Lappeenranta University of Technology

University of Oulu

Carboxymethyl Chitosan nanoparticles as Emulsifiers for Oil-Spill Treatment

Members of the research group:

Simo Kalliola, Eveliina Repo, Mika Sillanpää (LUT)

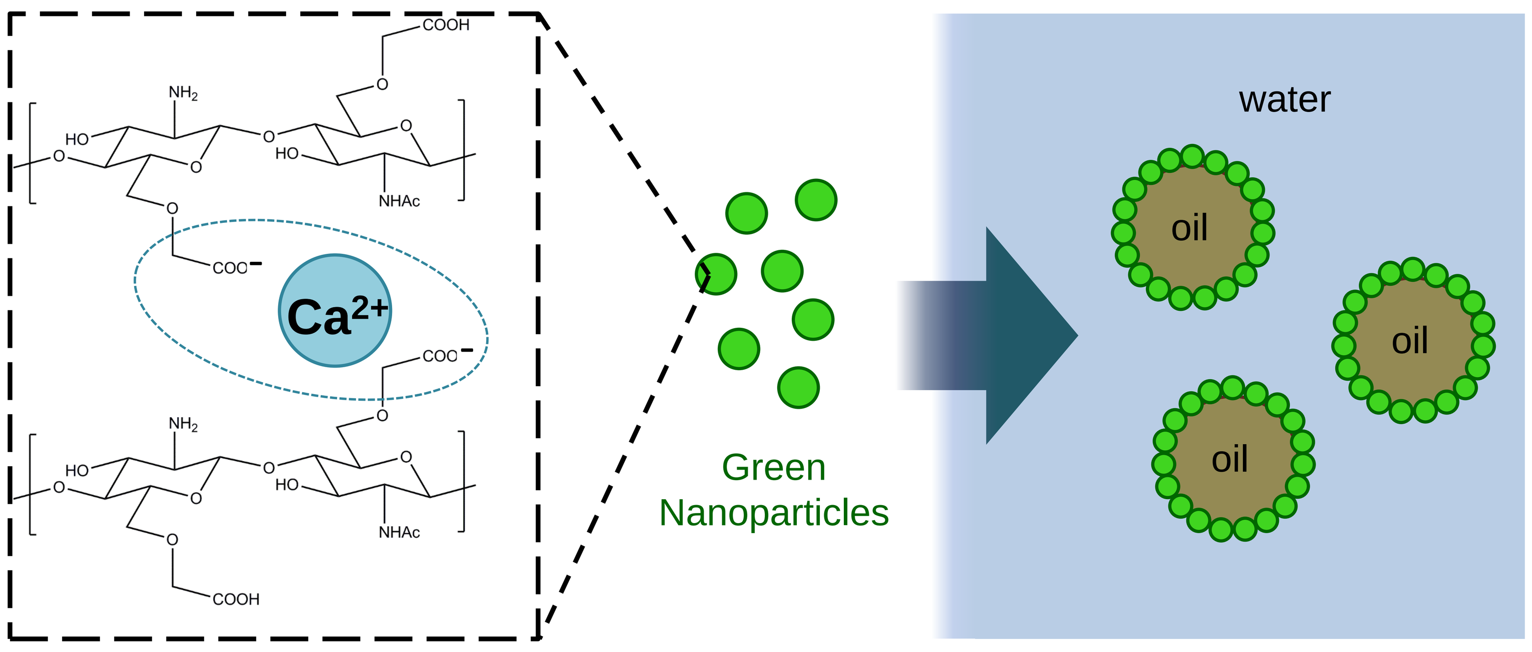
Jonna Ojala, Henrikki Liimatainen, Jouko Niinimäki (OY)

Project:

Towards Efficient and Sustainable Arctic Oil-Spill Response: Green Dispersing and Herding Agents Derived from Northern Bioresources

Introduction

The subject of this project is to develop green and sustainable nanoparticles for oil-spill treatment. For this purpose the materials need to be non-toxic, biodegradable and renewable. Therefore, we have chosen to use chitosan, a non-toxic and biodegradable biopolymer. Chitosan is derived mainly from the shells of crustacean that are a waste of food industry. Chitosan is a polysaccharide with reactive amino and hydroxyl groups. By introducing carboxylic groups into the polymer, it is possible to use calcium ions to cross-link the carboxymethylated chitosan (CMC) into nanoparticles (CMC-Ca). Calcium chloride is used for this purpose since there is already significant amounts of calcium and chloride in the natural sea water.



Materials and Methods

Chitosan is carboxymethylated with chloroacetic acid in heterogeneous and alkaline conditions at 50 °C. The nanoparticles are formed by addition of $CaCl_2$ or by pH adjustment. Oil-in-water emulsions are produced by vortex mixing for 10 s. Dodecane was used as a model hydrocarbon.

