)$$

T is the solution temperature in °C. Also

$$[NH_4^+] = [NH_3]_T - [NH_3] . \quad (5)$$

$[NH_3]_T$ is the total concentration of ammonia forms.

Rearrangement of this equation is

$$log_{10} \frac{[NH_3]}{[NH_3]_T - [NH_3]} = pH - \left[0.09018 + \frac{2729.92}{(273.2+T)}\right] . \quad (6)$$

Statistical Calculations

Statistical analysis of the study results was performed with “Minitab Release 17 for Windows” software. In terms of water parameters statistical significance among experimental

groups were evaluated by one-way analysis of variance (ANOVA) and means were compared using Fisher's range test at 5% level of significant [22].

Results and Discussion

When the data obtained in this study were evaluated, it was found that the amount of ammonium removal by zeolite and bentonite increased while water temperature decreased in the experiment. The pH in all samples increased in a small amount during the experiment (approximately 7.6 before mixing with zeolite and bentonite). Solution pH increased because calcium and magnesium carbonate compounds hydrolyzed after mixing with zeolite and bentonite [14, 17, 23]. TAN, NH_3, pH and dissolved O_2 values were presented in Table 2. In Table 2 all treatment groups were determined for different temperatures statistically.

Table 2. TAN, NH_3, pH and dissolved O_2 values in zeolite and bentonite added groups at the end of the experiments at three different temperatures (mean±SE)

	Water Parameters			
Trial Groups	**TAN (mg/l)**	**NH_3 (mg/l)**	**pH**	**Dissolved O_2 (DO) (mg/l)**
Zeolite*	9.012±0.28^b	0.132±0.00^a	7.655±0.01^a	8.292±0.06^a
Zeolite**	10.027±0.17^a	0.423±0.01^b	7.933±0.00^b	6.456±0.05^b
Zeolite***	10.103±0.11^a	0.743±0.01^c	8.089±0.00^c	5.573±0.05^c
Zeolite+Bentonite*	7.702±0.14^b	0.135±0.00^a	7.733±0.01^a	8.352±0.04^a
Zeolite+Bentonite**	9.282±0.15^a	0.495±0.00^b	8.039±0.01^b	6.543±0.04^b
Zeolite+Bentonite***	9.227±0.13^a	0.757±0.01^c	8.139±0.01^c	5.748±0.04^c
Bentonite*	6.594±0.14^b	0.150±0.00^a	7.852±0.01^a	8.559±0.04^a
Bentonite**	8.336±0.15^a	0.566±0.01^b	8.153±0.01^b	6.399±0.04^b
Bentonite***	7.933±0.17^a	0.717±0.02^c	8.182±0.01^c	5.552±0.04^c

*18°C, **24°C,*** 27°C, Means with different letter as superscript are significantly different in columns ($P<0.05$)

It was found that the TAN concentrations were significantly different at 18°C for trial groups ($P<0.05$). The experiment showed that the effect of natural zeolite and bentonite had a positive effect on aquaculture water conditions in terms of reducing the increasing TAN concentration levels. This result was found to be similar to the results of the study about the effects of zeolite and bentonite on the removal of ammonium [17, 24]. In general, most fish species will grow and thrive within a DO range of 5-12 mg/l (ppm). However, if levels drop below 4 mg/l they may stop feeding, become stressed and begin to die. Oxygen depletion usually occurs in the summer months because warmer water holds less oxygen than cooler water. As water temperatures rise, oxygen levels decrease. Higher temperatures also increase the metabolism of fish resulting in the need for more oxygen. Oxygen quantities were also determined in this study because they could change according to different water temperatures.

Ammonium removal efficiencies (%) of trial groups are given in Fig. 2.

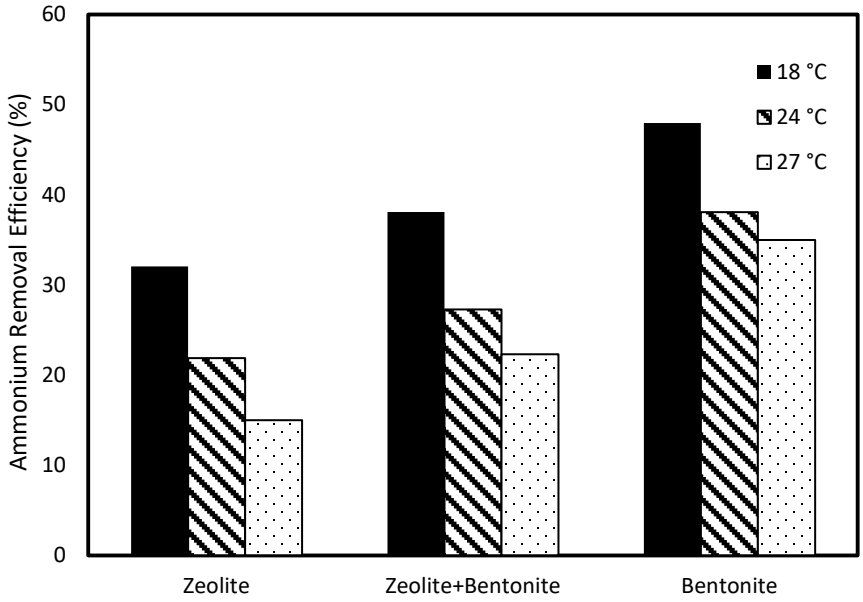

Figure 2. Ammonium removal efficiency (%) of zeolite and bentonite added groups at three different temperatures at the end of the experiment

