Technological Solution for the Treatment of Wastewater Resulting from Autochthonous Aquacultures in Order to Protect the Marine Water Quality

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This paper depicts the research conducted at a micro-pilot scale on autochthonous cultures in order to develop adequate technological solutions for the treatment of wastewater resulting from shrimp cultures (Palaemonidae) that would ensure the protection of the Black Sea ecosystem and constitute an applicable tool for the development of aquaculture in Romania. The proposed objectives were attained by adopting an integrated system of marine cultures shrimps-mussels-macrophyte algae, followed by a conventional chemical treatment step using aluminium sulphate recovered from metallurgical slags. This system together with wastewater treatment ensures an optimum development of species and a minimum load of pollutants in the aquatic environment.

Key words: aluminium sulphate, aquaculture, shrimp (Palaemonidae), wastewater treatment

Decapod were subjected to observation and research since ancient times. Although they are consumed on the Romanian seashore by the connoisseurs, they have not been the subject of specialised fishing and were more often captured accidentally. Lately, an increased interest in the exploitation of the natural stocks of shrimps has been observed among foreign investors. In this case, the mariculture may decrease the anthropic pressure exerted on the crustaceans by the fishing activities and may ensure a continuity for market supply.

One of the most important aquaculture resources is water, and its effective management is becoming an increasingly central issue in development and on environmental friendliness. The exploitation of shrimps growth ponds includes the systematic refreshment of water as well as water discharge for harvesting the shrimps (Figure 1) [1,2]. Shrimps growth is dependent on the food available in the pond and the the quality of the feed water [3-6]. In case of insufficient food, an additional fertilization based on urea and superphosphate is employed in order to maintain the growth of the phytoplankton followed by formulated food. Food residues and metabolites end up on the bottom of the pond where they may suffer anaerobic fermentation and may lead to water acidification; therefore neutralisation with calcium carbonate is employed.

Marine aquaculture generates wastewater significantly polluted wastewater that may affect the health of the culture and curing measures (use of antibiotics, disinfecting substances, anaesthetics) are undertaken, often with negative effects on the shrimp's quality [7,8]. Contrariwise, the significant volumes of generated wastewater and its highly diversified content (organic and inorganic substances, suspended matter, nutrients etc.) lead to problems related to the impact on the environment (persistent odour, toxic substances, microbial communities etc.); thus the development of an adequate wastewater treatment technology is required as an assurance for the protection of the marine ecosystem and human health [9,10].

Research on the minimisation of pollutant concentration in the effluent are conducted worldwide and physical, chemical and biological methods are employed. However, a unitary technology has not been developed so far. Available literature data show that high salinity affects negatively the rate of the gravitational sedimentation of suspended matter and the aerobic biological treatment using activated sludge. The techniques used for the treatment of wastewater resulting from shrimp cultures are various and may be grouped as follows: separation of suspended matter using sedimentation pond, natural treatment using wetlands, bioremediation using integrated aquaculture systems [11, 12].

This paper shows the results of the research conducted on the development of a technological solution for the treatment of wastewater resulting from a culture of autochthonous shrimp species (*Palaemon elegans*). A

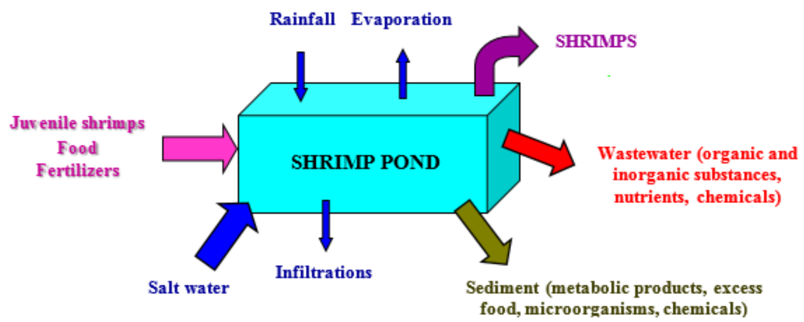

Fig. 1. Material flux in a shrimp's growth process

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contemporary theme related to the possibility to obtain an adequate quality of the effluents was addressed simultaneously with the use of compounds (aluminium sulphate) obtained through the recovery of metallurgical slags from secondary aluminium industry [13-15].

