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ZEOLITE FILTERS - TOOLS TO IMPROVE WATER QUALITY IN RECIRCULATING SYSTEMS IN AQUACULTURE

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Abstract

For the efficient and sustainable use of water in recirculating aquaculture systems, in order to improve water quality, zeolite filters have been used by retaining ammonia. The efficiency of the filters was tested in systems with volumes of 220 liters of water, populated with batches of 36 carp seedlings (Cyprinus carpio) in summer I. Horizontal filters with zeolite bed and composite filters, obtained from a granular mixture of silicate glass and zeolite, were used when filtering the water. For the determination of ammoniacal nitrogen, the continuous concentration criterion (CCC) and the maximum concentration criterion (CMC) were used. After 24 and 48 hours of water filtration using clinoptilolite filters, it was found that the maximum permissible values of ammonia in the water were not exceeded. Ammonia is absorbed in relatively large quantity, zeolite improves the filtration yield, which recommends the use of these types of filters in controlled recirculating systems in aquaculture.

Key words: *ammonia; continuous concentration criterion, clinoptilolite, maximum concentration criterion, organic recirculating systems.*

INTRODUCTION

At the World Conference on the Environment, held in 1992 in Rio de Janeiro, particular attention was paid to the concept of sustainability, which involves achieving a balance between economic growth and environmental protection as well as the use of alternative resources. Due to the current climatic conditions, it is necessary to use as rationally as possible the natural resources, especially the water. Aquaculture (FAO 2022) produced in 2020 49% of the total production of fish used for human consumption, i.e. 88 million tonnes, and this percentage is expected to increase in the coming years.

New technologies used in aquaculture ensure an increase in productivity. They must aim to protect the environment and the natural resource by reducing water and energy consumption and pollutant contaminants in the effluent waters of recirculating systems. Currently, more than 60 types of natural zeolites are known worldwide and more than 150 other types have been synthesized (Ghasemi et al., 2016). Natural zeolite bushes of very good quality are also found on the territory of our country. It is important to know and disseminate information on the efficiency of the use of zeolites in unconventional technologies (Mârza et al., 1991). Worldwide, it is tried to couple the adsorbent properties of the zeolitic - clinoptilolite volcanic tuff with various compounds (such as hydrotalcite – double hydroxycarbonate of magnesium and aluminum, which has anion exchanger properties) in order to obtain composites that have the property of retaining both cationic and anionic, inorganic or organic pollutants (Misăilă, 2004; Mishra & Jain, 2011). An economic and environmental advantage of the use of such filters is the low cost of adsorbent synthesis and the use of a matrix of natural origin that is not toxic and is widespread in nature. Zeolite volcanic bushes are an eco-alternative technological source of the future. They can be used as such, in membranes, in filters or in technological installations. Clinoptilolite zeolite has been registered in the European Community as a food additive DIN 53 770 since 2007 and declared safe for final consumers of meat, milk

or eggs from animals that have received zeolite in food or litter (Katsoulos et al., 2016; Pogurschi et al., 2017). A possibility to increase the mechanical strength and improve the absorption capacity of zeolites can be their incorporation into porous vitreous structures, with the obtaining of ecological zeolite-glass composites (Elisa et al., 2009; Sava et al., 2009; 2017).
The purpose of the work is to analyze the advantages of using filters based on clinoptilolite zeolite, as well as new filters, based on ecological clinoptilolite-glass zeolite composite in organic recirculating systems (SAR) populated with carp brood (*Cyprinus carpio*), especially with regard to the elimination by absorption of ammonia.

MATERIALS AND METHODS

The experimental researches, carried out in the Aquaculture Laboratory of the USAMV Bucharest, aimed at studying the influence of the natural clinoptilolite zeolite on the water quality and the development of the carp sapling (Cyprinus carpio) in summer I, from controlled systems. The duration of the experiment was 70 days. The controlled system used consisted of three aquariums with a capacity of 220 l each, the carp brood being divided into three batches of 36 individuals (Figure 1).

