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# Life in the *slip* lane: The effect of molecular level friction on algal adhesion

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## Background

The physical properties of a surface have a profound effect on the settlement and adhesion of fouling organisms. Concepts of fracture mechanics have been employed to describe and model release of hard foulers, e.g. barnacles, from fouling-release coatings. The adhesion strength of such organisms has been shown to be influenced by a range of physical factors including:

- Coating modulus.
- Coating thickness.
- Critical surface tension / surface energy.
- Friction and slippage.

For soft-foulers, e.g. algae, foul-release mechanics are less well defined, as the organisms often violate the conditions required by models by virtue of their small size and low modulus. This poster demonstrates the influence of surface friction on the adhesion strength of two species of fouling alga, *Ulva linza* and *Navicula perminuta*.

**This Study:** As the attributes of self-assembled monolayers (SAMs) can be closely controlled they provide useful model systems to investigate the influence of various surface properties on adhesive processes. In this study the adhesion of *Ulva* spores and *Navicula* cells to methyl-terminated alkanethiol SAMs of varying chain length and known frictional properties, was investigated. Varying the chain length of the alkanethiol from octyl ( $C_8$ ) to octadecyl ( $C_{18}$ ) results in a three-fold change in the frictional properties of the surface, whilst minimising the change in surface energy.

*Ulva* is a major fouling macro-alga that colonises new surfaces through motile spores. Spores adhere to newly colonised surfaces by the secretion of a preformed, fast curing, glycoprotein-rich adhesive that surrounds the spore and anchors it by wetting the surface<sup>1</sup> (Figure 1).

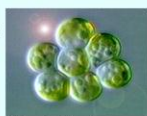


Figure 1: *Ulva linza* spores

*Navicula perminuta* (Figure 2) is a diatom (Bacillariophyceae), a member of a family of siliceous microalgae that are a major component of fouling microbial slimes. Diatoms colonise new surfaces by gravitational settlement and adhere through production of a, mainly, polysaccharide extracellular polymeric substance (EPS).

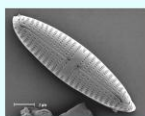
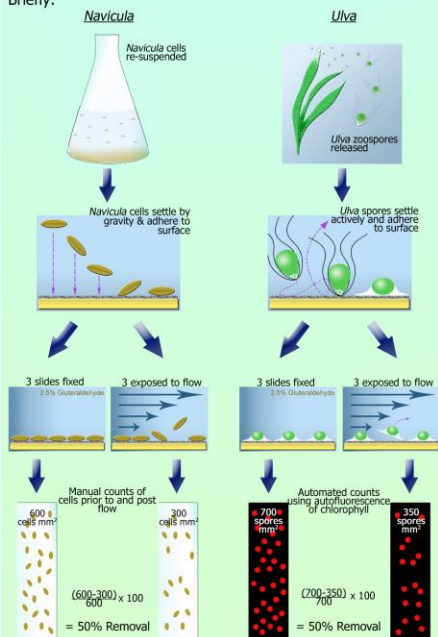


Figure 2: *Navicula perminuta*

## Methods

Methyl-terminated alkanethiol self-assembled monolayers (SAMs) of carbon chain length  $C_8$ - $C_{18}$  were formed from the relevant alkanethiol solutions in  $C_2H_5OH$ . SAMs were attached to a  $\sim 100$ nm thick Au film over a Cr adhesion promoter on a glass substrate. (Figure 3). SAMs were prepared shortly before the biological assays and were stored under  $N_2$  until required.

Biological assays. Biological assays were conducted according to the protocols detailed in references 1 and 4. Briefly:



## Results

Characteristics of the alkanethiol SAM series are shown in Table 1.

Table 1: Characteristics of a methyl-terminated alkanethiol series. <sup>1</sup> Thickness determined using a multi-spectroscopic ellipsometer. Wettability determined as advancing water contact angle. <sup>2</sup> Taken from reference 2, determined by Friction Force Microscopy. <sup>3</sup> As the friction coefficient of a  $C_n$  alkanethiol was not measured by Leggett, a value has been interpolated from the equation  $\gamma = -0.0301x + 0.7067$  ( $r = 0.9051$ ).

