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Review or Mini-review

Antifouling processes and toxicity effects of antifouling paints on marine environment. A review

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ABSTRACT

The production infrastructure in aquaculture invariably is a complex assortment of submerged components with cages, nets, floats and ropes. Cages are generally made from polyamide or high density polyethylene (PEHD). All of these structures serve as surfaces for biofouling. However, cage nets and supporting infrastructure offer fouling organisms thousands of square meters of multifilament netting. That's why, before immersing them in seawater, they should be coated with an antifouling agent. It helps to prevent net occlusion and to increase its lifespan. Biofouling in marine aquaculture is a specific problem and has three main negative effects. It causes net occlusion and so restricts water and oxygen exchange. Besides, the low dissolved oxygen levels from poor water exchange increases the stress levels of fish, lowers immunity and increases vulnerability to disease. Also, the extra weight imposed by fouling causes cage deformation and structural fatigue. The maintenance and loss of equipment cause the increase of production costs for the industry. Biocides are chemical substances that can prohibit or kill microorganisms responsible for biofouling. The expansion of the aquaculture industry requires the use of more drugs, disinfectants and antifoulant compounds (biocides) to eliminate the microorganisms in the aquaculture facilities. Unfortunately, the use of biocides in the aquatic environment has proved to be harmful as it has toxic effects on the marine environment. The most commonly used biocides in antifouling paints are Tributyltin (TBT), Chlorothalonil, Dichlofluanid, Sea-Nine 211, Diuron, Irgarol 1051 and Zinc Pyrithione. Restrictions were imposed on the use of TBT, that's why organic booster biocides were recently introduced. The replacement products are generally based on copper metal oxides and organic biocides. This paper provides an overview of the effects of antifouling biocides on aquatic organisms. It will focus on the eight booster biocides in common use, despite little data are available for some of them. Toxicity values and effects of these antifoulants will also be mentioned for different species of fish, crustaceans, invertebrates and algae.

1. Introduction

Marine biological fouling, usually termed marine biofouling, can be defined as the accumulation of microorganisms, plants, and aquatic animals on artificial surfaces immersed in sea water (Yebra et al., 2004). In the case of ships, biofouling is an unwanted phenomenon which may cause several problems such as increased fuel consumption due to water resistance, as well as increase in weight; in aquaculture, reduction of water exchange through net mesh, occurs (Champ, 2000; Cronin et al., 1999; Eckman et al., 2001; Phillippi et al., 2001).

To prevent the attachment of fouling organisms, antifouling paints have been developed and used (Koutsaftis and Aoyama, 2007). They contain chemical compounds (biocides), which are released from the paint matrix, to provide a constant threshold concentration of the biocide in water, therefore inhibiting the development of fouling communities (Boxall et al., 2000; Terlizzi et al., 2001). Tributyltin self-polishing copolymer paints (TBT-SPC paints), such as tributyltin oxide (TBTO: $C_{24}H_{54}OSn_2$) and tributyltin fluoride (TBTF: $C_{12}H_{27}SnF$) are the most successful compounds against biofouling. They belong to organotin biocides which contain at least one tin-carbon bond (Ingham et al., 1960; Omae, 2003). Unfortunately, TBT-SPC systems adversely affect the environment (Yebra et al., 2004). Due to its high toxicity to molluscs, fish reproduction and fish behavior at very low concentrations (Alzieu et al., 1980; Antizar-Ladislao, 2008; Bao et al., 2011; Dimitriou et al., 2003; Fent, 1991; Hongxia et al., 1998), the use of tributyltin (TBT) has been restricted since the early 1990s and marine paint companies have been developed alternatives to antifouling to substitute TBT (Alzieu, 2000).

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Currently, new alternatives to antifouling paints are based on copper compounds such as cuprous oxide (Cu_2O) and copper thiocyanate (CuSCN), with supplementation of booster biocides to control Cu resistant fouling organisms (Guardiola et al., 2012; Voulvoulis, 2006). Commercial boosters such as Irgarol 1051, Sea-Nine 211, Diuron, Chlorothalonil, and other metallic compounds like zinc pyrithione (ZnPT) and copper pyrithione (CuPT) are the most commonly used booster biocides (Konstantinou and Albanis, 2004). These biocides are intended to be environmentally less harmful compared to the organotin biocides. However, the problem of toxicity on several marine species remains (Bejarano et al., 2005; Braithwaite and Fletcher, 2005; Jacobson and Willingham, 2000; Ma et al., 2002; Mochida et al., 2010; Sherrard et al., 2003). In addition, the environmental effects such as toxicity and persistence of these biocides are not understood, as they have only been recently introduced (Maraldo and Dahllöf, 2004; Terlizzi et al., 2001).

This review is a comparative study of acute toxicities among TBT, copper and the six commonly used booster biocides (Chlorothalonil, Sea-Nine 211, Irgarol 1051, Zinc Pyrithione, Dichlofluanid and Diuron) on marine species essentially invertebrate, algae, fish and crustacean. Toxicity will be evaluated with numerous concentrations such as LC_{50}, LD_{50}, EC_{50}, LOEC and NOEC. All these toxicological dose descriptors will be detailed in the following sections.

