INNOVATIVE SOLUTIONS FOR REMOVING NITROGEN COMPOUNDS FROM WATER OF RECIRCULATING AQUACULTURE SYSTEMS USING CLINOPTILOLITE NATURAL ZEOLITES

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Abstract
From the constructive and functional point of view, a controlled aquaculture system can be assimilated with a classical water treatment system, functionally customized to the requirements of technology for intensive fish in confined spaces. A physicochemical process cheap, fast, secure which has the potential to replace the widespread technique of biologically removal of nitrogen compounds is based on the separation of nitrogen compounds from the water using zeolite. By using clinoptilolite, a zeolite with high affinity for nitrogen compounds, it was maintained in normal range the ammonia, nitrite and nitrate in a fish pound. The water recirculated in the controlled system was mechanically filtered and passed through the zeolite column. Clinoptilolite zeolite is an aluminosilicate from the microporous family solids which act as molecular sieve. The experiments were performed in the Laboratory of Fisheries and Aquaculture, Faculty of Animal Science, University of Agronomic Science and Veterinary Medicine of Bucharest. Advantages of this approach include: low dependence on temperature and absence of dependence on chemical toxins and bacterial predators, do not require a start-up period, the system can be turned off or on at will, fish is grown in much lower bacterial concentrations, reducing the possibility of disease or flavour loss.

Keywords: animal welfare, RAS, waste management, water purification, zeolite.

1. INTRODUCTION

The water quality in a recirculating system is determined by: concentration in dissolved oxygen, non-ionized ammoniacal nitrogen, nitrites, nitrates, carbon dioxide and water pH. For the success of closed-loop fish growth, the values and limits of variation of medial factors must be known, controlled and regulated (Cristea et al., 2002; Nicolae, 2007). In the controlled system, the biological filter, consisting of pure bacterial cultures of Nitrosomonas and Nitrobacter genes, was attempted to be replaced with zeolite. One of the zeolites that have a high affinity for ammonia and its compounds is clinoptilolite. It offers the possibility of removing ammonium and nitrate and nitrate compounds, as well as organic acids from aquaculture systems. Zeolite is cheaper than active carbon and also requires no conditioning prior to use (Gendel et al., 2013). These features recommend it as a first option for reducing the concentration of ammonium ions in controlled systems (Zabochnicka-Switek et al., 2010; Sava, 2015). An economic and ecological advantage

represented by the use of such filters is the low cost of absorbent synthesis as well as the use of a non-toxic matrix of natural origin that is widespread in nature (Çelik et al., 2001).

2. MATERIALS AND METHODS

In the Laboratory of Fisheries and Aquaculture of the Faculty of Animal Science, University of Agronomic Sciences and Veterinary Medicine, was developed a controlled system using a physico-chemical process cheap, fast and reliable using zeolite that has the potential to replace the biologically removal of nitrogen species from the water. The zeolite is an hydrated aluminosilicate from the family of microporous solids with infinite open three-dimensional structure, called molecular sieve, which has the ability to perform ion exchange at a very high level as well as high capacity of hydration-rehydration (Măicăneanu et al., 2008).

The system components were:
- 60 l capacity tank populated with carp fish species (*Carassius carassius*);
- zeolite with a grain size of 1-3 mm;
- water recirculation pump.

A number of 4 experiments were performed in which the zeolite was used both as a column and as a bed, in two amounts - 166 g and 400 g respectively. In the natural zeolite used in the experiment the mineralogical compound clinoptilolite is mostly in proportion of 90%.

The controlled system consisted of a 60 liter aquarium populated with common carp fish. The method used to determine the ammoniacal nitrogen, NH_4 and nitrate, NO_3, content was the manual spectrometric method, and for the determination of the nitrite, NO_2, content, the molecular absorption spectroscopy method.

3. RESULTS AND DISCUSSIONS

In the four experiments the water in the system was passed through two different amounts of zeolite - 166 g and 400 g and two different ways of layering of the zeolite - column and layer. An increase in NH_4 retention activity was observed by using a 2.4-fold higher zeolite in experiments 3 and 4 against experiments 1 and 2.