Compound	Thickness (nm) <sup>1</sup>	$\theta_a$ (°) <sup>2</sup>	Friction coefficient <sup>3</sup>
$C_8$	0.53 ± 0.06	111 ± 2	0.51 ± 0.03
$C_{10}$	0.70 ± 0.04	113 ± 2	0.35 ± 0.04
$C_{12}$	1.45 ± 0.06	113 ± 2	0.33 ± 0.02
$C_{14}$	1.54 ± 0.08	115 ± 1	0.29*
$C_{16}$	1.73 ± 0.04	116 ± 2	0.23 ± 0.02
$C_{18}$	2.14 ± 0.08	115 ± 1	0.18 ± 0.05

Progressive extension of the thiol chain length is verified by the increasing thickness of the coating in the nanometre range. Wettability of the series varied by only 5° but the friction coefficients decreased with increasing length of the thiol chain, this is a consequence of changes in the molecular organisation of the SAM (see Discussion).

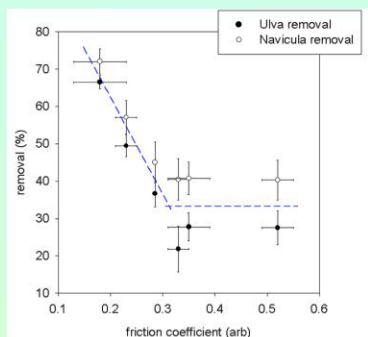


Figure 4: The removal of *Ulva* spores and *Navicula* cells from the alkanethiol SAM series ( $C_8$ - $C_{18}$ ) as a function of the friction coefficient of the SAMs. Y error bars = 2 × Standard Error derived from arcsine transformed data, X error bars = Standard Deviation.

Figure 4 reveals a similar, biphasic, removal dynamic for both *Ulva* and *Navicula* from this SAM series. Cell / spore removal from  $C_8$ - $C_{18}$  SAMs is insensitive to changes in friction coefficient, removal remaining around 25% for *Ulva* and around 40% for *Navicula*. On SAMs of thiol length  $C_{12}$  and greater, removal of both species scales linearly; as friction coefficient decreases (chain length increases) removal of both species increases.

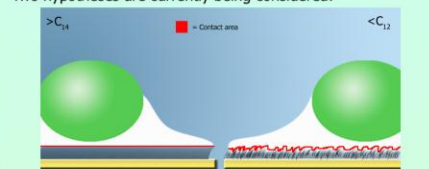
## Discussion

Table 1 shows that as the length of the thiol chain increases from  $C_8$  to  $C_{18}$  the friction coefficient of the surface drops. This is a consequence of the intermolecular organisation of the monolayer. Short chain length thiols are disordered structures. The reduced number of methylene groups in the chain limits the potential for intermolecular interactions, primarily van der Waals forces. The resulting monolayer has a 'fluid-like' amorphous nature, which is readily deformable and therefore experiences high levels of surface friction. As chain length increases the SAM becomes more ordered as interactions between the thiol chains increase. This gives the monolayer a more rigid crystalline structure, which is less deformable and consequently has lower friction.

**The change from fluid-like to crystalline packing occurs at thiol lengths of  $C_{12}$ - $C_{14}$ . This coincides with the onset of increasing spore / cell removal.**

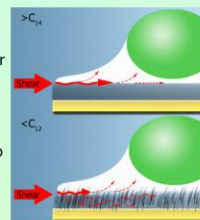
The mechanism that accounts for this change in adhesive strength is not yet certain. As Figure 4 shows however, the removal of *Ulva* and *Navicula* has the same dynamic. This suggests that the underlying mechanism is independent of the specific composition of the adhesive employed.

Two hypotheses are currently being considered:



1) The amorphous nature of the short chain length thiols may simply provide a greater available surface area for the wetting and interaction of the adhesives.

2) The short chain length SAMs have a lower elastic modulus (i.e. are more deformable) than the longer chain length, crystalline, SAMs. This may confer the potential for increased energy dissipation through molecular motion. As shear stress (energy) is applied to the adhered spores / cells, an amorphous SAM has the ability to 'absorb' more of the energy.



These results indicate that the frictional properties of a surface affect the dynamics of adhesive release in a consistent manner for these two algal species. Newby and Chaudhury<sup>2</sup> described the importance of friction, lubricity and slippage in the foul-release properties of PDMS (siloxanes). Although the mechanisms they invoked to explain high removal from thick cross-linked polymers cannot be directly applied to release from a monolayer, these results suggest that frictional characteristics are of fundamental importance to the foul-release nature of a surface.

## Acknowledgements

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