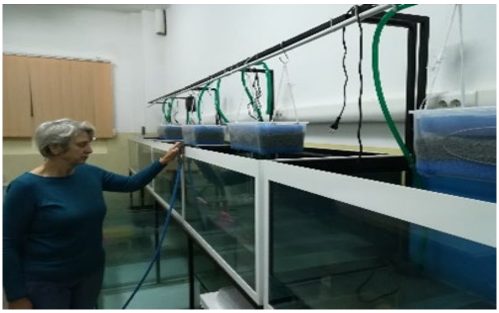

Figure 1. Controlled fish breeding system (original photo)

Clinoptilolite zeolite, used as a substitute for biological filters, is, from a chemical point of view, a natural aluminosilicate, with alkaline and alkaline-earth metals, crystalline and hydrated, which belongs to the group of tectosilicates (Emadi et al., 2001; Mansouri et al., 2013). The clinoptilolite chemical formula is:

$$(Ca, K, Na_2, Mg)_4Al_8Si_{40}O_{96}\ 24H_2O$$

From the mineralogical point of view, the zeolite used is of the clinoptilolite type. In its predominant chemical composition is silicon oxide (SiO_2) in the proportion of 68.75-71.30 followed by aluminum oxide (Al_2O_3) with a weight of maximum 13.10% (Table 1).

Table 1. The chemical and mineralogical composition of the clinoptilolite zeolite used (Zeolites Development data sheet)

Compound	Precent (%)
Chemical composition	
SiO_2	68.75-71.30
Al_2O_3	11.35-13.10
CaO	2.86-5.20
K_2O	3.17-3.40
Fe_2O_3	2.10-1.90
MgO	1.18-1.20
Na_2O	0.82-1.30
Calcination loss	9.77
Mineralogical composition	
Clinoptilolite	87-90
Plagioclase	2-5
Anherite	2-3
Cristobalite	4-5

According to the elemental chemical analysis (Figure 2), in the clinoptilolite zeolite the largest peaks belong to the main elements (silicon and aluminum), preceded by calcium, potassium, magnesium, iron, oxygen. From the category of microelements are distinguished titanium, zinc, zirconium, phosphorus and traces of sulfur, vanadium, chromium, copper and rubidium.

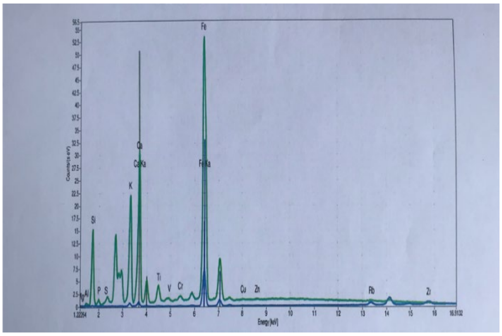

Figure 2. Chemical analysis of clinoptilolite zeolite powder (Zeolites Development data sheet)

The physico-chemical properties of clinoptilolite highlight the high porosity of zeolite, up to 44%, with a pore diameter of 0.4 nm, as well as the chemical resistance to the action of acids and bases (Table 2).

Table 2. Physico-chemical properties of clinoptilolite zeolite (Zeolites Development data sheet)

Property	Value
Softening temperature	1250°C
Melting temperature	1320°C
Flow temperature	1400°C
Appearance and smell	Gray-green, odorless
Porosity	32-44%
Pore diameter	0.4 nm
Mohs hardness	3.5-4
Water absorption	34-36%
pH	9
Density	2.377±0.002 g/cm^3
Chemical resistance	Resistant to the action of acids and bases
Thermal stability	up to 450^{0}C
Water solubility	Insoluble
Dangerous decomposition	Not applicable
Dangerous polymerization	Not applicable
Toxicity	Nontoxic
Total cation exchange capacity	175 meq/100 g

Water filtration was conducted using simple and composite zeolite filters (Sava et al., 2017). To make a simple filter, the amount of 4 kg of clinoptilolite was used, with the initial granulation of 3-5 mm, subsequently 2-3 mm. Zeolite was regenerated at 48 hours with saline (Ghasemi et al., 2016; Nicholas et al., 2017).
The filtration of residual solids from the water of recirculating systems for breeding carp juveniles was done before the water came into contact with zeolite, using sponges and filter cotton wool (Figure 3).

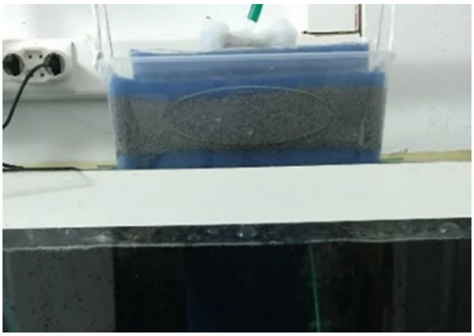

Figure 3. The filter with clinoptilolite zeolite (original photo)

For the realization of the composite filters sintered glass-clinoptilolite, called FSZ 1 and FSZ 2, glass with a silico-chalco-sodium composition was used (Table 3).

