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Preparation and stabilization of D-limonene Pickering emulsions by cellulose nanocrystals

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ABSTRACT

The aim of this study was to investigate D-limonene Pickering emulsion stabilized by cellulose nanocrystals (CNCs) and factors that may affect its properties. CNCs were prepared by ammonium persulfate hydrolysis of corncob cellulose, and D-limonene Pickering emulsions were generated by ultrasonic homogenizing method. The morphology and size of the prepared emulsions with different CNCs concentrations were studied by optical microscopy and laser light diffraction. In addition, factors that may affect the stability of emulsions such as ionic concentration, pH and temperature were also studied. As indicated by the experiment data, when temperature rose, the stability to of emulsions would be increased, and the stability of emulsions was reduced with low pH or high salt concentration due to electrostatic screening of the negatively charged CNC particles. In conclusion, high stability of D-limonene Pickering emulsions could be obtained by CNCs.

1. Introduction

D-Limonene (4-isopropenyl-1-methylcyclohexene) is a major flavor component of citrus fruits. It is reported that D-limonene has bactericide, antioxidant, chemo-preventative and therapeutic activities, so it is widely used in cosmetics, foods, and other consumer products (Li & Chiang, 2012). However, since D-limonene is insoluble in water and easy to oxidative degradation, it is difficult to keep the lemon-like flavor especially in the areas such as water-rich phases and liquid–solid interfaces. Therefore, it is very important and necessary to utilize a delivery system to protect D-limonene from chemical degradation and improve its water-solubility. Recently, much attention has been paid to emulsion technology to solve the above problems.

Emulsions are heterogeneous systems consisting of droplets of a liquid dispersed in another non-miscible or partly miscible liquid, and stabilized by surfactants, surface-active polymers, solid particles or natural polymers such as proteins and polysaccharides (Bouyer, Mekhloufi, Rosilio, Grossiord, & Agnely, 2012; Chen et al., 2011). However, the classical synthetic emulsifiers get more and more limited with increasing legal and consumer requirements such as non-toxicity, biocompatibility and high ecological acceptability (Marku, Wahlgren, Rayner, Sjöö, & Timgren, 2012; Zoppe, Venditti, & Rojas, 2012). Pickering emulsions are emulsions of any type, either oil-in-water (o/w), water-in-oil (w/o), or multiple, stabilized by solid particles instead of surfactants (Aveyard, Binks, & Clint, 2003; Binks, 2002). Because of the highly enhanced stabilization against coalescence and Oswald ripening, Pickering emulsions could conserve the droplets under high concentration of dispersed phase. There has been increasing interest in renewable, environment-friendly biomaterials recent years, and it is a good choice to introduce these materials into solid particles preparation to stabilize Pickering emulsions. Several investigations have reported to use cellulose to stabilize oil in water emulsions (Kalashnikova, Bizot, Cathala, & Capron, 2011a; Kalashnikova, Bizot, Cathala, & Capron, 2011b). Cellulose nanocrystals (CNCs) are regarded as ideal biomaterial due to its nice properties, such as low density, chemical tunability, environmental sustainability, and anticipated low cost (Leung et al., 2011).

In this study, CNCs were prepared from corncob cellulose hydrolyzed by ammonium persulfate. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA) techniques were used to investigate cellulose structure, crystallinity index and thermal stability respectively. Then D-limonene Pickering emulsions were successfully prepared by sonicating D-limonene and CNCs aqueous dispersion, and their properties were studied by laser particle size analyzer and

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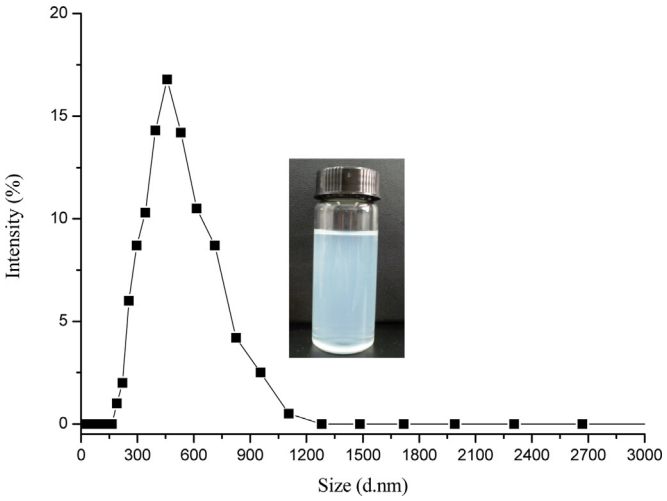

Fig. 1. Size distribution of CNCS by volume and CNCs suspension (0.2 wt%) after treatment with 1 M APS.