Results

In our previous studies it was concluded that the CMC-Ca nanoparticles are fairly stable against increased NaCl concentration but more susceptible against variations in pH. The nanoparticles were also able to stabilize oil-in-water emulsions by adsorption onto the oil-water-interface **[1]**.

The instability of CMC-Ca nanoparticles in alkaline pH was found to be due to the decreased interaction between amino and carboxyl groups as a result of the deprotonation of the amino groups. The interaction between amino and carboxylic groups is manifested by the formation of nanoparticles near the isoelectric point of the polymer without the addition of $CaCl_2$ **[2]**.

The emulsion stability increases as pH is decreased due to the aggregation of CMC (Fig. 1). At lower pH, the CMC nanoparticles are formed and the emulsion stability no longer depends on oil/water ratio. The nanoparticle formation is reversible since the nanoparticles can be formed by only adjusting the pH without the addition of cross-linking agents. This allows for the reversible emulsification of oil by pH adjustment and mixing (Fig. 2).

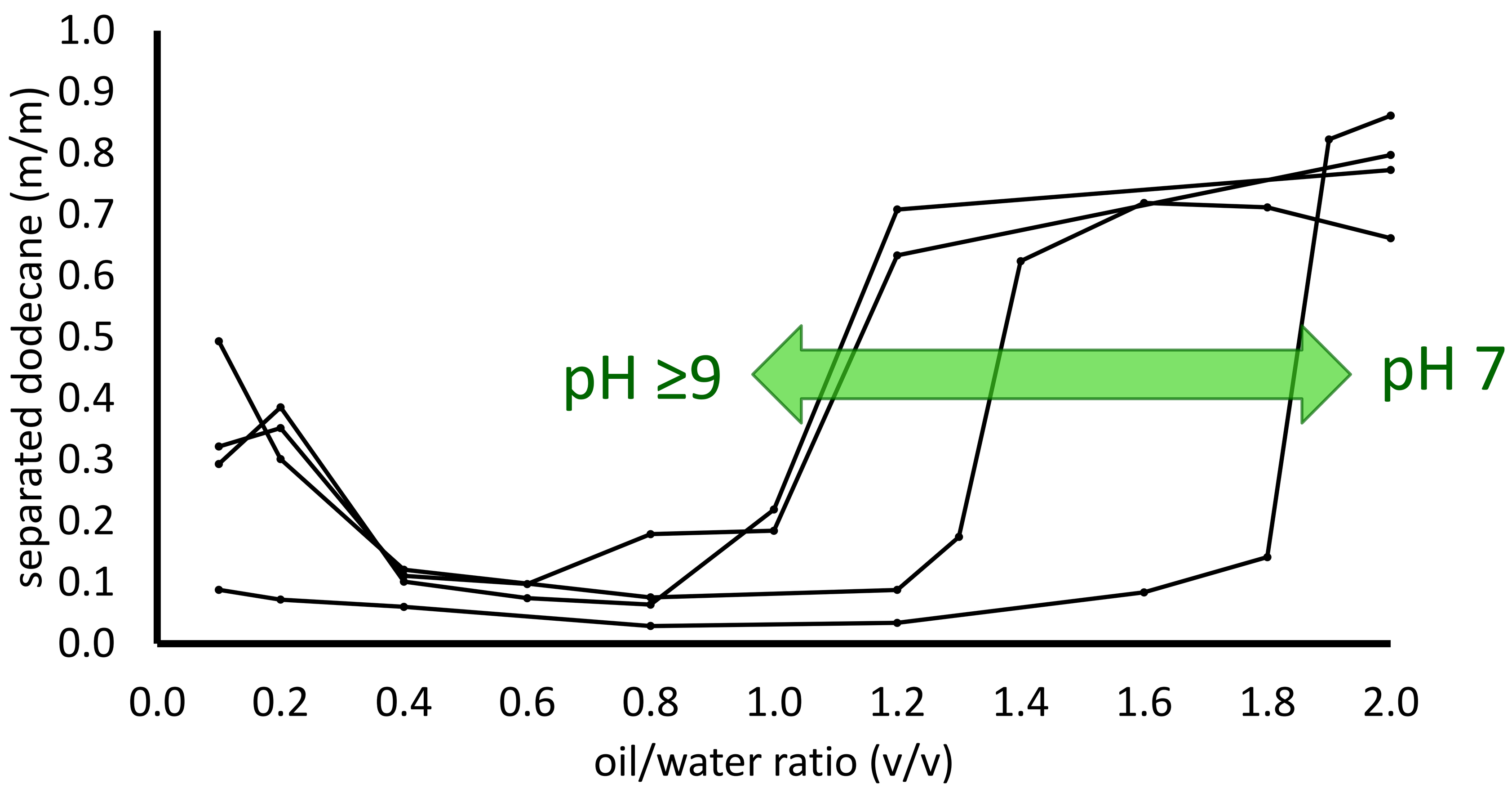


Figure 1. Emulsion stability increases as the pH is decreased from 9 to 7.