2. Marine biofouling problems

When a pristine object is placed in seawater, it is not long before fouling with vegetable and animal organisms becomes a significant problem. In the case of ships, the adverse effects caused by this biological settlement are well known. Firstly, it produces high frictional resistance, combined with increased of weight, which reduces speed and maneuverability, as well as increasing fuel consumption by up to 40% (Champ, 2000).

In the case of aquaculture field, biofouling causes two problems: firstly, fouling communities constrict net openings, and left unchecked, this leads to a significant increase in the weight of netting (Phillippi et al., 2001). In the other hand, it reduces the flow through fouled net mesh or tray perforations so restricting nutrient exchange, removal of waste products and oxygen supply (Cronin et al., 1999; Eckman et al., 2001). All of these factors can affect the health of fish stock and also impact the local environment (Folke et al., 1997).

3. Marine biofouling details

The colonization of a substratum in the aquatic realm has been viewed as proceeding through a four- step process (Maki and Mitchell, 2003; Wahl, 1997):

- Primary film formation
- Biofilm formation
- Diatom and protozoan colonization
- Settlement of invertebrate larvae and algal spores

This scenario can be modeled as shown in Fig. 1:

3.1. Primary film formation

Biofouling usually begin by an abiotic surface conditioning, i.e. the formation of a non −living chemical/biochemical film (Characklis, 1981; Marshall et al., 1971; Mitchell and Kirchman, 1984). This process starts with a spontaneous and rapid adsorption of organic molecules already present in the water, such as proteins, polysaccharides, nucleic acids, humic acids and possibly inorganic compounds onto the substrate. It will be achieved within minutes of exposure of surfaces to seawater (Abarzua and Jakubowski, 1995; Callow and Fletcher, 1994).

Through the modification of the physicochemical properties of the surface, this film promotes bacterial adhesion on it by constituting a source of nutrients and specific interaction between bacteria and organic molecules (Dunne, 2002; Walker and Marsh, 2004).

3.2. Biofilm formation

The figure below (Fig. 2) presents the different growth times of the biofilm using the SEM (Fernández et al., 2008):

The formation of the biofilm is a process taking place in several stages as shown in Fig. 3 (Brian-Jaisson, 2014):

- The first step is the transport of bacteria to the surface. Bacteria are transported to the conditioned area due to many factors including gravity, Brownian movement, diffusion, dynamics of fluids, electrostatic interactions and cell mobility (Fig. 3-a) (Bos et al., 1999; Carpentier and Cerf, 1993; Dunne, 2002; Harbron and Kent, 1988; Palmer et al., 2007; Wahl, 1989).
- The second step is termed reversible adhesion. When the bacteria approach a conditioned surface, weak interactions occur (Van Der Waals attraction, electrostatic and hydrophobic interactions) between the bacteria and the support. These interactions lead to partial immobilization of the bacteria on the surface, and it can be detached simply by rinsing or by shear conditions (Fig. 3-b) (Dunne, 2002; Harbron and Kent, 1988).
- The third step is called irreversible adhesion. After the bacteria initially interact with the primary film, permanently attachment occurs in minutes through their production of extracellular polymeric substances (EPS). The existence of these adhesive exudates and the roughness of irregular microbial colonies help to trap more particles and organisms (Fig. 3-c) (Wahl, 1989; Yebra et al., 2004).
- The fourth step follows in days, and is termed maturation and dispersion. This involves the settlement and the growth of larger marine invertebrates together with the growth of macroalgae (seaweeds) (Yebra et al., 2004). Thanks to nutrients present in the conditioned film and those present in the surrounding fluid, the biofilm is developed by involving several mechanisms such as binary division, mobility on the surface and co-adhesion (Fig. 3-d) (Hall-Stoodley and Stoodley, 2002; Kumar and Anand, 1998). At an advanced stage of maturation of the biofilm, individual cells or parts of the biofilm can be separated from the heterogeneous mass due to the decrease of nutrients, to the occurrence of anaerobic conditions, or under the effect of shear forces or other environmental stress. This step is illustrated in Fig. 3-e (Dunne, 2002; Walker and Marsh, 2004).

3.3. Diatom and protozoan colonization

The settlement of unicellular eukaryote typically begins within days to weeks after immersion of new substratum. These cells are subjected to the same physical forces as bacteria. But due to larger cell size and higher motility, their contribution to the adsorption process relative to behavioral aspects should be smaller. After contacting the substratum, the cells attach with polysaccharide or protein glues to biofilm, conditioning film or substratum surface (Wahl, 1997).

3.4. Settlement of invertebrate larvae and algal spores

This is the longest and final step in biofouling process. It needs several days to weeks after biochemical conditioning. It involves the settlement and the growth of larger marine invertebrates together with the growth of macroalgae (Fig. 4). Additionally to the roughness of the irregular microbial colonies, the existence of adhesive exudates (EPS), such as polysaccharides, proteins, lipids and nucleic acids helps to trap more particles and organisms. These are likely to include algal spores, marine fungi and protozoa (Yebra et al., 2004).