

Strategies for Material Protection in Aquatic Environment

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Introduction

Settlement of micro and macro and microorganisms over the submerged materials is called biofouling. If a material is immersed in aquatic environment it will experience an initial formation of biofilm. This is due to the adsorption of proteins, polysaccharides, macro and micro organic molecules over the surface. This complex nutrient rich surface attracts bacteria, fungi, diatoms and micro algae, and this layer is called biofilm [Avelelas et al 2017]. Organisms like barnacles, mussels, sponges, polychaetes, oysters etc attach over the biofilm and this results in degradation of materials or change the physico-chemical characteristics.

Aquaculture industry is coming up in India and provides cheapest protein food for the growing population and for export. The government and planners look upto aquaculture as one of the important items to meet the food security challenge of the growing population [FAO 2014]. The vast coastal line of about 8041 km, 3million hectares of reservoirs and 1.2 million brackish water resources can contribute enormously to improve the fish production through aquaculture. NFDB report of 2017-18 showed that 67% of the total fish production is coming from inland and culture sector. India's position in aquaculture production is 2nd in the world and it plays an important role in employment, labor, exports and economy. Biofouling is the major issue in the aquaculture industry and it eats away 25% of the project cost. Biofouling of the cages increases the weight of the cages, close the lumen, blocking the circulation of wastes, and its cleaning increases the turbidity and hence affect the growth of the fish in the cages. Biofouling in the cage nets will affect the growth of the fish thereby the economic loss.

Current strategies

In the shipping industry the biofouling is effectively prevented by using different coating technologies. Initially copper oxide based coating was used. Later effective chemicals like Tributyl tin oxide (TBTO) and their analogue compounds were used for protecting the ship hulls. TBTO was effective and popular among the ship builders and boat manufacturers. TBTO was banned world over due to its accumulation in the bottom crawling organisms and due to its toxic nature. Currently new generation antifouling paints are manufactured based on self-polishing, low surface energy coatings and other new generation organic molecules. For fishing boats and other submerged materials such as pillars, dam shutters mainly employed CuO based antifouling paints are mainly employed. World over aquaculture is growing and no effective coating methods were used to prevent biofouling in the cages. Antifouling strategies in aquaculture is very sensitive issue since it directly enters into the human body. Hence it requires detailed impact assessment studies. Current methods to combat biofouling in aquaculture system is manual or mechanical cleaning, which is very labour intensive and detrimental to the fish grown in cages. Popular antifouling strategies in aquaculture cages are treating low level copper based chemical coating and it leaching the aquatic environment in fixed amount will deter the foulers. Treatments usually

last only for one season of culture. The cost for treating the net is very high and the major problem is the disposal of the net after use. Also these types of nets are heavily coated with copper and the aquatic body will expose higher copper concentration. Different other methodologies suggested are biological control using grazers, silicon base coatings, acetic acid based coatings, cage net modification to prevent oysters and natural material principled antifouling coatings. Still these are under research stage and most of them are not suitable to aggressive marine environments. Introduction of nano technology open up the application of nano materials against biofouling organisms.

Nano technological solutions

The principle of nano technology is that those materials with known properties and functions will exhibit different behaviour and functions at nano sized state. Particles with dia 1 to 100 nm sized materials are considered as nano materials. The surface area of a unit weight materials are enormous compared to the normal molecules. The nano materials are extensively employed for solving the problems of drug delivery, sensors, catalysis, surface coating and antibacterial applications. The activity of the nano materials were very high and hence very low amounts of material be having high efficiency. Nano materials are extensively used as biocides and can be applied as antifouling agent.

Nano application in aquaculture cage nets

Nano copper oxide coated HDPE cage nets

Polyethylene fibres are extensively used to manufacture aquaculture cage nets. Polyethylene is nonpolar polymeric molecule and difficult to introduce the biocide over the molecule. Generally, biocide coatings were made over the cage nets using adhesives. The major disadvantages of biocides like copper oxide coating over the cage net is leaching to the aquatic environment and disposal of nets after use. The major advantage of nano materials as biocide very less quantity used, increased surface area of exposure and exhibit higher efficiency. Since polyethylene is nonpolar we have undertaken different methodology to make the polyethylene surface polar. The surface was coated with in situ synthesised polyaniline, a conducting polymer. Over this surface nano copper coated and their characteristics were studied. Uniform coating of polyaniline and copper was showed by Scanning electron micrograph and Atomic force micrographs. The formation of the biocide was verified by analysing FTIR spectra (Ashraf et al 2017). Polyaniline coated polyethylene showed IR absorption was shifted from 1362 to 1396 cm^{-1} indicating the attachment of polyaniline over PE. Quinonoid peak of $\text{NH}_4^+/\text{NH}^+$ in polyaniline was exhibited at 1047/1161 cm^{-1} and the same was shifted further to 1070 / 1179 cm^{-1} due to nano copper coating over polyaniline.

The field evaluation of the cage net showed the excellent biofouling resistance after 90 days exposure in the estuarine environment. The experiment was repeated by constructing a cage with treated and control panels and exposed in the Vizhinjam coast for 7 months (fig 1). The fishes grown in the cages and controlled environments were compared and exhibited significant difference in growth was shown.