Palaemon elegenans, popularly known as *rockpool shrimp* (fig. 2) is the shrimp usually found on the Romanian seashore, on the sandy bottom covered with algae. Generally, it is a euryhalin and euribiont species that may be encountered even on the rocks of Sulina dam. It is a petricol species that endures winter conditions and it is not affected by high turbidity of water. *Palaemon elegans* may be considered omnivorous, using algae, detritus, small animals and fish residues as feed. This species reproduces from the end of May until September and is found only in the Lusitanian sector of the Atlantic Ocean, the Mediterranean, the Adriatic and the Black Sea [16,17].

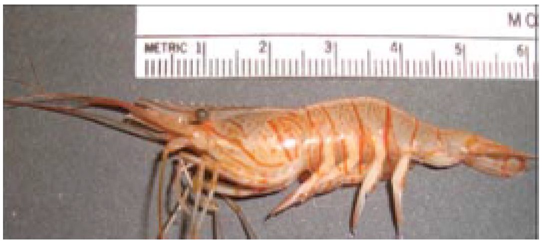


Fig.2. Palaemon elegans (Source: Salem Sound Coastwatch)

Experimental part

The experiments involving wastewater treatment were conducted using an integrated system of marine cultures shrimps-mussels-macrophyte algae consisting of:

a). reservoir for the cultivation of juvenile shrimps fed with 6 week-old *Palaemon elegans* (obtained by directed natural reproduction) at a growth density of 3000 samples/m^3. The reservoir was continuously fed with sea water (operating flow Q = 8 L/min) and pressurised air that ensured the oxygen required for the organism development to take place. Once a day food was supplied and it consisted of fresh minced fish mixed with fishmeal, 30% of the body weight. Upon completion of the experiment, shrimp were aged 15 weeks and an average length of 32 mm, the growth ratio of 1.4 (final / initial) and the survival rate of about 60% [16].

b). filtering sieve with mesh diameter of 33μm. High concentration of suspended matter may inhibit the rate of the biofiltration of mussels; therefore a filtration step was added.

c). reservoir populated with mussels *Mytilus galloprovincialis* at a growth density of 50 kg/m^3.

d). reservoir populated with macrophyte algae *Enteromorpha sp*.

The growth of the organisms was conducted outdoor, in natural environmental conditions (temperature, light regime etc.). The system has a cascade functioning and the water flows gravitationally. Phytoplankton, zooplankton and bacterial load from the feed water and growth reservoirs were monitored during the entire growth period.

A chemical coagulation-flocculation step was added to the technological solution for the treatment of wastewater within the integrated aquaculture system. The chemical treatment of wastewater was conducted using a Jar test, which simulates the coagulation and flocculation processes on small scale and highlights the efficiency of the chemical treatment [17]. First the optimum operating conditions were established, whereupon the removal of pollutants from wastewater was achieved based on the experimental plan.

The substances used for wastewater treatment were: aluminium sulphate recovered from metallurgical slags using a Romanian patented method [13, 14], commercially available aluminium sulphate Kemira ALG (EN 878:2004, Kemwater Cristal Comp.) considered as benchmark and a flocculation agent Floerger FR 1023 (anionic polyelectrolyte).

The wastewater treatment process was conducted in the following conditions: pH = 6.5, coagulant dose = 200 mg/L aluminium sulphate 10%, flocculant dose = 3 mg/L flocculant 1‰, rapid mixing at 160 rpm for 2-3 min during the coagulation step and slow mixing at 40 rpm for 20 min during the flocculation step, gravitational sedimentation of the chemical sludge for 120 min.

