Clay nanotube Pickering emulsions for spill oil bioremediation

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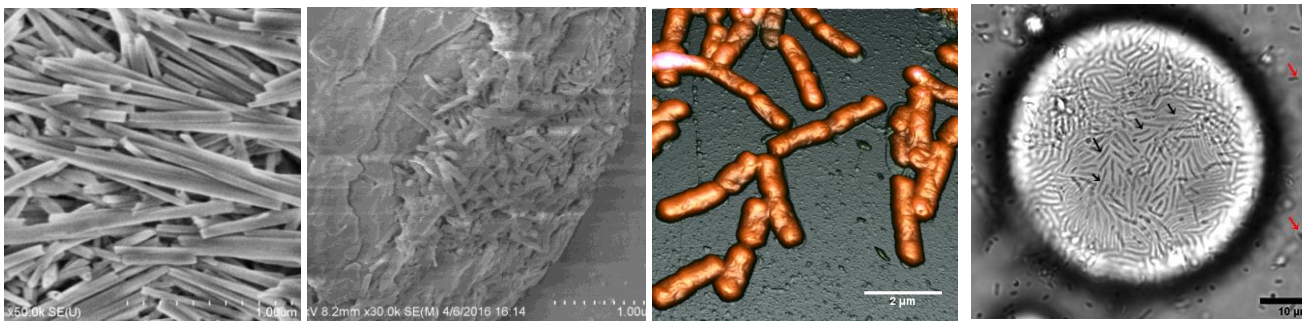
Motivated by the Deepwater Horizon oil spill, this work presents a model study of the biofriendly remediation of nanoclay oil emulsions by bacteria. Halloysites as tubular aluminosilicates are introduced as biocompatible and cheap nanoparticles to form and stabilize oil-water emulsions. Pickering emulsification can proceed with energies low enough to be afforded by ocean turbulence and stability of droplets extends over more than a week. We used model oil representing the Gulf of Mexico petroleum. Cell viability is affected by halloysite addition only little, and therefore the system is environmentally safe and most promising for further development. Optimization of the nanotubes' length between 0.4 and 1.5 μm and their surface hydrophobicity through silanization allowed designing oil droplets with dimeters of 3-5 μm stable in pure water and even in 0.6 M sodium chloride model sea water making this technology applicable for sea spilled-oil dispersion [1-2].

The emulsion micro-droplets have a rough surface coated with laterally located clay nanotubes (Fig.1 a-b) which drastically improved bacteria proliferation. Petroleum degrading bacteria *A. borkumensis* has shown ten-time enhancement in the number of microorganisms attached to the oil droplets when optimally hydrophobized halloysite were used (Fig. 1c). These clay nanotubes are safe natural materials available in thousands of tons at low price, which makes halloysite-based technologies scalable for large industrial applications.

In collaboration with R. v. Klitzing, D. Stehl, T. Pogrzeba, R. Schomäcker**,** Tech University of Berlin, J. Koetz, University of Potsdam and H. Möhwald, Max Planck Institute-Golm, the stabilization of oil emulsions by halloysite is also shown to be very effective in general interface catalytic reactions. Yield, selectivity and product separation can be considerably enhanced for the hydroformylation reaction of dodecene to tridecanal.



a **b** **c** **d**

Fig. 1, a - SEM of halloysite clay nanotubes; **b** –cryo-SEM image of oil droplet coated with clay nanotubes; **c** – oil decomposing *A. borkumensis* bacteria, AFM image; **d** - bright field optical microscopy images of droplets formed with 1% halloysite and completely covered with bacteria after 1 week incubation. Small black arrows indicate bacteria attached to the surface of oil droplets. Red arrows indicate free bacteria, clay nanotubes are not visible at this magnification.

References:

1. Y. Lvov, W. Wang, L. Zhang, R. Fakhrullin, ***Adv. Mater***., v.28, 1227–1250, 2016, " Halloysite Clay Nanotubes for Loading and Sustained Release of Functional Compounds"

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