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Fabrication, Characterization and Biodegradability of Oil–in–Water Pickering Emulsions Stabilized by Cellulose Nanocrystals

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Introduction

Over the last decade, while the development of nanotechnologies allowed generating highly dispersed particles in an amount sufficient to satisfy the needs of industry, the amount of studies of Pickering emulsions has been rising steadily. Pickering emulsions are widely used in the food, cosmetic, medical, and oil refining industries. In the oil industry, which is prone to frequent oil spills, the use of Pickering emulsions is relevant for dispersing crude oil during a spill response.

In order to form stable emulsions, a particle should exhibit good wettability of both hydrophilic and hydrophobic components. Kalashnikova et al. [1] shows that the faces of CNC are structurally non-equivalent and the amphiphilicity of Iα and Iβ cellulose is based on (200) β / (220) α-hydrophobic edge plane. The following factors which influence the formation and stability of nanocellulose-based Pickering emulsions can be distinguished: the geometry of nanoparticles, the chemical nature of the surface and its charge, the ionic strength and pH of a dispersed medium [2].

Although sulfuric acid hydrolysis is one of the commonly used methods of CNC particle generation, yet the sulfated CNC cannot effectively stabilize oil droplets due to strong repulsion between nanoparticles, which inhibits their adsorption on the oil/water interface. Research has shown [1] that sulfated CNC with surface charge exceeding -50 mW cannot effectively stabilize oil droplets because of strong electrostatic repulsion between the nanoparticles in the area of the oil/water interface. Additional treatment of CNC, that is, removal of sulfate groups from the surface of nanocrystals, leads to reduction of the surface charge down to -35 mW, which has a favorable effect on their emulsifying ability.

At the same time, because of its double hydrophilic/hydrophobic nature and non-toxicity, CNC has a great potential as a green emulsifier, stabilizer and gelling agent for prospective biotechnologies used for elimination of crude oil spills without consequential damage to the environment. In particular, the work [3] showed that *Serratia marcescens* stock can effectively process saturated hydrocarbons in Pickering emulsions in co/w systems stabilized by sulfated CNC.

In this study, we aimed developing eco-friendly oil emulsifiers based on CNC and assessing the effectiveness of oil emulsions biodegradation after the introduction of target oil-destroying microorganisms. For this, we have studied the influence of CNC on the formation and stability of Pickering emulsions in a crude oil/water system depending on component ratio, ionic strength, pH of the medium, and examined the biodestruction of obtained emulsions by natural microorganisms.

Cellulose nanocrystalls (CNC)

CNC in the form of hydrosols was obtained by acid-catalyzed solvolysis of cellulose (CH_3COOH/octanol-1/0.2 mol.% $H_3PW_{12}O_{40}$). The method makes it possible to obtain particles with a partially acetylated surface (CNC_{Ac}), and also, after hydrolysis, with a surface close to natural cellulose (CNC_H).

Tabl. Colloid-chemical properties of CNC_{Ac} and CNC_H hydrosols

Type of hydrosol CNC	ζ-potential, mV	pK of surface acid-base centers	number of surface acid-base sites, mmol/g
CNC_{Ac}	-35	pK_{COOH}=3.95	q_{COOH}=0.245
		pK_2=6.35	q_2=0.035
CNC_H	-10	pK_{COOH}=5.45	q_{COOH}=0.058
		pK_2=7.70	q_2=0.272

Rod-like particles with native (CNC_H) and partially acetylated (CNC_{Ac}) surfaces, with average geometric dimensions of approximately 200 nm (length) and 8 nm (width, thickness), that were characterized by a highly ordered structure (crystallinity index of 0.88) were obtained by cellulose solvolysis.

