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SUSTAINABLE CONSERVATION OF THE AQUATIC BIO-RESOURCES THROUGH USE OF ABSORBENT MINERAL ADDITIVES AS ZEOLYTES TYPE

CONSERVAREA DURABILĂ A BIORESURSELOR ACVATICE PRIN UTILIZAREA DE ADITIVI MINERALI ABSORBANȚI/ADSORBANȚI, DE TIPUL ZEOLIȚILOR

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Present scientific paper propose to evidence the chemical composition and the effect of the volcanic tuff, for a water quality maintenance at the optimum parameters, for technologies of semi-intensive and super-intensive rearing, and the distribution as ingredients in fodders and its effect in breeding and physiological state for different fish specie with economical value. During the last years, zeolytes represent a material used frequently in environment protection technology, which is based on the capacity of ionic changing and the absorption capacity. By reason of these chemical proprieties the intension is their implementation in Romanian aquaculture regarding technological water with optimum physic-chemical properties for fish species rearing.
Key words: preservation, aquatic bioresources, zeolytes

Introduction

Water quality management was and still is considerate to be one of the most important aspects of aquaculture in recirculating systems.

Regarding a sustainable preservation of aquatic bioresources, it could be used mineral additives, absorbents or adsorbents, zeolytes type for recirculating systems with the goal of gases noxes decreasing (ammonia, sulphuretted hydrogen) and of organic charge (CCOCr, CBO_5), resulted from metabolism after eutrophisation process.

During the last years, natural zeolites represent a material used frequently in environment protection technology which is based on the capacity of ionic changing and the absorption capacity.

Zeolyte used in experiment belongs to natural zeolytes group, named clinoptilolit. Specialty literature show that the zeolyte is successfully used in water

treatment, results from domestic, zootechnical and industrial activities, by reason of its chemical proprieties, and specially, ions exchanging. This ionic exchanging capacity increase when these goes trough the deallumination process. Exchange capacity values are influenced by some factors of chemical nature of zeolite and by parameters of exchange process, as: ions concentration, temperatures, time, rapport solution/zeolite, other ions presence etc.

Natural zeolytes (like volcanic tuff) are the most frequent rocks on the earth, with complex structures, with different granulations, composed from a mineral complex mixture: feldspars, illites, muscovite etc.

By reason of these chemical properties the intension is their implementation in Romanian aquaculture regarding technological water with optimum physic-chemical properties for fish species rearing.

In this paper it is presented the demonstrative model for water treatment in conditions of fishy material rearing in recirculating system, with the goal of water quality maintenance in fish rearing units that used this kind of system.

Materials and Methods

The performances of experimental module were verifying trough rearing operations of *Huso huso* sturgeon specie. Rearing experiment developed during a 144 days period trough a monitoring of hydro chemical parameters of the system's technological water, using as filter the zeolyte.

Regarding the experiment development was accomplished a system for fish species rearing, compounded from:

- *2 rearing units*, each unit has double walls from PVC for a good water circulation in closed system. Each module has a volume at almost 600 liters, populated with the same fishy material with the same population density;

- *units for water quality conditioning, compound from: unit of water filtration; unit of water aeration and oxygenation*

Filtration installation with zeolytes, constructional and functional point of view, is compounding from:

- vertical mechanical filter, with clarification bed with quarts sand, with role in suspensions removing, which have dimensions bigger than 1μm;
- chemical filter, with clarification bed with natural zeolytes, with a granulation of 1,6-1,8 mm and a specifically weight lower than 2-2.3 g/cm^3, with a role in ionic changing process, between electrolyte ions, fixed in adsorbent mass (ions changer) and water ions (which become in contact).

- *installation for water distribution to rearing module*

Installation for water distribution to rearing module it is accomplished trough a centrifugal pump for delivery. The centrifugal pump has an automatic function, stopping and starting trough a button switch with level traductor, with a role of automatic protection if the water level

decrease. The water circuit was assuring by centrifugal pump with a debit of 7000 liters/minute, at 5 m evacuation length.

Filtration installation with zeolytes was installed in one of experimental unit, and the other one was used as testifier.

Trough this installation followed the influence of zeolyte on physic-chemical parameters of water as filtration agent and for its effect assessment on these parameters correction.