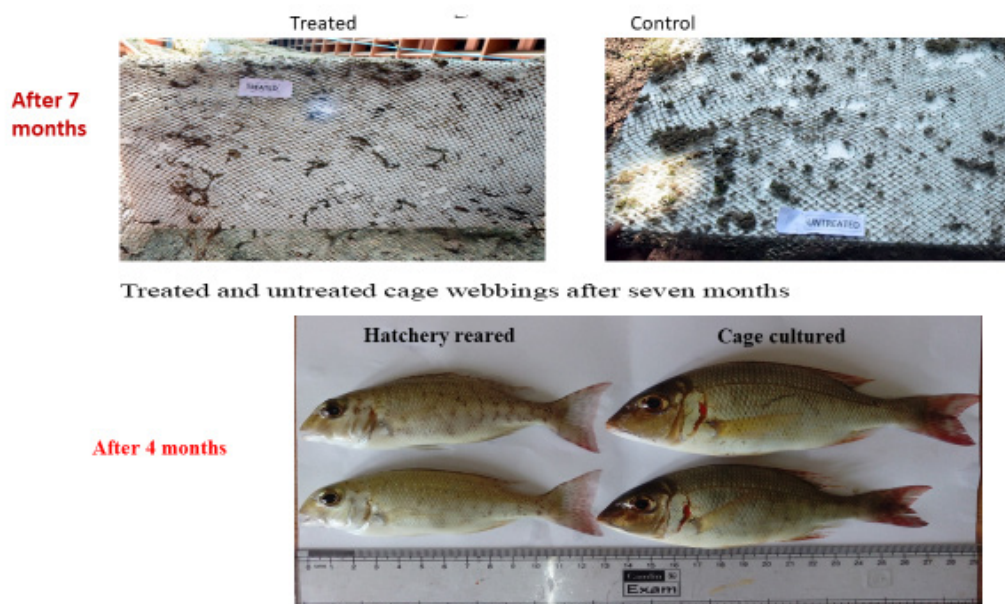


Fig. 1. Control and treated net after 7 months exposure in the marine environments

Different tests to verify the biofouling resistance are mentioned in detail by Ekbalad et al 2008. Deterrence of biofouling organisms to the treated surface was tested by cyprid assays. The treated surfaces were exposed to the testing organisms in natural or artificial seawater at controlled environments. Callow et al 1997 described assays using microorganisms like *Ulva* zoospore over the treated surface. The exposed surface in controlled environment were evaluated based on the attachment of spores. Callow et al (2002) and Schultz et al (2000) described about the determination of adhesive strength using a calibrated flow channel. Diatom assays were generally carried out using *Navicula perminuta* (Pettitt et al 2004) by suspending the treated surface in artificial seawater containing chlorophyll a $0.30 \mu\text{g ml}^{-1}$. After 2 h exposure the surface was evaluated for the adherence and deterrence of organisms. Antibacterial property of the biocide treated surfaces were evaluated using two marine bacteria viz *Cobetia marina* and *Marinobacter hydrocarbonoclasticus* (Akesso et al 2009; Ista, et al 1996). The former bacteria are considered first settled microbes over marine exposed surfaces. The measurement was carried as per the protocols described by Akesso et al 2009.

Nano copper oxide incorporated hydrogel

Hydrogels are considered eco-friendly and hydrophilic in nature. Hydrophilic nature of polyethylene glycol hydrogel will deter the adsorption of proteins and this will reduce the attachment of microorganism and biofilm formation. Thereby reduced accumulation of macro foulers. The major disadvantage of hydrogel is that it will degrade after sometime and susceptible for biofoulers attack. We tried to synthesise with more efficient hydrogel by incorporating nano biocide (Ashraf PM 2019). The problem of non-polar nature of polyethylene was overcome by synthesising nano copper oxide incorporated hydrogel in situ by microwave method. The hydrogels were strongly bonded over the cage net which was evidenced by SEM, FTIR and AFM studies. Field evaluation was carried out to understand the biofouling resistance of the coating

and showed 53% more efficient than control. The mechanism was explained due to the formation of semi hydrophilic in nature, defect free, compact structure and the nano copper oxide acted as a point source to deter the attack of micro and macro organisms.

Mixed charged Zwitterionic polymeric hydrogel

Polyethylene glycol hydrogel is having less surface energy difference with surrounding water and this will increase the probability of adsorption of foulers over the surface. A new class of hydrogels considered are environmentally safe, zwitterionic hydrogel polymers, which is having equal number of cations and anions and super hydrophilic. It was generally synthesised using S, carboxy or phosphor betaines. Mohan and Ashraf (2019) synthesised a nano silicon oxide incorporated mixed charged polymeric hydrogel through microwave method over aquaculture cage nets. Mohan and Ashraf [25] synthesised a nano-sized SiO₂-incorporated poly (N-isopropylacrylamide-co- 2-(methacryloyloxy) ethyl]- Trimethylammonium / 3-sulfopropyl methacrylate) mixed-charged zwitterionic polymeric hydrogel in situ over a polyethylene aquaculture cage netting material treated with polyaniline. The SEM, AFM and FTIR studies confirmed the formation of hydrogel. Its efficiency was tested by exposing in the estuarine environments and showed the biofouling resistance at two months.

Conclusion

Aquaculture industry is facing severe biofouling problem and its management incurs huge expenditure. Current technologies are sustainable due to its low impact on environment. Nano technology offers excellent solution to combat biofouling and the technology needs further refining. The advantage nano materials are low in quantities for application and increased efficiency.

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