The amount of NH_4^+ ion removed from aqueous solution decreased by rising temperature from 18 to 27°C. Fig. 3 shows that, contact time is an important factor in this study because it affects the adsorption capacity of an adsorbent at different temperatures and for different adsorbents. Ammonium removal capacity of the bentonite (18 °C) was higher than other experiment groups. The results were consistent with those reported by other researches [24, 25]. The best ammonium removal efficiency was determined at 18°C (Fig. 4), and the values were 32%, 38% and 48% for zeolite, zeolite+bentonite and bentonite, respectively. As the temperature increased, the desorption of the solution from the interface increased, resulting in better efficiency of ammonium removal at low temperatures [24].

In order to increase the efficiency of the zeolite and bentonite adsorption process, methods such as conditioning, changing the physical and chemical properties of the solution and using with a different adsorbent were used [26, 27].

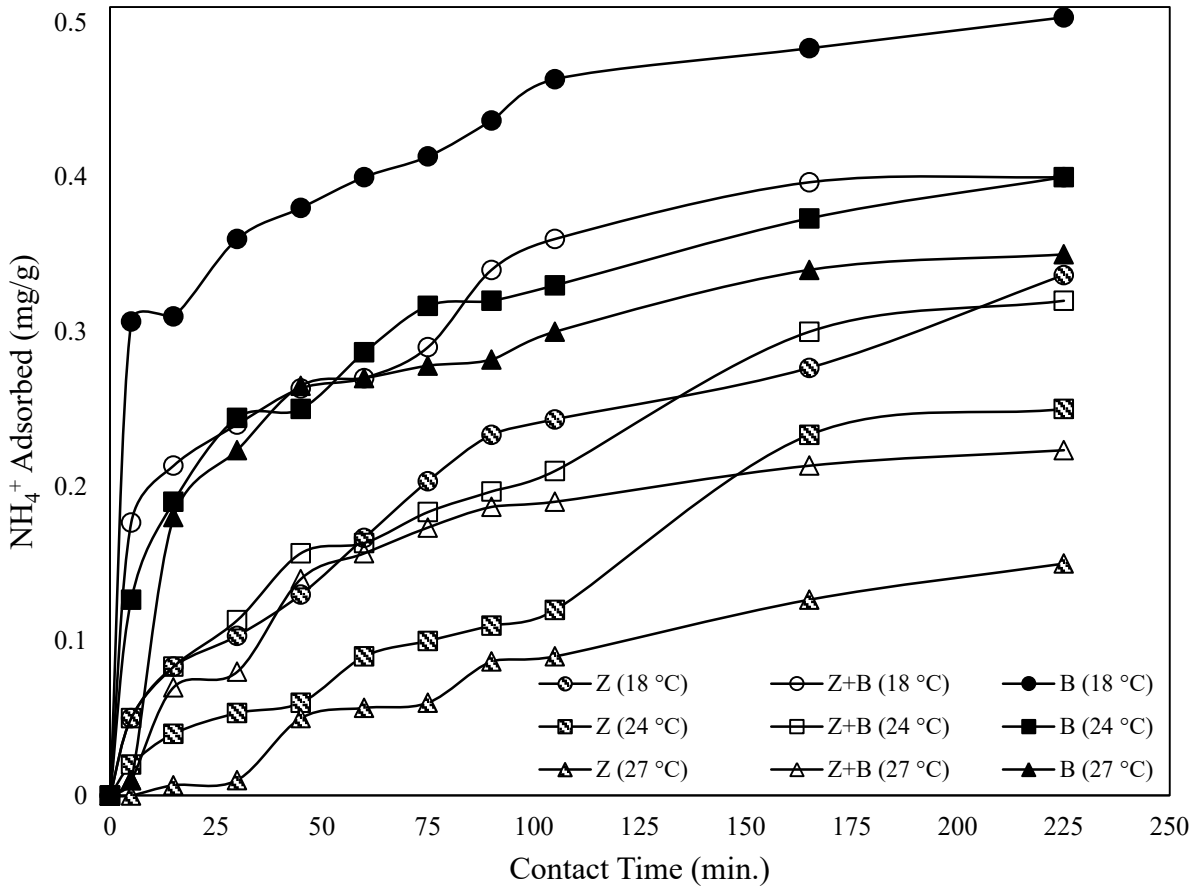

Figure 3. Effect of contact time at different temperatures on ammonium removal by Z, Z+B, B during 225 min