Table 3. Glass composition (Krystal Clear - Intex data sheet)

No.	Oxide	Percentage (%)
1	SiO_2	72.07
2	CaO	9.54
3	MgO	3.25
4	Na_2O	13.79

The glass was used in the form of granules with a maximum size of 0.50 mm and had a powder density of 1.6 x 10^3 kg/m^3 (Table 4).

Table 4. Glass properties (Krystal Clear - Intex data sheet)

No.	Property	Value
1	Absolute density	2.4 x 10^3 kg/m^3
2	Powder density	1.6 x 10^3 kg/m^3
3	Grains dimension	0.25-0.5 mm
4	Uniformity coefficient*	1.6

* According to (Radu and Ibriș, 2004)

The zeolite in the FSZ 1 composite filter had the finest grain below 0.125 mm, and the coarse one of 1.25 mm (Table 5).

Table 5. Particle size distribution of the zeolite used in composite filters

Particle size (mm)	Percentage (%)
0.5-1.25	6.24
0.25-0.50	12.39
0.125-0.25	1.01
Under 0.125	0.36
Total	20

In obtaining the FSZ 1 filter, a zeolite/glass ratio of 1: 4 and 20 g of zeolites and 80 g of glass was used. For pressing and binding of granules was used a solution of polyvinyl alcohol (PAVN) 8% in distilled water, in the proportion of 10%, relative to 100% granular glass-zeolite mixture. In this first variant, the composite filters with a diameter of about 20 mm were made in raw (Figure 4), by pressing with a hydraulic press, with a force of 2.5 Tf on the entire surface.

Figure 4. Composite filter - type 1 (FSZ 1) (original photos)

The pressed composite filter was inserted into an electric furnace with molybdenum disilicide bars Nabertherm - Germany. The thermal sintering treatment was aimed at obtaining a mechanical resistance high enough to cope with the passage of water. Even though the sintering temperature reached 600ºC, a porosity was retained large enough for this passage to be possible (Malherbe et al., 2006) (Table 6).

Table 6. Thermal treatment parameters for the obtaining of composite filter type 1 (FSZ1)

Temperature domain (ºC)	Duration (hours)
20-110	1
110	1
110-250	2
250	1
250-600	3
600	2
600-20	6
Total	16

The shrinkage of the diameter of the FSZ 1 filter after sintering is 1.4%, and the height contraction is 1.9%. The weight loss of the filter is 9.4% and the open porosity represents 49% of the total porosity (Table 7).

Table 7. Composite filter properties FSZ 1 type

Property	Value
Green diameter	20.24 mm
Sintered diameter	19.94 mm
Diameter contraction	1.4 %
Green height	17.41 mm
Sintered height	17.0 mm
Height contraction	1.9 %
Green mass	10.35 g
Sintered mass	9.38 g
Mass loss	9.4 %
Green volume	5.6 cm^3
Sintered volume	5.33 cm^3
Volume contraction	4.82 %
Green density	1.848 g/cm^3
Sintered density	1.759 g/cm^3
Absolute density *	2.36 g/cm^3
Theoretical volume	3.97 cm^3
Total porosity**	25.45 %
Open porosity***	12.47 %

The absolute density of the composite was calculated by a simple additive relationship:

$$d_c = d_s \times m_s + d_z \times m_z \quad (1)$$

where:
d_c = composite absolute density
d_s = glass absolute density
m_s = glass weight %
d_z = zeolite absolute density
m_z = zeolite weight %

The total porosity was calculated with the formula:

$$P_t = \frac{V_c - V_t}{V_c} \times 100 \quad (2)$$

where:
P_t = total porosity
V_c = sintered composite volume
V_t = theoretical volume

The open porosity was calculated with the formula:

$$P_d = \frac{P_t \times A_z}{P_z} \quad (3)$$

where:
P_d = open porosity
A_z = water absorption zeolite (Aquatech) = 16.21 %
P_z = total porosity zeolite (Aquatech)=33.08%.

