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Environmental risk assessment on capsaicin used as active substance for antifouling system on ships

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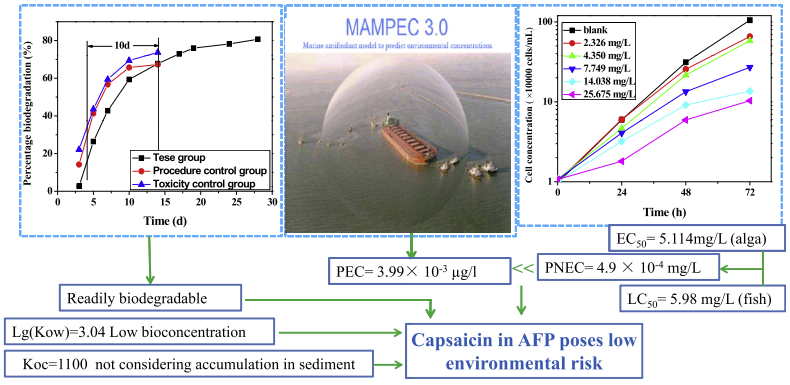
HIGHLIGHTS

- The biodegradation experiments show capsaicin was readily degradable.
- The fish toxicity tests showed LC_{50} for *Brachydanio rerio* was 5.98 mg L^{-1}.
- The alga growth inhibition tests show EC_{50} for *Selenastrum capricornutum* was 114 mg L^{-1}.
- The calculated PEC is much less than the calculated PNEC for capsaicin.
- Capsaicin used as active substance in paints poses low risk to marine environment.

GRAPHICAL ABSTRACT



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ABSTRACT

Biodegradation experiments were carried out with capsaicin to evaluate its degradability. The results show that capsaicin was readily biodegradable under aerobic conditions. The values of K_{ow} and the calculated bioconcentration factor indicate that capsaicin have a low potential for bioconcentration. The fish acute toxicity tests conducted with *Brachydanio rerio* show LC_{50} for capsaicin was 5.98 mg L^{-1}. The tests of alga growth inhibition conducted with *Selenastrum capricornutum* suggest EC_{50} for capsaicin was 114 mg L^{-1}. The calculated PNEC (Predicted No Effect Concentration) was 4.9×10^{-4} mg L^{-1}. The average PEC (Predicted Environmental Concentration) for OECD-EU commercial harbor and marina were 3.99×10^{-6} and 2.49×10^{-5} mg L^{-1}, respectively. These indicate that the PEC was much less than the PNEC for capsaicin. The low K_p value of capsaicin suggests the data about the risk of capsaicin to sediment organisms can be waived. According to the results from the analysis of the degradation, bioaccumulation, toxicity and accumulation in sediment, it can be concluded that capsaicin used as active substance for antifouling system on ships poses relatively low risk to marine environment.

1. Introduction

The attachment of organisms such as barnacles and algae on the submerged parts of a ship's hull increases the propulsive resistance of the hull to passage through water. In order to prevent such circumstance, antifouling paints are applied onto the hull of the ship. Most of antifouling paints contain one or several active substances, which are the key materials to prevent the attachment of organisms. As active substances have general or specific action such as mortality and growth inhabitation on unwanted organisms, their harmful effects on marine organisms and human health have been of global concern. Dichlorodiphenyltrichloroethane (DDT) has ever been used as active substance in antifouling paints for ships. As it

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poses severe environmental and human health risk, the paint industry voluntarily withdrew DDT from use during the early 1960s (Thomas and Brooks, 2010). Since the 1960s, tributyltin (TBT), a toxic metal-base compound, has been widely used as active substance in antifouling paints. TBT is also harmful to marine organisms, and can accumulate in sediment in high concentration, facilitating toxic biomagnification in bethnic communities. For these reasons, the International Convention on the Control of Harmful Anti-fouling Systems on Ships prohibits the use of tributyltin (TBT) antifouling coatings on ships (Thomas et al., 2000; Diego et al., 2004; Xu et al., 2005). Even the approved biocides, such as chlorothalonil and Irgarol 1051, pose the danger of causing a nonselective toxicity (Scarlett et al., 1999; Yonehara, 2000; Thomas et al., 2001; Voulvoulis et al., 2002).

In the recent years, the researchers have never stopped investigating suitable nontoxic or less toxic alternatives. One of the alternatives is to generate antifouling paint with the incorporation of less toxic antifoulant compound, such as natural product. Capsaicin is one of the most promising natural products used for antifouling system. It was also reported in some references that capsaicin possessed much more attractive properties than the current toxic antifoulants (Xu et al., 2005; Angarano et al., 2007; Qian et al., 2009). As a good active substance for antifouling paint should be not only technically and economically viable but also environmentally friendly, it is significant to study the environmental risk on the use of capsaicin in antifouling paint on ships before it is placed into market. To evaluate environmental risk in marine environment, the degradation, bioaccumulation, acceptable toxicity risk assessment and accumulation in sediments should be considered according to the principle of environmental risk assessment. In the recent years, some of these considerations were taken into account for capsaicin. LaHann et al. (1989) reported that the $\log K_{ow}$ (the logarithm of the octanol–water partition coefficient) and K_{oc} (the soil sorption coefficient) for capsaicin were 3.04 and 1100, respectively. Cope et al. (1997) concluded that the EC_{50} for capsaicin obtained from the toxicity tests with zebra mussels was 4.9 mg L^{-1}. However, other essential properties about capsaicin such as the biodegradation, the fish acute toxicity and alga growth inhibition toxicity were rarely studied. The knowledge is so limited that it is difficult to systematically evaluate the environmental risk of capsaicin used as active substance for antifouling system on ships.