To determination of the main parameters who are implied in quality assessment, from chemical point of view, were respected the work protocol, indicated in analyzing standard methods for surface waters, and also, the methods from domain literature, using reactive kitts already prepared, regarding, when it was possible, a decrease of working time, obtaining accurate results.

Results and Discussions

After analyzes on water from experimental unit, it could be make the following observations (tabel nr.1):

Table nr. 1

Chemical parameters from experimental unit – using zeolite as „filter"

Chemical parameters determinates	U.M.	Sample 1 Water without zeolite	Sample 4 water with zeolite before population	Sample 5 water with zeolite – populated with fishes	Max. Val. Adm. by Ord.no. 161/2006 for class II of quality	Maximum values admissible by specialty literature
0	1	2	3	4	5	6
pH	upH	7,98	8.16	7.96	6.5 – 8.5	
Organically substance	mg $KMnO_4$/l	49,67	44.96	58.33	-	60
CCO-Mn	mg O_2/l	12,41	11.24	14.58	10	15

0	1	2	3	4	5	6
Ammoniac nitrogen $N\text{-}NH_4^+$	mg/l	0.212	0.051	0.174	0.8	-
Ammonia NH_3	mg/l	0.01	0.003	0.007	-	0.2
Ammonium NH_4^+	mg/l	0.262	0.062	0.216	-	2
Nitrites NO_2^-	mg/l	0.621	absence	0.445	0.03	-
Nitrates NO_3^-	mg/l	2.9	2.4	25.1	-	0.2
Phosphates PO_4^{3-}	mg/l	0.229	0.120	0.702	-	3
Carbonates CO_3^{2-}	mg/l	absence	absence	absence	-	20
Bicarbonates HCO_3^-	mg/l	134.2	146.4	134.2	-	600
Total alkalinity	mval/l	2.2	2.8	2.2	-	6
Calcium Ca^{2+}	mg/l	32	36	48	100	160
Magnesium Mg^{2+}	mg/l	17.01	14.58	9.72	50	50
Ca^{2+}/ Mg^{2+}		1.8	3	4.9	-	5/1
Total hardness	°D	8.41	8.41	8.97	-	20
Chloride Cl^-	mg/l	43.42	59.67	80.74	50	40
Sulphate SO_4^{2-}	mg/l	25.1	28.0	29.0	120	80

- **pH** – represents the concentration of hydrogen from water and, in conformity with this, water will has an acid or alkaline character. pH have values in 0-14 upH interval, and for aquatic resources protection it is recommended water with values between 6.5 – 8.5 upH.

In laboratory, pH of water samples was measured with a digital pH-meter.

Water pH has a decrease initially, with values between 7.98 upH, for initially water, to 6.90 upH for water with zeolyte, and after that to 7,96 upH in unit with fishes. A maintenance of pH value is by reason of the contain increase of calcium and bicarbonates ions, which lead to an improvement of water tamponade capacity.

- **Organically substance**, expressed trough the chemical consumption of oxygen at potassium permanganate, was detected trough volumetric method that based on the oxidation of oxidable substances in water (especially organically substances) with potassium permanganate.

Analyzes results could be expressed in two ways: mg $KMnO_4$/l and mg O_2/l. Contain of oxidable organically substances, expressed in mg $KMnO_4$/l, has values between 49.67 mg $KMnO_4$/l, for initially water, 41.31 mg $KMnO_4$/l for

water with zeolite, and after that to 58.33 mg $KMnO_4$/l in unit with fishes, in all of these cases being under the maximum admissible for fishy water, respectively 60 mg $KMnO_4$/l. Correlated with this, the chemical consumption of oxygen at potassium permanganate (CCO-Mn), expressed in mg O_2/l, has a similarly evolution.

It could be observe a decrease at organically substance in zeolyte presence, due to its adsorption capacity, trough its retention in net, but also the aggrandizement of environment with oxygen and its mineralization.

- **Ammoniac nitrogen (NH_3 şi NH_4^+)**, and also, **ions of nitrogen (NO_2^-)** were determinate with spectrophotometer using kitts of reactive, at a spectrophotometer with molecular adsorption VIS, DR 2800 type. These have lower concentration in water filtered trough zeolitic material than water trough testifier unit and than water treated with zeolite, by the reason of a better capacity of this to stocks ions in its net.