In the second type of sintered composite filter, FSZ 2 (Figure 5) the proportions of glass and zeolite were preserved, and the grain of the zeolite used was between 0.5 and 1.25 mm. In this case, a 5 % PAVN solution was used in distilled water at the rate of 8% per 100% granular mixture of zeolite-glass.
The thermal sintering treatment was performed at a temperature of 620ºC, higher by 20ºC than in the case of the FSZ 1 filter (Table 8).

Figure 5. Composite filter - type 2 (FSZ 2)

Table 8. Thermal treatment of the composite filter type 2

Temperature domain (ºC)	Duration (hours)
20-110	1
110	1
110-250	2
250	1
250-620	3
620	2
620-20	6
Total	16

The shrinkage of the diameter of the FSZ 2 sintered filter is 12.08%, and of the height of 3.67%, higher than in the case of the FSZ 1 filter, but the weight loss is less than 7.66 g. The open porosity represents, as in the case of the FSZ 1 filter, 49% (Table 9).

Table 9. Composite filter properties FSZ 2 type

Property	Value
Green diameter	20.15 mm
Sintered diameter	19.73 mm
Diameter contraction	12.08 %
Green height	16.37 mm
Sintered height	15.77 mm
Height contraction	3.67 %
Green mass	9.41 g
Sintered mass	8.69 g
Mass loss	7.66 %
Green volume	5.22 cm^3
Sintered volume	4.82 cm^3
Volume contraction	7.66 %
Green density	1.804 g/cm^3
Sintered density	1.804 g/cm^3
Absolute density	2.36 g/cm^3
Theoretical volume	3.68 cm^3
Total porosity	23.57 %
Open porosity	11.55 %

Hanna Instruments' Aquaculture Photometer HI3303 and specific reagents from the same company were used to measure the water parameters, and to determine the temperature, thermometers for aquariums.

The continued concentration criterion (CCC) is the limit value of total ammonia resulting in unacceptable effects, i.e. more than 20 % decrease in survival, growth and/or reproduction (Eddy, 2005)

The maximum concentration criterion (CMC) is half of the final acute value of total ammonia (Eddy, 2005)

For the testing of the FSZ 1 and FSZ 2 filters, an assembly consisting of a PVC pipe was made inside which the filter was inserted, fixed with silicone. The filtration system was positioned vertically using a clamping system and through it was passed the amount of 100 ml of water coming from the aquarium and 100 ml of ammonia solution in distilled water, of different concentrations, between 1 and 2.3 mg/l.

Several consecutive crossings were made, after which the filters were regenerated with distilled water and reused, in order to follow the efficiency of zeolite regeneration.

RESULTS AND DISCUSSIONS

The initial use of zeolite with a grain size of 3-5 mm when filtering water from aquariums kept the ammonia values high. Although the regeneration of clinoptilolite was carried out at 24 hours, the ammonia values continued to increase slightly (Table 10). The water temperature was constant, of 22ºC, the pH value was between 7.5 and 7.6, and that of dissolved oxygen (DO) was 6.5-6.7.

Table 10. Water parameters

Aquarium	NH_4^+ (mgL^{-1})	NH_3 (mgL^{-1})	NH_3-N (mgL^{-1})
Initial	0.68	0.65	0.53
1	1.28	1.21	1.00
	1.48	1.39	1.15
	1.73	1.63	1.34
	1.89	1.79	1.47
Initial	0.70	0.66	0.54
2	1.22	1.15	0.94
	1.57	1.48	1.22
	1.66	1.56	1.29
	1.98	1.87	1.54
Initial	0.73	0.69	0.56
3	1.30	1.01	0.87
	1.84	1.74	1.43
	1.85	1.74	1.43
	1.99	1.88	1.55

By using the smaller-grained zeolite, respectively 2-3 mm, the values of ammoniacal compounds were lower after 24 hours, due to the smaller size of the zeolite particles (Table 11) (Asgharimoghadam et al., 2012).

The water samples were taken and analyzed 24 hours and 48 hours after the zeolite change.