At the end of the experimental procedure, the effluent was analysed and the degree of pollutant removal was evaluated. The main water quality indicators and the properties of the chemical sludge were determined based on standardised methods [18, 23].

Results and discussions

The treatment of wastewater resulting from aquaculture was conducted in an integrated system that works on the principle that the effluent resulting from shrimp culture may constitute the medium for the growth of other autochthonous marine cultures. As may be seen in Table 1, mussels have a good biofiltration capacity and they reduce the concentration of suspended matter and they uptake the biodegradable organic substances from water (expressed as BOD_5). The effluent resulting from this reservoir attained the quality required for mussel's growth as regards to the content of organic substances (expressed as COD-Mn) and a better quality as regards to the content of suspended matter. This step is followed by a step that employs macroalgae treatment that leads to the removal of nutrients present in feed water from the Black Sea together with the nutrients resulting from shrimp and mussel culture.

Table1

WATER QUALITY IN THE INTEGRATED AQUACULTURE SYSTEM FOR WASTEWATER TREATMENT THROUGH BIOLOGICAL ABSORPTION

Indicator de calitate Quality indicator	Unit	Sea water	Shrimps	Mussels	Macrophyte algae
pH	pH unit	8.1 - 8.2	8.0 - 8.2	8.0 - 8.2	8.2 - 8,4
COD-Mn	mg O_2/l	2.5 - 2.7	8.5 - 10.3	5.3 - 6.4	6.1 - 6.2
BOD_5	mg O_2/l	-	2.1 - 3.1	1.3 - 1.9	1.5 - 1.8
Suspended matter	mg/l	277 - 286	183 - 252	146 - 156	134 - 140
Total nitrogen	mg/l	0.8 - 3.1	1.2 - 4.5	0.8 - 3.1	0.4 - 1.4
Total phosphorus	mg/l	0.04 - 0.06	0.06 - 0.08	0.05 - 0.06	0.03 - 0.04

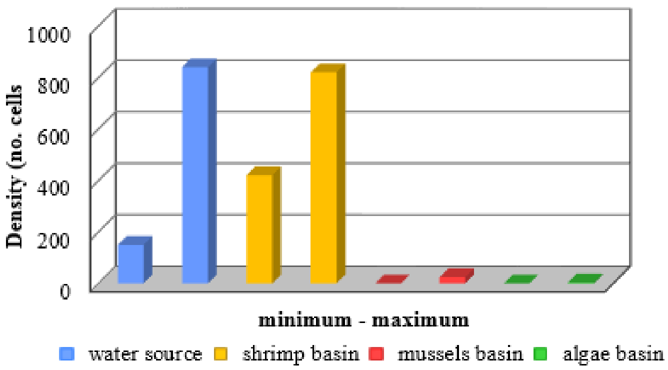
The phytoplankton showed no substantial growth, as its density was insignificant and did not alter the culture medium. Zooplankton was hardly present in the feed source (sea water) and in the experimental reservoirs, which facilitated the supply of inert food during the experiment (fig. 3).

The monitoring of the bacterial load of the effluents showed a significant decrease as the water passed through the reservoir filled with mussels, as follows: saprophytic heterotroph bacteria were reduced from 1000-18000 no/mL in feed water to 0-1000 no/mL in the mussel reservoir and total coliforms were reduced from 170-1090 no/L in sea water to 0-170 no/L in the mussels reservoir. The germs from the Vibrio genre were present in all samples at a level of 0-50 no/mL, without a significant reduction, probably due to small number present in feed water.

Overall, the integrated aquaculture system leads to removal efficiencies of approximately 40% for organic substances and suspended matter and 50-60% for nitrogen and phosphorus. The efficiencies attained in the micro-pilot treatment plant are within the acceptable range for the removal of pollutants through biological absorption on experimental marine cultures as reported in specialised literature.