In treated water, but with fish's presence, its values have an increase, but lower than water from testifier unit and than water treated with zeolite by the reason to an increase of organically substances quantities from fodder and fishes metabolism.

- Regarding **ion of nitrogen (NO_3^-)** - were determinate with spectrophotometer using kitts of reactive, at a spectrophotometer DR 2800 – do not observe significance variations, except water with fishy material, where was a significance increase of nitrogenous, appreciatively 8 fold, a fact that could be explained trough a mineralization in optimum conditions of organically substance from this water.

- Quantity of PO_4^{3-} determinate with spectrophotometer decrease in water treated with zeolite from 0.229 mg/l in testifier sample until 0.120 mg/l, but increase again in water with fishy material, solving in bigger quantities, in optimum conditions of pH and till 0.702 mg/l.

- **Concentration of calcium** ions has been volumetric determined trough the complexing of calcium ion with disodic salt of etilen-diamino-tetraacetic acid (Complexon III), in the presence of the mixture between murexid indicator and β-naphthol green.

- **Magnesium** concentration from water has been volumetric determined trough the complexing of calcium and magnesium ions with disodic salt of etilen-diamino-tetraacetic acid (Complexon III), in the presence of the indicator ericrom T black and effectuating the difference between the amount of calcium cation and magnesium and calcium catione, previously detected.

Variations in calcium ion concentration are connected with magnesium ion variations. Ionic changing at zeolite surface is divided between these two ions, in conformity with pH value.

Lower values of pH encourage magnesium retention and the increase of calcium in water. In addition, Ca^{2+} is determining also by exhaustion grade (a decrease of changing capacity) of zeolite. During the experiment the quantity of

Ca^{2+} has a subtle increase, but continuous in compared with untreated water, but concentration of Mg^{2+} ion decrease compared with untreated water, and than maintain constantly until the unit was populated with fishes, when it has a decrease again.

The report Ca^{2+}/ Mg^{2+} is supra-unitary, net favorable to Ca^{2+} increasing from 1.8 value in uncured water to 2.4 in water treated with washed zeolite and finally to 4.9 in water treated with unwashed zeolite.

Water hardness was relatively constantly maintained independent from report exchange between both cations.

- **Bicarbonates** were volumetric determined and the method's principle consists in titrating them with chlorine hydride in presence of methyl-orange.

Water bicarbonates quantity has continuous increased in treated water beside untreated water and decreasing in treated fishy water. This thing, alongside the growth of solved calcium quantity has conduced to improvement of environment buffering capacity.

Water alkalinity has had the same variation as bicarbonates due to their presence in water.

- The value of **ion (Cl^-) and sulphate (SO_4^{2-}) -** volumetric determined through Mohr method and spectrophotometric respectively - they have intervened soft increases of concentrations in treated water beside the uncured control sample, being released from zeolite material network through desorption process.

Conclusions

Accomplished study started to the theoretical proprieties of natural zeolites, composites based on allumino-silicated, to function as ions changer and to correct some essential chemical parameters of technological water used in fishes breeding.

Trough comparative analyze of water from experimental units with zeolite filter and without zeolite filter, appear the following conclusions: it is confirmed the action of volcanic tuff used as filtration element, detected in laboratories analyses, regarding a decrease of NH_3, NH_4, NO_2^- concentrations, by the reason of changing capacity of aluminous-silicates and its adsorption proprieties in the holes of structural net. Ionic change is realized selective in conformity with holes dimensions from structural net of changing ions volume, of pH, the utilization grade of volcanic tuff – and in this case it is imposed a regeneration of volcanic tuff, because the water (testifier) passed trough the tuff, presents a high contain in organically substances and suspensions. We could mention the double usability of volcanic tuff due to ions contain.

From chemical composition of volcanic tuff are observed the following proprieties:

- a high affinity for water (this entered trough the net holes) and it is known as zeolitical water, that it could be alienated trough a gradual hitting till 300-400 ^{o}C without zeolite structure modification;
- a low specifically weight 2-2.3 g/m^3, high porosity due to the net holes;
- a good capacity of ionic change that represent a selective character determine by volcanic tuff nature, respectively by the structure and chemical composition of zeolite, being admitted only the smaller ions (cation) or equals with the dimensions of net holes, respectively of discarded ions;
- presents the selective adsorption propriety of different molecules, due to the surface structure as a molecular net of surface;
- a high catalytic activity.

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