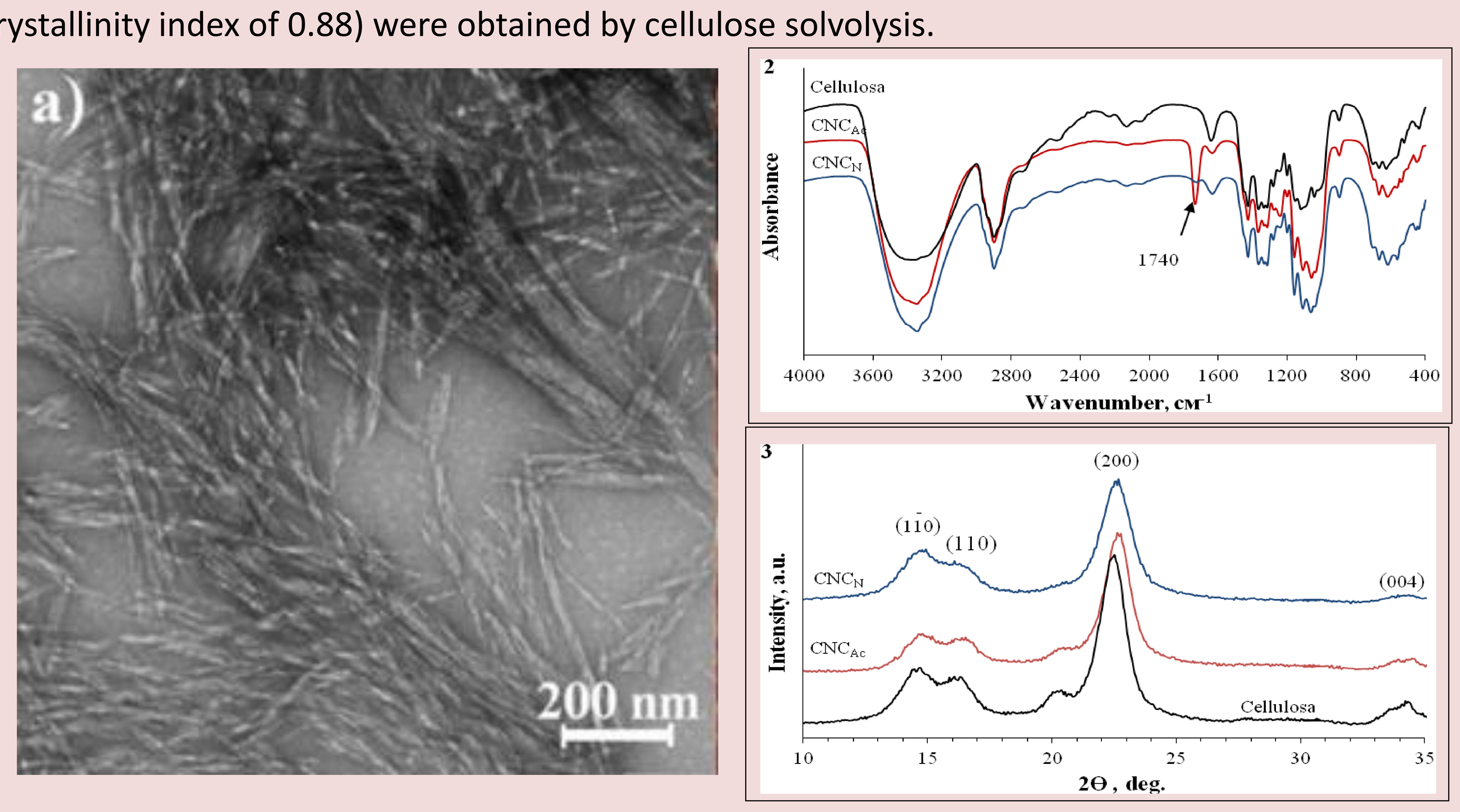

Fig. Photomicrographs (TEM, 1), FTIR spectra (2) and diffraction patterns (XRD, 3) of CNC

Due to the low surface charge, CNC_H has a low aggregative stability compared to CNC_{Ac}. Therefore, in the work, to obtain emulsions with reproducible parameters, cellulose nanocrystals with an acetylated surface were used, as they are more stable with stable colloidal chemical characteristics.