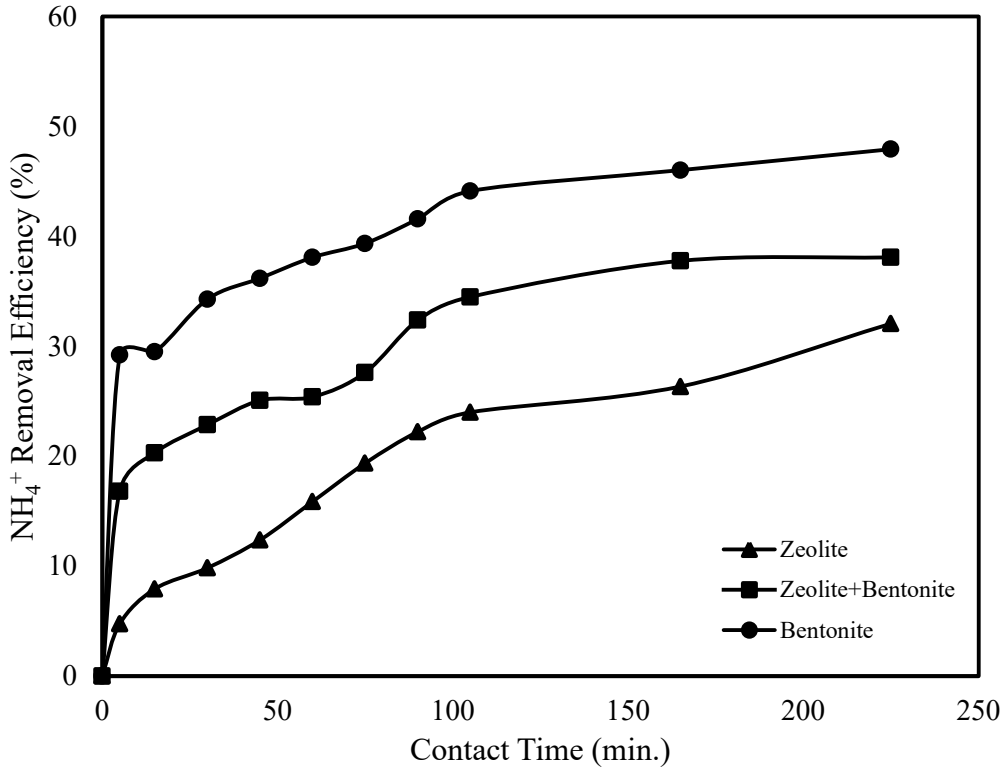

Figure 4. Effect of contact time on the NH_4^+ removal efficiency of zeolite and bentonite added groups during the 225 min. at pH 7.7, 18°C

Keeping water conditions within the ideal range is one of the most important activity to be performed for fish. The most important factors affecting water conditions are metabolic waste of live animals and unconsumed feed. It is reported that toxicity of unionized ammonia (NH_3) begins at 0.05 mg/l, while it causes death at 2 mg/l for many fish species [28]. In this study, the use of natural zeolite and bentonite as a filter materials were investigated. Ammonium adsorption of natural minerals such as zeolite and bentonite changes with the amount, pore size, surface area, mining area of minerals; the initial concentration, the pH, the temperature and the presence of other cations of the solution [29]. Similarly in this study, at the end of the 225 min.; it was found that ammonium removal efficiencies (%) of the group of bentonite reduced with increasing water temperatures at a statistically significant level compared to the other trial group. Adsorption experiments have demonstrated that the contact time and temperature have significant effects on NH_4^+ adsorption [4, 30]. One of the most important factors in the ammonium removal of natural adsorbents is the initial ammonium concentration. The remediation at low ammonium concentrations is lower than the ammonium removal efficiency at high ammonium concentrations. About 48% of the ammonium removal efficiency in this study is due to the work at low initial concentrations.

Conclusions

The characteristics of Turkish (Manisa-Gördes) natural zeolite and (Tokat) natural bentonite and their efficacy in removing ammonium for different temperatures were investigated. The results obtained from this study are presented below as articles:

(1) Adsorption process is a powerful alternative among the other NH_4-N removal technologies due to ease of operation.

(2) Gördes zeolite and Tokat bentonite are influential alternative adsorbents for the removal of NH_4-N from aquatic solution.

(3) The zeolite and bentonite showed the highest performance in low water temperature (18°C) in terms of removal efficiency.

According to the all results, it is finalized that zeolite and bentonite have a good adsorption performance and can be successfully used for NH_4-N removal from aquatic solution, but bentonite has better performance than zeolite in same aquatic conditions because the particle of zeolite and bentonite used in the study are different from each other. The efficiency of ammonium removal of zeolite is lower than bentonite, probably due to the particle size. Natural zeolite and bentonite removal efficiency increasing processes were not applied in this study. Under these conditions, the removal efficiencies were below 50%. When the studies were examined, it was determined that removal efficiency increasing processes were mostly performed [5, 31]. In these studies it has been found that removal efficiencies are higher in modified materials than natural adsorbents. In the next studies ammonium removal efficiency is planned to be higher by modifying zeolite and bentonite which are natural adsorbents.

Conflict of Interest

The authors declare that there is no conflict of interest.

Acknowledgment

We would like to express our appreciation to the company, Rota Mining Company and Samaş Industrial Materials for providing us with the trial material zeolite and bentonite.

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