Preliminary Results on the Antifouling Potential of Copper Wire and Dyneema® Fiber Combined Twines for Aquaculture Net Cages

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Abstract: - Antifouling management for aquaculture cage nets has developed over the years to reduce the costs of cleaning the nets and minimize the damages caused to the nets by the encrustation of benthic organisms. There have been various approaches to this end such as using toxic paints (TBT-SPC, etc.) and nanomaterial coatings, mechanical cleaning using brushes, and constructing the net using copper alloys instead of nylon (or other) material, etc. We designed and constructed experimental fish farm nets substituting Dyneema® fibers with uncoated copper wire 0.15-0.2 mm in diameter by 5%, 10%, 20%, and 40% and deployed them in a commercial operating fish farm for almost 7 months. We examined their antifouling performance based on the percentage of mesh openness remaining by the end of the experimental period. The results showed that the antifouling performance increased with copper substitution level and peaked at a level of 29.79% and maximum mesh openness at 46.5%.

Key-Words: - antifouling, aquaculture cage nets, copper wire, Dyneema® fibers, marine aquaculture

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1 Introduction

It should be noted that typical nets are usually made from synthetic fibres like nylon, polyester, HDPE, etc. Nylon is mostly preferred due to its breaking load and durability, [1]. However, these nets are more expensive than standard synthetic materials and affected by UV radiation when exposed to the sun, [2]. A major problem in aquaculture is the fouling of the nets from benthic fauna and flora creating many problems to the health of the cultivated organisms and the net material characteristics, [3], [4].

Antifouling management for aquaculture cage nets was developed over the years to reduce the costs of cleaning the nets and minimize the damages caused to the nets by the encrustation of benthic organisms. At the same time, the benefits of the prevention of fouling are numerous including reduction of net drag, increased water circulation within the nets, and improved rearing performance for the cultivated organisms. The main method so far has been the painting of the nets with a paint that includes among others, a toxic metal – mainly copper and zinc - which prevents the establishment of a biofilm which is the basis for the development of bacteria colonies at first, and subsequently other organisms, [5], [6], [7], [8], [9]. These paints are the most preferred method of anti-fouling until today due to their results. However, it has been shown that they are harmful to the marine environment even in small concentrations, [6], [10], [11]. High copper concentrations have been observed in sediments near marine fish farms where antifouling paints are used such as in the cases of salmon, [12], and European seabass and Gilthead seabream farms, [6]. Previous studies in Greece have shown that zinc and copper can be measured in the tissues of European Seabass and Gilthead seabream fish but at levels much lower than those allowed for food for human consumption, [6]. Such findings led to the establishment of guidelines for the use of such paints all over the world and mainly the restriction of their use and reduction or even elimination of

TBT-holding compounds in such products, [13]. In addition, they are listed in the EU Directive for dangerous substances (67/548/EEC) [see, [10], for an analysis].

Another approach tested was the design and manufacture of fish nets made of pure copper alloy, [14], [15]. In Greece, for example, there are at least 2 companies that produce such nets: Hellenic Copper and Aluminum Industry SA and VIOHALCO SA (Greek Branch). Even though these nets showed very excellent anti-fouling properties, they are heavy and expensive, very difficult in handling and require large storage space.

Most recently, metal oxide nanoparticle paints have been developed, [16]. Most are using nanoparticles of Cu_2O in the paint, following the modification of the surface of the net twines with substances such as polyaniline, [17], [18], [19], [20]. These nanomaterial coatings have advantages as they show improved adhesiveness on the net twine surface and do not alter the basic technical characteristics of the net such as elasticity, mechanical strength, and plasticity. On the other hand, their main disadvantage is their instability and leaching, [17], [21].

Having considered the above approaches and their advantages and disadvantages, we have concluded that the main criteria, *inter alia*, for an anti-fouling approach should be low cost, preservation of the technical characteristics of the net material, easy handling, maintenance and storage and high performance in terms of environmental impact (leaching or otherwise). Therefore, 100% metal alloys and TBT-type paints based on Cu cannot be the modern solution. Our proposed solution is to design a completely new thread composed of made of Dyneema® synthetic fibers and copper cable. These new combined twines were used for the construction of fish farm nets and studied for 7 months for their performance. This paper aims to present our preliminary results on the performance of these nets in terms of anti-fouling properties in an actual environment of an operational coastal cage sea bass and seabream farm in Greece.