Crude oil

We used crude oil from the Usinsk oil field (Russia)

Tabl. General characteristics of crude oil

Parameter	Value
Density at 20 °C, $kg{\cdot}m^{-3}$	877.5
Water, wt%	0.09
Mass concentrations of chloride salts, $mg{\cdot}dm^{-3}$	22.1
Sulfur, wt%	1.24
Mechanical impurities, wt%	0.0092
Paraffin, wt%	7.2
Resins, wt%	15.66
Asphaltenes, wt%	3.81
Crystallization temperature, °C	+7
Mass fraction of organic chlorides, ppm	< 1
Mass fraction of hydrogen sulfide, ppm	9.7
Mass fraction of methyl-ethyl mercaptan, ppm	6.2

1. I. Kalashnikova et al. New Pickering emulsions stabilized by bacterial cellulose nanocrystals, Langmuir 27 (12) (2011) 7471–7479. doi: 10.1021/la200971f
2. I. Kalashnikova et al. Cellulosic nanorods of various aspect ratios for oil in water Pickering emulsions, Soft. Matter, 9 (3) (2013) 952–959. doi: 10.1039/C2SM26472B
3. S. Parajuli et al.. Surface properties of cellulose nanocrystal stabilized crude oil emulsions and their effect on petroleum biodegradation, Colloids Surfaces A Physicochem. Eng. Asp, 596 (2020)124705. doi: 10.1016/j.colsurfa.2020.124705