In this study, the degradation experiments, the tests of fish acute toxicity and alga growth inhibition were conducted with capsaicin to obtain its properties of persistence and toxicity. Also the bioaccumulation and accumulation in sediments for capsaicin were studied. According to the results from these studies, the risk assessment of capsaicin in marine environment was investigated to evaluate its use as active substance for antifouling system on ships.

2. Materials and methods

2.1. Chemicals

Capsaicin (8-methyl-N-vanillyl-6-nonenamide) with high purity of 95% was purchased from Beijing Jiuzhou Longling High-tech Co., Ltd., (China). Capsaicin has limited water solubility (saturated concentration ~60 mg L^{-1}). To prepare the stock solution for the experiments, 0.700 g capsaicin was firstly dissolved in 350 mL chlorine-free distilled water and then treated by ultrasound for 10 min. The resultant suspension was diluted to 7000 mL, stirred for 24 h and filtered with 0.45 μm membrane. After filtration, the stock solution was obtained. The theoretical concentration of capsaicin was 100 mg L^{-1}. Before use, the stock solution was diluted to the desired concentration with chlorine-free distilled water according to the demand of the experiments.

HPLC system (Agilent 1200, USA) was used to determine the actual concentration of capsaicin in the solution for the experiments. It was equipped with a diode array detector and C18 column (Agilent XDB, USA, 4.6 × 150 mm, 5 μm). The mobile phase was the mixture of phosphoric acid solution (the concentration was 0.5%) and methanol (V/V = 35:65). Its flow rate was 1.0 mL min^{-1}. The detection wavelength was 230 nm. During the analysis the column temperature was controlled at 30 °C. Analyzed the test standard solution with the concentration of 0.2142 mg L^{-1}, signal to noise ratio (S/N) was 5.39921. The LOD (limit of detection) was 0.1190 mg L^{-1} calculated by three times of signal to noise ratio and the LOQ (limit of quantification) was 0.3967 mg L^{-1} calculated by ten times of signal to noise ratio. A calibration curve was constructed which was $A = 9.07622 \times C - 1.29659$ (r = 0.99996).

In the biodegradation experiments, mineral salts medium was prepared according to the OECD guidelines for the testing of chemicals (OECD 301B, 1992). The medium used in the tests of alga growth inhibition was also prepared according to the OECD standard procedure (OECD 201, 2006).

For the calculation of the leaching rate of capsaicin from antifouling paint, two types of antifouling paints were used. One was labeled as #1, which was purchased from Xiamen Sunrui Ship Coating Co., Ltd., (China). The other was labeled as #2, which was purchased from Beijing Jiuzhou Longling High-tech Co., Ltd., (China). Their main properties are shown in Table 1.

2.2. Test organism

The tests of fish acute toxicity were conducted with Zebra fish (*Brachydanio rerio*). The length and weight of fish were 20.86–23.99 mm and 0.103–0.173 g, respectively. Before the tests, the fish were acclimated for 25 d under the same conditions as the tests. Daily feed was stopped 24 h prior to the tests. The mortality of 7 d was 0.32%.

The tests of alga growth inhibition were carried out with green alga (*Selenastrum capricornutum*), which was bought from the Chinese Academy of Science. Algal cells were precultured for 3 d under the same conditions as the tests.

2.3. Biodegradation experiments

The biodegradation experiments (CO_2 Evolution Test) were carried out according to the OECD standard procedure (OECD 301B, 1992). Six 3-L flasks were used for the experiments. Two flasks containing capsaicin (for capsaicin TOC = 12.1 mg L^{-1}) were designated as the test group. One flask containing sodium benzoate (for sodium benzoate TOC = 12.2 mg L^{-1}) was designated as the procedure control group. One flask containing both capsaicin (for capsaicin TOC = 12.1 mg L^{-1}) and sodium benzoate (for sodium benzoate TOC = 12.2 mg L^{-1}) was attribute to the toxicity control group. The left two flasks were set as blank group. With the dilution of the mineral salts medium, the final volume of the solution in every flask reached 2 L. The concentration of inoculums in every flask was 30 mg L^{-1}.

Table 1
Data for calculating the leaching rate of capsaicin in two Chinese antifouling paints.

Samples	Contents of capsaicin (%)	Solids constituent (%)	Specific gravity (g cm^{-3})	Dry film thickness (μm)	Lifetime (months)
#1	0.5	75	1.8	60	12
#2	0.3	60	1.6	70	12