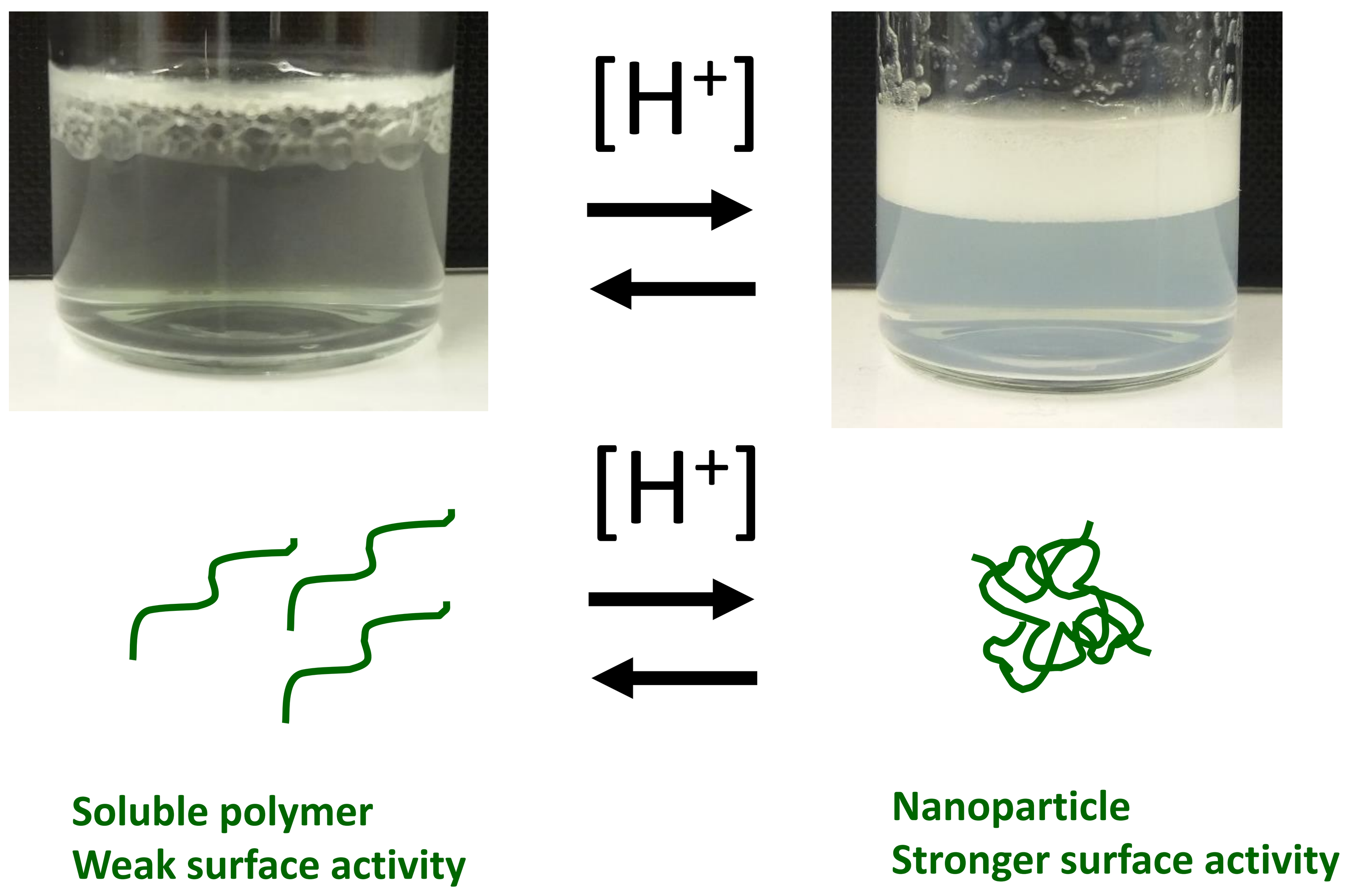


Figure 2. Reversible emulsification of oil by pH adjustment and mixing using CMC.

CONTACT

Simo Kalliola, M.Sc, LUT
simo.kalliola@lut.fi

Mika Sillanpää, Prof., LUT
mika.sillanpää@lut.fi

Eveliina Repo, D.Sc, LUT
eveliina.repo@lut.fi

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2. Kalliola S., Repo E., Srivastava V., Heiskanen J. P., Sirviö J. A., Liimatainen H., Sillanpää M., The pH sensitive properties of carboxymethyl chitosan nanoparticles cross-linked with calcium ions, Colloids and Surfaces B: Biointerfaces 153 (2017) 229-236.