Conditions for formation and stability of emulsions

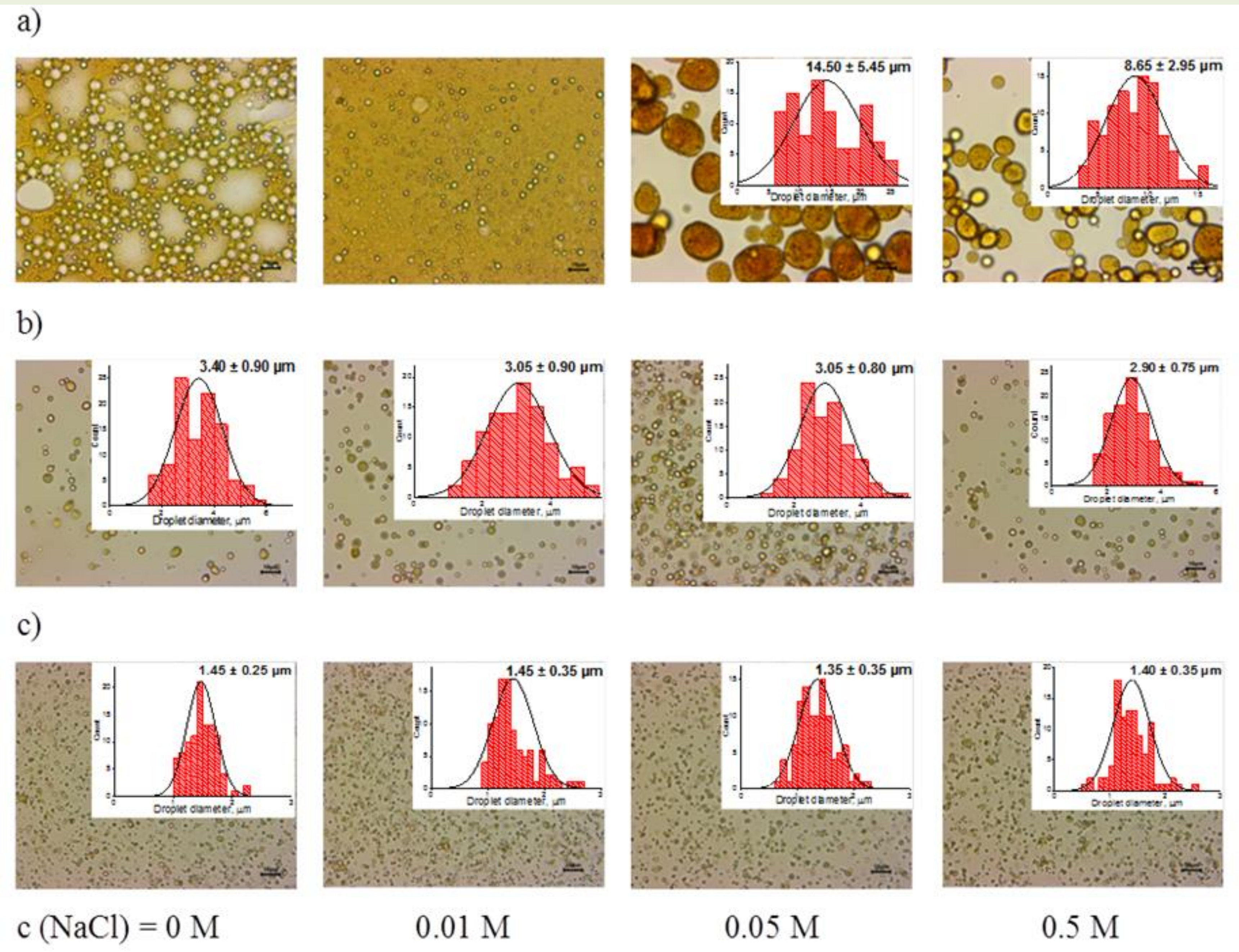

Fig. Changes in sizes of emulsion droplets in the co/w system based on the optical microscopy data, depending on CNC content: a) 3.5; b) 7; c) 14 mg/mL.

In all the systems studied, at a cellulose concentration above 7 mg/mL, the formation of kinetically stable emulsions is observed; this is the minimum and sufficient concentration of NC required for the formation of time-stable emulsions.

Study of acid-base and rheological properties of emulsions

Table. Constant values of ionization of surface CNC groups and Pickering emulsions (pK_i), their concentrations (q_i) and packing of active acid-base centers on the surface (N_S)

Sample	c(NaCl), M	pK_i, Δ±0.15	q_i, mmol/g, Δ±0.005	N_S, pcs/nm²
CNC	0.001	pK_{COOH}=3.95	q_{COOH}=0.245	0.354
		pK_{OH}=6.35	q_{OH}=0.035	0.051
	0.1	pK_{COOH}=3.95	q_{COOH}=0.060	0.087
		pK_{OH}=6.50	q_{OH}=0.030	0.043
CNC-crude oil	0.001	pK_{COOH}=5.60	q_{COOH}=0.057	0.082
		pK_{OH}=6.65	q_{OH}=0.032	0.046
	0.1	pK_{COOH}=5.60	q_{COOH}=0.053	0.077
		pK_{OH}=6.55	q_{OH}=0.045	0.065

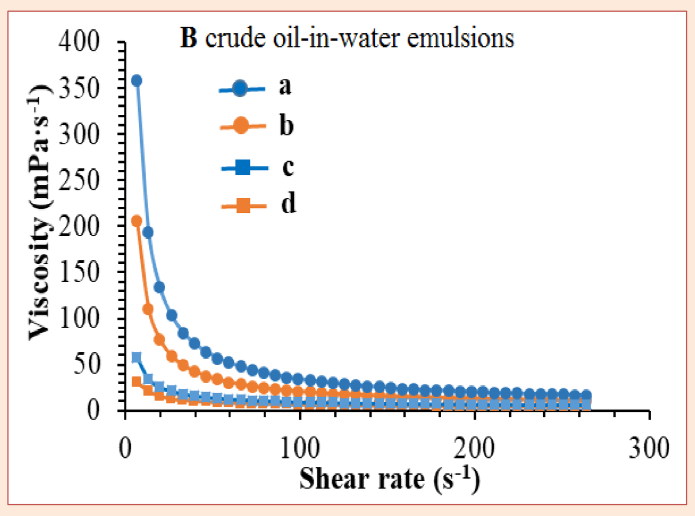

Fig. Flow profiles and the effect of NaCl addition and CNC concentration on the viscosity of nanocellulose stabilized o/w emulsion (a) CNC concentration 14 mg/mL, NaCl 0.511 M; (b) CNC concentration 14 mg/mL, NaCl 0 M; (c) CNC concentration 7 mg/mL, NaCl 0.511 M; (d) CNC concentration 7 mg/mL, NaCl 0 M.

The formation of emulsion accompanied interaction of the compounds of polar groups of crude oil with cellulose surface centers. This leads to additional shifting of the dissociation of carboxyl groups towards pK_{COOH}=5.6 and to a decrease in the centers involved in this equilibrium to 0.05 pcs/nm². Also, such interactions lead to a higher pK_{OH} as compared to the emulsions containing liquid paraffin and water dispersion of CNC. The rheology of this emulsion type can be effectively controlled by both introducing outside electrolytes and varying the concentrations of a dispersant.

