Biocide Leaching Rates and Electrochemical Methods for Antifouling Marine Paints

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Subsurface Biosphere Initiative
Research and education focused on life below Earth's surface.

Introduction:

Marine vessels such as ships and wave energy converters lose functionality and efficiency due to biofouling in marine environments. Marine biofouling is the accumulation of biomass such as bacteria, algae, and barnacles on a submerged surface. This growth adds mass, increases drag, and can cause seizure in moving parts. The solution to this problem has been the development of antifouling paints which incorporate biocides. An experimental antifouling method currently under scrutiny is using conductive marine paints and surfaces.
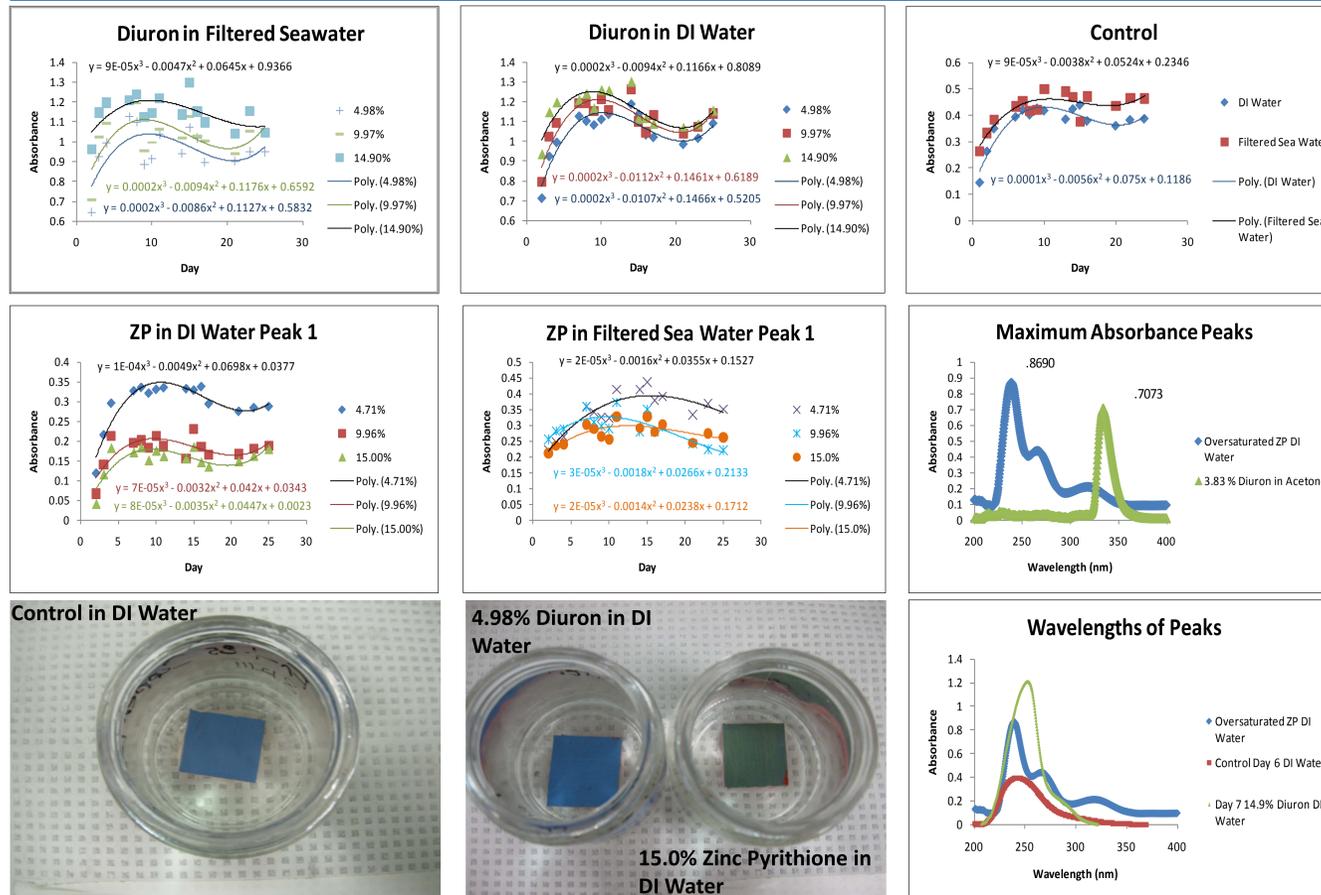
Biocides are chemical agents added to paints that deter and or kill organisms so they do not attach to marine surfaces[1]. Using Biocides is the most common method for prevention of biofouling; however, the total environmental impact as well as bioaccumulation problems remains to be determined[1]. Modeling the release rates of the most common biocides is a vital key to fulfilling this information, as well as making predictions for potential new biocides.