Table 11. Water analysis after 24 and 48 ore of zeolite use

Aquarium	NH_4^+ (mgL^{-1})	NH_3 (mgL^{-1})	NH_3-N (mgL^{-1})	NH_4^++NH_3 (mgL^{-1})
1 Initial	1.29	1.20	1.01	2.49
(24 h)	1.76	1.66	1.37	3.42
(48 h)	2.99	2.82	2.32	5.81
(24 h)	1.16	1.09	0.90	2.25
(48 h)	3.30	3.11	2.56	6.41
(24 h)	1.21	1.15	0.94	2.36
(48 h)	3.25	3.07	2.52	6.32
(24 h)	1.54	1.45	1.09	2.99
(48 h)	2.68	2.53	2.08	5.21
(24 h)	0.98	0.92	0.73	1.90
(48 h)	2.62	2.47	2.04	5.09
(24 h)	0.82	0.78	0.64	1.60
(48 h)	2.18	2.06	1.69	4.24
2 Initial	1.47	1.38	1.13	2.85
(24 h)	1.86	1.75	1.44	3.61
(48 h)	3.22	3.04	2.50	6.26
(24 h)	0.76	0.72	0.59	1.48
(48 h)	3.42	3.23	2.66	6.65
(24 h)	1.13	1.06	0.87	2.19
(48 h)	3.43	3.24	2.66	6.67
(24 h)	0.92	0.87	0.72	1.79
(48 h)	2.39	2.26	1.86	4.65
(24 h)	0.82	0.77	0.64	1.59
(48 h)	2.92	2.80	2.30	5.72
(24 h)	0.96	0.91	0.75	1.87
3 Initial	1.37	1.29	1.05	2.66
(24 h)	1.83	1.72	1.42	3.55
(48 h)	2.97	2.80	2.30	5.77
(24 h)	0.64	0.61	0.50	1.25
(48 h)	2.78	2.63	2.16	5.41
(24 h)	0.85	0.80	0.66	1.65
(48 h)	3.18	3.01	2.47	6.19
(24 h)	1.48	1.39	1.15	2.87
(48 h)	3.53	3.33	2.74	6.86
(24 h)	0.95	0.90	0.74	1.85
(48 h)	3.19	3.01	2.40	6.20
(24 h)	0.92	0.87	0.71	1.79
(48 h)	2.39	2.26	1.86	4.65

The pH values of the water during the experiment were between 7.5-7.6, and those of dissolved oxygen between 6.5-6.7 mg/l, both parameters being within the normal permissible limits. The water temperature was 21-22°C.

Total ammonia values (NH_3 + NH_4^+) after 24 hours of filtration were between: 1.60 mg L^{-1} - 3.42 mg L^{-1} in the first aquarium; 1.59 mg L^{-1} - 3.61 mg L^{-1} in the second aquarium and 1.25 mg L^{-1} - 3.55 mg L^{-1} in the third aquarium.

The upper limit of total ammonia did not exceed the accepted limit of the continuous concentration criterion (CCC) which is 3.8 mg NH_3 + NH_4^+ mg L^{-1} (Eddy, 2005).

After the 48-hour filtration interval, the total ammonia values exceed the accepted limit of the continuous concentration criterion in all three aquariums, ranging from 3.42 mg L^{-1} to 6.86 mg L^{-1}.

The limit of the maximum concentration criterion (CMC) for the carp species is 8.4 mg NH_3 + NH_4^+ mg L^{-1} (Eddy, 2005).

The CMC criterion values were not exceeded either after 24 or after 48 hours of water purification using clinoptilolite zeolite (Ip et al., 2001).

Total ammonia nitrogen values, in all cases, after 24 and 48 hours, were well below the concentration of 15 mg L^{-1}, which is the limit for a 27 % decrease in survival rate (Farhangi et al., 2013).

Since CCC values after 48 hours have been increased, it is concluded that zeolite should be regenerated after 24 hours of continuous use.

In the fish organism, the decrease in ammonia toxicity can be achieved by decreasing its production, increasing the excretion of ammonia or converting ammonia into less toxic compounds intended for storage or excretion (Randall & Tsui, 2002). After exposure to higher ammonia values, plus endogenous ammonia, the organism of some species, including the common carp (Cyprinus carpio), can synthesize glutamine from glutamate and NH_4^+. Glutamine is stored in tissues and can subsequently be used as an oxidative substrate. The disadvantage lies in the high energy consumption of the body to perform detoxification (Eddy, 2005).

In the case of composite filters FSZ 1 and FSZ 2, the ammonia retention capacity testing was carried out by successive passages of either aquarium water or water and ammonia solutions.

Through the FSZ 1 filter, 10 passages of aquarium water with an NH_3 concentration of 1.57 mg/l were carried out at a temperature of 24°C.