Biodegradation of CNC-stabilized o/w emulsions

Optical microscopy

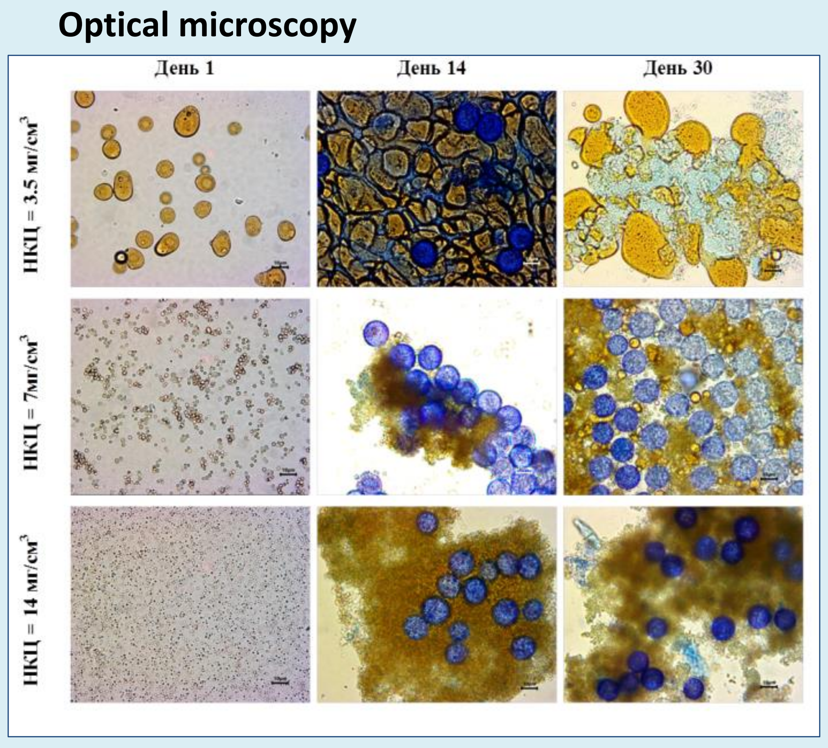

Fig. Stages of biodegradation of oil droplets at different emulsifier content (colored with methylene blue)

Gas-liquid chromatography

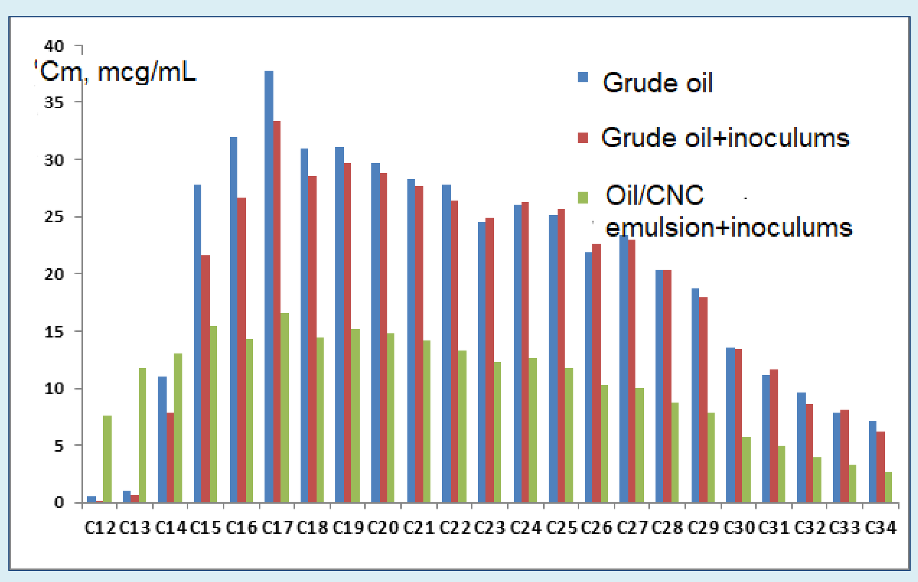

Fig. Comparison of the content of n-alkanes after the introduction of inoculums into the oil emulsion and into crude oil (control sample - crude oil without inoculums)

The use of oil and CNC as a basis for the formation of Pickering emulsions ensures the preservation of water/air contact at the interface, encouraging more effective oxidation of oil by bacteria Rhodococcus egvi in aerobic environment provided there are mineral salts of nitrogen, potassium and phosphorous in the environment. The results obtained are a scientific basis for the development of technologies for the disposal of oil spills on water surfaces.