Using electrochemical methods for the prevention of biofouling is relatively new. It was proven that applying a voltage to a graphite and carbon black urethane resin surface decreased the amount of biomass that accumulated[3]. Electrochemical methods for antifouling could be a cleaner and safer method for the environment compared to biocide paints. Finding different conductive materials as well as determining the actual mechanism that prevents fouling is key to developing new and improved methods for surface antifouling.
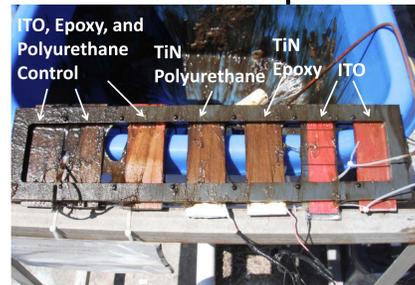
Methods/Experiments:

Biocide Leaching Rates:
Biocides diuron and zinc pyrithione were mixed with a copper base (45 weight percent) non-self-polishing paint in 5%, 10% , and 15% wet weight percentages. These paints were then applied to 1" by 1" fiberglass plates. The samples were each placed in 100mL of water, with one set in DI water and the other in filtered sea water. Using UV/Vis spectrometry the concentrations of diuron and zinc pyrithione in the water were measured.
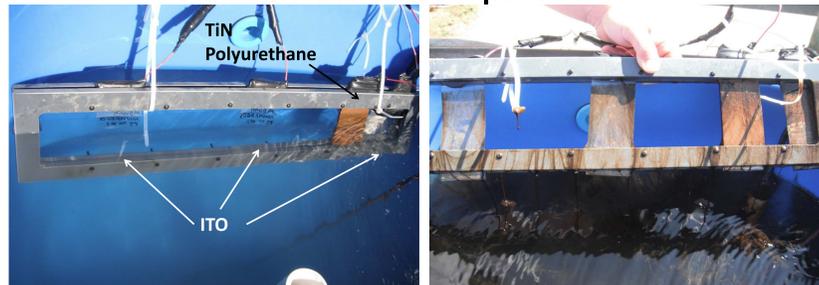
Results/Analysis

Diuron in Filtered Seawater

Diuron in DI Water

Control

ZP in DI Water Peak 1

ZP in Filtered Sea Water Peak 1

Maximum Absorbance Peaks

Control in DI Water

4.98% Diuron in DI Water

15.0% Zinc Pyrithione in DI Water

Wavelengths of Peaks

HMSC Water Tank Experiment 1

ITO, Epoxy, and Polyurethane Control   TiN Polyurethane   TiN Epoxy   ITO

HMSC Water Tank Experiment 2

TiN Polyurethane

ITO

Methods/Experiments Continued:

Electrochemical Methods:
Titanium nitride was mixed with epoxy and polyurethane to make paint coatings. These coatings were applied to 2" by 6" fiberglass plates. Indium tin oxide coated polyethylene terephthalate was cut into 2" by 6" pieces and applied to fiberglass glass plates as well. These samples were put into a frame that was submerged in ocean water at the Hatfield Marine Science Center. A potentiostatic circuit held the potential of each plate constant.

Future Work:

Biocide Release:
- Modeling biocide leaching rate with a flow rate. This will help determine how self polishing and non self-polishing rates differentiate
- Modeling rate with respect to the number of layers or thickness of paint.
- Finding reaction consequences of zinc pyrithione and cuprous oxide in paints.

Electrochemical Methods:
- Determine the relationship of current density and sheet resistance and their antifouling abilities.
- Determine if electrochemical methods can be used to 'clean' surfaces that are already fouled.
- Continue proof of concept experiments

Acknowledgements:

References:

1) Konstantinou, I.K., and T.A. Albanis. "Worldwide occurrence and effects of antifouling paint booster biocides in the aquatic environment: a review". Environmental International 30 (2004): 235-248. Science Direct. Web. 11 July 2011.
2) Sakkas, V.A., A.D. Dimou, V.I. Boti, and T.A. Albanis. "Photodegradation study of the antifouling agent diuron in aqueous media under simulated solar irradiation Proceedings of the 9th International Conference on Environmental Science and Technology. Rhodes island, Greece. 1-3 Sept. 2005.
3) T. Matsunaga, T. Nakayama, H. Wake, M. Takahashi, M. Okochi, and N. Nakamura, "Prevention of marine biofouling using a conductive paint electrode," Biotechnology and Bioengineering, vol. 59, 1998, pp. 374-378.

Conclusion:

Zinc pyrithione's largest wavelength absorbance peak is approximately the same wavelength of cuprous oxide. This means that their absorbance spectrum overlaps in the samples (since the samples are made of a copper base paint and either zinc pyrithione or diuron). There is more cuprous oxide in the paint (45 weight %) than zinc pyrithione. This means that zinc pyrithione's absorbance spectrum and the cuprous oxide's spectrum are added together in the absorption spectrum. A different method and or a way to distinguish zinc pyrithione's peaks and copper's peak is needed. There was a color change on the zinc pyrithione's samples that increased with intensity as weight percentage of zinc pyrithione increased. This indicates that a reaction is taking place most probably between the cuprous oxide and zinc pyrithione. The diuron samples show decreasing concentration at later times, likely due to degradation[2]. The diuron and zinc pyrithione both appear to have either reached saturation or an equilibrium where release rates are equal to reaction consumption rates.

On both HMSC water tank experiments it appears that the method works as there is less biomass on the samples compared to the controls; however, the tests remain inconclusive since the microcontrollers seem unable to keep enough current running through the samples. Further testing on the capacity of the microcontrollers is needed before results can be conclusive.