The filter contains 1.87 g of zeolites and retained 62.42% of the ammonia in the test sample, i.e. 0.98 mg. One gram of clinoptilolite retained 0.52 mg of ammonia in a span of 4 hours and 39 minutes (Table 12).

Table 12. Water analysis after passing through the FSZ 1 filter

Parameter	Initial value	Final value	% absorption
pH	6.5	6.7	
NH_4^+	1.67 mg/l	0.62mg/l	62.87
NH_3	1.57 mg/l	0.59mg/l	62.42
NH_3-N	1.29 mg/l	0.48mg/l	62.79

The regeneration of the filter was conducted by washing with two liters of distilled water, to eliminate the retained ammonia. Through the regenerated filter, a new series of 5 passes of aquarium water with an NH_3 concentration of 1.85 mg/l was carried out. The total time interval was 5 hours and 15 minutes.

After regeneration, the FZS 1 filter retained only 60% ammonia from the test sample (Table 13).

Table 13. Water analysis after passing through the regenerated FSZ 1 filter

Parameter	Initial value	Final value	% absorption
pH	6.5	6.9	
NH_4^+	1.96 mg/l	0.78 mg/l	60.20
NH_3	1.85 mg/l	0.74 mg/l	60.00
NH_3-N	1.52 mg/l	0.61 mg/l	59.87

The filter was evaluated with aquarium water, which contained alongside ammonia, nitrites and nitrates, which reduced its ability to retain ammonia. Slower filtration and lower yield can be explained by plugging part of the pores of the sintered filter (Malherbe et al., 2006).

The FZS 2 composite filter was sintered at a temperature 20ºC higher than FSZ 1 in order to prevent the pores from plugging. For testing the filtering capacity of this type of filter, a laboratory-prepared ammoniacal solution was used. The aqueous ammonia solution with 2,07 mg NH_3/l was subjected to 10 successive filter passes.

Table 14. Ammoniacal solution after passing through the FSZ 2 filter

Parameter	Initial value	Final value	% absorption
pH	6.5	7.7	
NH_4^+	2.19 mg/l	0.08 mg/l	96.35
NH_3	2.07 mg/l	0.08 mg/l	96.14
NH_3-N	1.70 mg/l	0.06 mg/l	96.47

1.74 g of zeolite from the filter retained 96.14% of the ammonia present. During the experiment - 7 hours and 51 minutes, one gram of zeolite retained 1.14 mg of ammoniac (Table 14).

After regeneration, the filter was subjected to a new series of five passes of an ammonia solution with a concentration of 2.14 mg NH_3/l.

Following the second series of passes, which lasted 10 hours and 20 minutes, the 1.74 g of zeolite retained 97.66% of ammonia, which means that one gram of zeolite retained 1.20 mg of ammonia (Table 15).

Table 15. Analysis of the ammonia solution after passing through the regenerated FSZ 2 filter

Parameter	Initial value	Final value	% absorption
pH	6.5	7.7	
NH_4^+	2.27 mg/l	0.05 mg/l	97.8
NH_3	2.14 mg/l	0.05 mg/l	97.66
NH_3 - N	1.76 mg/l	0.04 mg/l	97.73

Although the sintering temperature was increased by 20ºC, from 600ºC to 620ºC, the filter showed the same tendency to increase filtration time after regeneration, which shows that either the filter pores clump after the first filtrations, or the open porosity decreases by potential chemical reactions inside the filter. It follows that, in future research, the cause of this decrease in open porosity will be precisely established, resulting in an increase in filtering time.

CONCLUSIONS

In the present study it was aimed at improving the quality of water in recirculating systems in aquaculture by using clinoptilolite zeolite. When using simple horizontal filters with a zeolitic bed, it was observed that in none of the cases presented were the values of the continuous concentration criterion (CCC) and the maximum concentration criterion (CMC) for ammoniacal nitrogen exceeded, both after 24 and after 48 hours of zeolite water purification. To improve the filtration efficiency, composite filters consisting of sintered glass and zeolite were made and tested. The FSZ 2 composite filter revealed an increased ability of zeolite to retain ammoniacal compounds, which means that the inclusion of clinoptilolite in glass does not lead to a decrease in this property. A problem that needs to be solved further is that both composite filters have filtered in increasingly longer times, which means that their open porosity has shrunk during filtering.

The clinoptilolite used to filter the water contributed to the maintenance of the medial conditions favorable to the growth and development of the fish from the controlled systems used, but also to ensuring a 100% survival rate.

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