Calculations were performed for the specific zeolite absorption per 100 g zeolite in all four experiments and the graphical comparison of the zeolite performance in all experimental variants.

The first experiment consisted of passing the water through the zeolite column, with a mass of 166 g, after a mechanical filtration.

The results obtained after the water quality test for the first experiment, are presented in Table 1.

Table 1. Chemical analysis of the samples in the first experiment.

Hour/Compound	0	8	16	24
NH_4 (mg/l)	0.176	0.100	0.132	0.232
NO_2 (mg/l)	0.569	0.398	0.190	0.294
NO_3 (mg/l)	67.950	68.285	70.566	72.645

The most intense activity of the ammonium retention in zeolite is in the first 8 hours, after which it begins to decrease, and after 16 hours the effect is much diminished. The NO_2 group has a similar evolution to that of ammonium, the concentration decreasing in the first 16 hours, and then slightly increasing up to 24 hours. In the first 8 hours, the decrease is 30% and the next 8 hours bring a more pronounced decrease of 0.208 mg / l, i.e. 36.5%, relative to the initial concentration. After 24 hours, the NO_2 concentration is still lower than the initial one, with 48.3%. Evolution of NO_3 is different from that of ammonium and nitrites in that it has a continuous increase in concentration throughout

the experiment. In the first 8 hours the growth is very low, only 0.33 mg / l, i.e. 0.5%. Up to 24 hours, the increase is more pronounced and linear, of 4.36 mg / l, i.e. 6.4%, in total, of the initial nitrate concentration. When using the same amount of zeolite but disposed as a horizontal layer (experiment 2), the results showed that this arrangement is far less efficient. The results are shown in Table 2.

Table 2. Chemical analysis of the samples in experiment 2.

Hour/Compound	0	2	4	6	8	10	12	14	16
NH_4 (mg/l)	0.118	0.134	0.101	0.107	0.099	0.145	0.167	0.170	0.181
NO_2 (mg/l)	0.138	0.136	0.134	0.129	0.119	0.124	0.143	0.151	0.168
NO_3 (mg/l)	38.767	40.120	39.529	42.048	41.647	41.595	43.090	44.531	41.754

It is noted that due to the small contact surface of the water with the zeolite, its activity was only 8 hours, after which there was an increase of the nitrogen compounds level. In the first 8 hours, the nitrite concentration decreased by 0.019 mg / l, i.e. 13.7% of the initial concentration, and in the next 8 hours the increase in concentration was 0.049 mg / l, i.e. 35.5% of the initial concentration.

The concentration of nitrates increased, with fluctuations, in the first 12 hours, when some temporary decreases in this concentration were recorded. The maximum concentration was reached after 14 hours, being greater with 5.764 mg / l, i.e. 14.8%, than the initial concentration. During the last 2 hours, a NO_3 concentration decreasing of 2.773 mg / l, i.e. 7.1% of the initial concentration, was recorded, so that over the entire 16-hour period the increase in nitrate content was 2.991 mg / l, i.e. 7.7% relative to the initial concentration.

In experiment 3 (Table 3), the vertical column of zeolite was used again, but the mass was increased to 400 g.

Table 3. Chemical analysis of the samples in experiment 3.

Hour/Compound	0	4	8	12	16	20
NH_4 (mg/l)	0.26	0.19	0.13	0.21	0.21	0.18
NO_2 (mg/l)	0.30	0.25	0.11	0.10	0.12	0.11
NO_3 (mg/l)	99.64	77.50	77.50	99.64	99.64	99.64

In the first 8 hours, a 50% decrease in ammonium concentration is recorded. An increase in ammonium content is then recorded, followed by a slight decrease after 16 hours, so that 20 hours after the start of the experiment, the content of ammonium is lower than the initial one by 0.08 mg / l, i.e. 30.7%. This shows that the zeolite is still active, 20 hours after the beginning of the experiment.