2 Problem Formulation

The objective of our study is to create an innovative new twine material that will exhibit equal or better characteristics than the ordinary standard nylon or nowadays, Dyneema fibre net, and which will be more environmentally friendly than the standard Cu painted nets, more stable than the recent nanoparticle net coatings when exposed in seawater and easier to handle in comparison to the metal alloy nets.

To achieve these objectives, we attempted to combine the existing antifouling approaches by designing a new aquaculture net based on the combination of pure non-varnished copper wires 0.1-0.2 mm in diameter (commonly used for transformer windings) with 0.1-0.2 mm in diameter Dyneema® fibres and creating a new metal-polyethylene (M-Pt) combined twine for braided knotless nets. The design and construction of this M-Pt twine were carried out with the cooperation of DIOPAS SA (a Greek company specialising in the manufacture of fisheries and aquaculture ropes and nets since special machinery is required to knit the fibres and wires into a single twine and then use this twine to create cage nets. The nets were then tested under normal fish farm conditions at the Sagiada AZA (allocated zone for aquaculture), North Greece.

3 Problem Solution

3.1 Methodology

Uncoated and unvarnished Cu wire with a diameter of 0.15-0.2 mm was purchased from China and used to create a fish net cage twine in combination with Dyneema fibres. A typical fish cage twine is 210d/24 (appx. 0.6 mm in diameter) even though the denier number of each net depends on the buyer's specifications regarding strength. We have designed a series of fish cage nets with a mesh of 16 mm (hexagonal) using M-Pt twine which contained 0% copper fibers (control; 100% from Dyneema®), 5% (5% copper-95% Dyneema®), 10% (10% copper-90% Dyneema®), 20% (20% copper-80% Dyneema®) and 40% (40% copper-60% Dyneema®). In addition, another 2 nets were constructed: the first was painted with the standard Cu_2O-based antifouling paint (Jotun Hellas Ltd; Cu_2O 12%), and the second with a modern nanoparticle-based non-Cu antifouling coating. A total of 7 nets were constructed. Each net was circular (cylindrical in 3D) and exhibited 12 m in diameter and 11 m in depth. They were used for fish production in an operating fish farm constantly immersed in the sea until all the meshes were closed by encrustations and fouling. The experimental period started on October 8, 2022, and ended on April 20, 2023 (a total of approximately 7 months). On a bimonthly basis, close-up photographs were taken from each net. A series of high-resolution photographs (Canon EOS cameras and lenses) were taken from each net (100x100 cm area in all cases).

The photo gallery then was fed into ImageJ image analysis software to create a database of areas and dimensions and thus, calculate the area of the mesh that is clogged by fouling organisms at each time point and calculate the overall fouling percentage. The time series of average covered area data enabled the comparison of the antifouling effectiveness of each approach based on the progress of the area covered by fouling organisms and the time required to completely cover the mesh since the first immersion of the net in the sea.

3.2 Results

The results are shown in Figure 1. Overall there are 2 main results obtained from this study: (a) first and as expected, the standard Cu/Zn paint-coated nets showed the best performance in terms of fouling prevention during the experimental period of almost 7 months; (b) all of the nets except the control, showed sufficient antifouling characteristics during the period in which, under normal circumstances, the fish farm staff changes the nets (for example 15 days for meshes up to 10 mm, and up to 1 month for larger meshes). Small-mesh nets clogged faster than large-mesh nets. Finally, the nets which included copper wire showed a gradual resistance to fouling in the experimental period of 7 months constantly immersed in seawater.

The antifouling performance measured as the percentage of unclogged surface started from 20.2% for a net with 5% substitution and reached a maximum of 43.7% for a net with 20% substitution. Nets with a 40% substitution showed a performance at 41.5% which is statistically similar to the value obtained for 20% substitution levels.