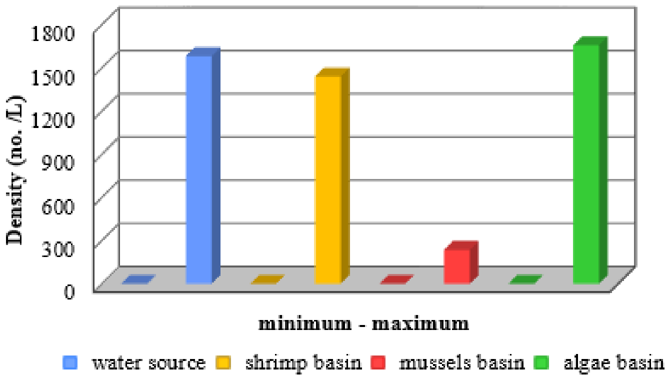
The effluent resulting from the integrated aquaculture system does not meet the quality requirements provided by the Romanian normative NTPA 001/2005 [24] as regards the content of suspended matter. Together with the fact that at industrial scale, the values may exceed the limits of other specific indicators, the technological solution of an integrated aquaculture treatment system was followed by a chemical coagulation-flocculation step. As coagulation agent, the aluminium sulphate recovered from metallurgical slags was tested by comparison with commercially available aluminium sulphate in order to determine its efficiency in wastewater treatment. The experimental results and observations on the treatment process are summarised in table 2.

The product based on recovered aluminium sulphate conducted to high efficiency for the removal of pollutants: 29% COD-Mn, 79% suspended matter, 76% total nitrogen and 99% total phosphorus. The efficiency of water treatment using commercially available coagulant is: 32% COD-Mn, 75% suspended matter, 82% total nitrogen and over 99% total phosphorus. The dynamics of the sludge sedimentation process was good in both cases, with a wastewater flow of 10 mL/L and 95% humidity. The results prove the remarkable coagulation properties of the aluminium sulphate recovered from metallurgical slags similar to the benchmark and promote its use in wastewater finishing process in order to achieve the criteria required at the discharge in the aquatic environment.



(a) phitoplankton

Fig. 3. The variation of total phytoplankton (a) and total zooplankton (b) in the marine aquaculture reservoirs



(b) zooplankton

Table2

THE QUALITY OF CHEMICALLY TREATED WATER

Quality indicator	Unit	Analysed values	
		Using commercial aluminium sulphate	Using recovered aluminium sulphate
COD-Mn	mg O_2/L	4.1 – 4.3	4.2 – 4.5
Suspended matter	mg/L	33 – 35	27 - 31
Total nitrogen	mg/L	0.08 – 0.24	0.14 – 0.31
Total phosphorus	mg/L	BDL (0.005)	BDL (0.005)
Observations:		small flocs, clear supernatant, chemically stable sludge	

Conclusions

Shrimp cultures generate wastewater with different pollutants so that this activity has to be conducted in parallel with the development of a technological solution for adequate treatment in order to protect the production and to avoid the degradation of water resources.

This experimental study focused initially on the possibility to employ the bioremediation procedures by means of an integrated system of autochthonous marine cultures shrimps-mussels-macrophyte algae for the removal of pollutants from wastewater.

The proposed technological solution combines the marine cultures and conventional chemical coagulation-flocculation wastewater treatment using aluminium sulphate recovered from metallurgical slags. Chemical treatment has proven to be a simple and easy to apply method that ensures the achievement of the quality requirements so that the final effluent may be recirculated as growth medium in the pond or discharged in the marine environment as regulated by the national legislation.

By conducting an overall evaluation for proving the feasibility of this treatment solution, it may be observed that it leads to an advanced removal of organic pollutants, suspended matter and nutrients from wastewater. Moreover, a chemical compound recovered from a hazardous waste (secondary aluminium slag) that poses serious problems regarding its landfilling on platforms is used.

An interest for pollution prevention and identification of recovery solutions for useful materials exists worldwide and the research depicted in this paper is part of the joint concerns aiming at an integrated approach between the economic development, environmental protection and the quality of life.

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