As for the nitrite content, it drops steeply in the first 8 hours, lighter in the next 4 hours, and shows a slight increase over the next 4 hours. Thus, there is a decrease of 67% in the first 12 hours. In the last 12 hours, the nitrite content remains constant, even if slight variations are recorded, demonstrating that the used zeolite retains its ability to regulate the NO_2 content within 20 hours of the beginning of the experiment.

The nitrate content decreases in the first 4 hours, then a level within the next 4 hours, followed by an increase to initial values, followed by a new level, up to 20 hours. The variation is 22.14 mg / l, i.e. 22.2%.

Experiment 4 sought to highlight the efficacy of using the same amount of zeolite as in experiment 3 but regenerated by treatment with an alkaline base of 0.01N concentration.

The results obtained with the evolution of various components of nitrogen in water are summarized in Table 4.

The ammonium content decreases by 70% in the first 12 hours to continue to increase slightly after another 4 hours, which means that zeolite activity starts to decrease.

NO_2 content values record an increase of 0.042 mg / l in the first 4 hours, i.e. 19.6%, followed by a slight decrease, up to 12 hours and level, up to 16 hours. The value recorded after 16 hours is 0.191 mg / l, less than the initial value by 0.023 mg / l, i.e. 10.7%.

Table 4. Chemical analysis of the samples in experiment 4.

Hour/Compound	0	4	8	12	16
NH_4 (mg/l)	0.28	0.11	0.08	0.08	0.11
NO_2 (mg/l)	0.21	0.256	0.210	0.191	0.191
NO_3 (mg/l)	42.96	46.50	38.97	36.76	37.64

The NO_3 content is similar to that recorded for NO_2. Thus, a slight increase is recorded in the first 4 hours, followed by a slightly more pronounced decrease and a return to an increasing trend, 16 hours after the beginning of the experiment. The increase in the first 4 hours is 3.54 mg / l, i.e. 8.2%, and the final value after 16 hours is 8.86 mg / l lower than the initial value, i.e. 20.6%.

In the last two experiments, the pH values were monitored (Table 5).

Table 5. pH variation during experiments 3 and 4.

Hour	pH	
	Exp 3	Exp 4
0	7.45	7.29
4	7.70	7.58
8	7.70	7.81
12	7.72	7.81
16	7.72	7.72
20	7.76	-

The pH variation in experiment 3 occurs in the basic range starting at pH 7.45 with a rapid increase in the first 4 hours, reaching pH 7.7, followed by a slow increase over the next 16 hours, to 7.76. This increase in pH can be due to the decrease in nitrite content, which reduces the acidity of the solution.

Similarly, in experiment 4, where pH increase can be explained by decreasing the NO_2 and NO_3 content.

4. CONCLUSIONS

In the first two experiments, where 166 g of zeolite was used, the results showed that the maximum zeolite action was recorded in the first 16 hours in experiment 1 and in the first 8 hours in the second experiment, leading to decreases in NH_4 content of 43% and 16%, respectively.

Better absorption of ammonia was noted when column-shaped zeolite was used, not in the form of a bed, which means that in order to capture ammonia, the zeolite needs a longer period of time in contact with used water.

In experiments 3 and 4 where it returned to the zeolite vertical column but increased the amount to 400 g, the results showed how the ammonium content dropped in the first 8 hours by 50%,

continuing to remain low, up to 20 hours, and the pH has been steadily increasing, which may be due to the decrease in nitrite content.

In experiment 4, which sought to highlight the use of regenerated zeolite, the results were particularly encouraging, with the ammonium content dropping by 70.7%.

The slight increase in pH from 7.29 to 7.81 can also be explained by lowering the NO_2 and NO_3 content.

The zeolite used - clinoptilolite - maintains in the normal media parameters the water from the controlled system, both in the natural state and regenerated, and proves to be a successful replacement of the biological filters.

5. ACKNOWLEDGEMENTS

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