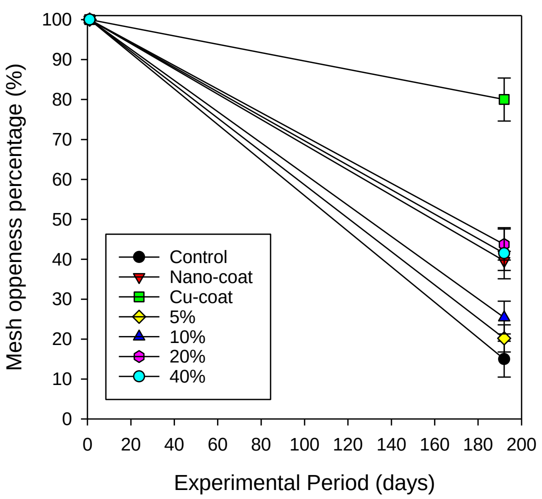

Fig. 1: Comparison of experimental net antifouling performance among the 7 different types of nets used in the experiments after 7 months of constant immersion in seawater.

In particular, the results showed 3 groups of experimental nets:

A low-performance group which includes the control, the 5%/95% net and the 10%/90% net (the first percentage indicates the copper wires and the second the Dyneema® in the twine). The worst performance was observed for the control (remaining openness 15.1±4.4%) while the other 2 nets showed 20.2±3.4% and 25.4±4.1% remaining openness respectively and an average of 20.2±5.15%,

A middle-performance group composed of the nanomaterial-coated net and the 20%/80% and 40%/60% nets with remaining openness values 39.6±2.4%, 43.7±3.9% and 41.5±6.4%, respectively and on average 41.6±2.05%

Finally, a group with the best performance with the net coated with the common TBT-based copper paint used in Greece. The remaining openness measured for this net reached 80.2±5.4%. ANOVA test showed a zero probability that the 3 average values of remaining openness are equal (P=0; a=0.05; df=8). In addition, LSD multiple range test (Fisher's least significant difference) showed 3 distinct groups of the data confirming the qualitative results of Figure 1.

The equation that describes the relationship between the copper (Cu%) substitution levels and the mesh openness (%) followed the quadratic model $y=a+bx+cx^2$, and was found:

$$\text{Oppeness}(\%) = 5.900 + 2.725\ (\text{Cu}\%) - 0.046\ (\text{Cu}\%)^2$$

$$r^2 = 0.980, \text{std. error} = \pm 3.99\%$$

The maximisation of the above equation using the linear SIMPLEX algorithm showed that the best results can be obtained with copper substitution of not more than 29.79% to achieve a maximum mesh openness of 46.5% after almost 7 months of constant immersion in the sea and at the same time use the minimum amount of copper wire in the twine to achieve this result (Figure 2).

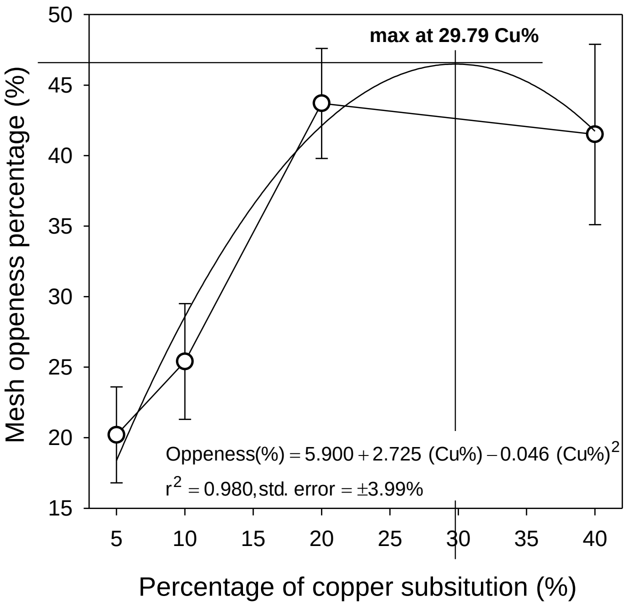

Fig. 2: Relationship between mesh openness (%) and copper substitution levels (%).

4 Conclusions

Biofouling is the accumulation of benthic organisms on a submerged surface affecting many different sectors of the economy including, *inter alia,* the marine aquaculture sector, [22]. The development of an organic substrate of micro- and macrobenthos on the immersed surfaces and especially the nets and ropes has negative effects on the structures by the decrease of water circulation, the increase of the forces imposed on the structures from the waves and currents, [23], [24], the increase of the structural weight and the increase of the probability of accidents such as breaking of the nets or ropes or create openings from which fish may escape, [25], all of which will have a very high financial cost to the farm, [22]. Some common antifouling methods used in marine aquaculture are: a. chemical antifouling i.e. the use of biocides (copper, zinc, and tributyltin) or coatings to prevent the growth of fouling organisms; b. biological antifouling i.e. the use of natural predators or competitors to control fouling organisms; c. mechanical antifouling i.e. the use of mechanical devices to physically remove fouling organisms (brushes, scrapers, and jet sprays) and d. use new materials i.e. the manufacture of nets and ropes using new materials that have inherent antifouling properties either due to their surface which prevents fouling organisms to settle or materials that have biocide characteristics such as nets made of copper alloy instead of nylon. The objective of this paper was to follow up on these approaches through the manufacture of a new twine for aquaculture nets made of Dyneema® fibers and copper wire to provide a new solution to the problem with good antifouling properties and at the same time a positive cost/benefit ratio and ease of handling. To fulfil this objective we studied the anti-fouling performance of fish farm cages made of a combination of Dyneema® fibers and uncoated copper wire and at percentages of Dyneema® substitution equal to 0%, 5%, 10%, 20% and 40%.

Starting with the design of the net material itself (Dyneema® fibers), several major advantages were gained: reduced weight, thinner fibers and therefore less surface for fouling, the requirement for lower coating amounts (even in the case of TBT-based anti-fouling paints) and resistance to UV radiation and abrasion. The partial addition of pure uncoated copper wire with the Dyneema® fibers, added strength to the overall net, reduced elasticity i.e. reduced deformation due to waves and currents, and increased strength to cuts from fish bites especially in the case of gilthead seabream, [26]. It is known that Dyneema® (an UHMWPE) as a material exhibits 4-5 times more tenacity, 6-8 times less elongation at break (%) 20% less specific weight, and zero moisture absorption in comparison to PA, PES, PP or PE net materials, [27]. In addition it is 15 times stronger than steel and 40% stronger than Kevlar, [27].

The results on remaining openness showed that there are 3 distinct groups of nets with minimum openness ranging between 15.1% for the control net and 80.2% for the TBT-based copper-coated net. These results indicate that such nets maintain a sufficient antifouling potential for a period much longer than the typical time between net changes within the frame of a coastal fish farm operation (normally not more than 1 month). From a cost/benefit point of view, a twine made of 70% Dyneema® and 30% of copper fiber shows optimum antifouling results and cost in terms of the amount of copper wire used (30%/70%) from the others, even though its performance is almost half of the TBT-based coated nets under the same experimental conditions.

An important observation is the performance of the nanomaterial-based Cu coating which was significantly similar to the performance of a 20-40% Cu/60-80% Dyneema® combined twine nets. Therefore, if there will be a full ban on the use of TBT-based coatings and paints in the future, the nanomaterial coatings are very good candidates for antifouling means depending on their procurement cost compared to Cu wire/Dyneema® fiber combinations. Making some summary calculations based on an average price of 8.3 € per kilo of copper wire 0.1 mm in diameter (from China) and the requirement of approximately 150 km of copper wire to cover a 30% replacement of synthetic fibers in the net twine (approximately 105 kg), gives an extra cost of 871.50 € per net (diameter 12 m, depth 11 m) when such net costs between 9000-13000 € currently in Greece i.e. the copper wire cost extra charge contribution is approximately 6.7-9.6% per net.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghost writing Policy)

-Alexis Conides carried out the net design and was responsible for the writing of this paper. He was also the coordinator of the research project which funded the work herein.
-Efthimia Cotou was responsible for the laboratory analyses of Cu toxicity and participated in the writing of the paper.
-Ilias Kallias, Panos Georgiou, and Ioannis Gialamas were responsible for all fieldwork, sample handling, and data collection.
-Dimitris Klaoudatos was responsible for the image analysis work and the proofing of the paper. He occasionally participated in the fieldwork

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Conflict of Interest

The authors have no conflict of interest to declare.