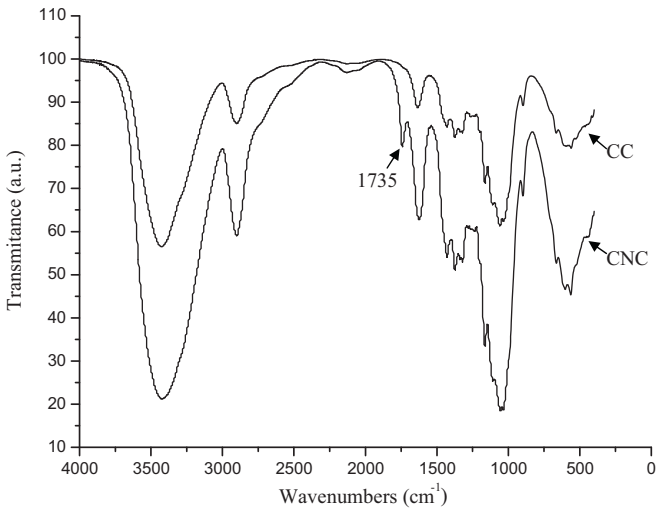

Fig. 3. FTIR spectra of CC and CNCs.

microscope. Furthermore, effects of different environmental factors on the stability of Pickering emulsion were analyzed in detail.

2. Materials and methods

2.1. Materials

Corncob cellulose was supplied by Fustian Pharmaceutical Co., Ltd. (Shan Dong province, China). Ammonium persulfate (APS), sodium chloride and sodium hydroxide were all of reagent grade and purchased from Beijing Chemicals (Beijing, China). D-Limonene was obtained from Shanghai Meishuang Company (Shanghai, China).

2.2. Methods

2.2.1. Cellulose nanocrystals preparation

Two gram of corncob cellulose (CC) was added to 100 ml of 1 M APS solution, and the mixture was heated to 60 °C for 16 h (Leung et al., 2011), and then a suspension of CNCs was obtained. The suspension of CNCs was washed by repeated centrifugations at 5000 rpm for 10 min until the solution conductivity was ≈5 μS cm^{-1} (pH 4), close to that of deionized water.

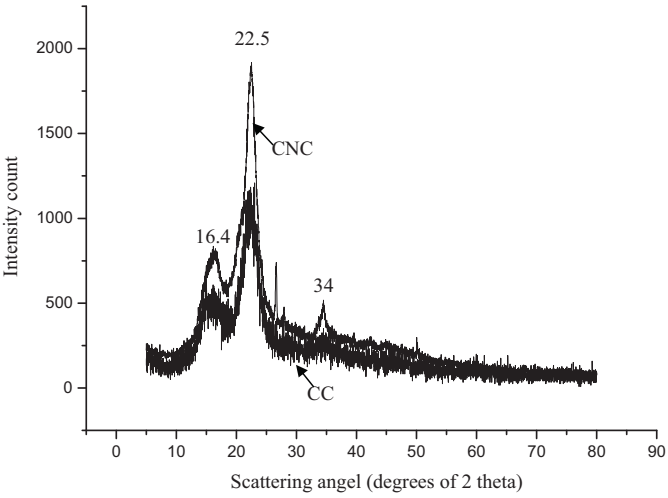

Fig. 2. X-ray diffraction patterns for CC and CNCS.

2.2.2. X-ray diffraction (XRD)

The X-ray diffractograms of CC and CNCs were obtained at room temperature within a 2θ ranging from 5° to 80° and a scan rate of 0.02° min^{-1}. The equipment used was a diffractometer Shimadzu LabX XRD-6000, operating at a power of 40 kV with a current of 30 mA and Cu Kα radiation (1.5406 Å). Before performing the XRD, two samples were dried at 80 °C for 16 h in a vacuum drying oven. The crystallinity index (CRI) of CNCs was then estimated using the empirical method, as shown in the follow equation.

$$\mathrm{CRI} = \frac{I002 - Iam}{I002} \times 100\%,$$

where I_{002} and I_{am} are the peak intensities of crystalline and amorphous materials, respectively (Sheltami, Abdullah, Ahmad, Dufresne, & Kargarzadeh, 2012).

2.2.3. Fourier transfer-infra red (FTIR) spectroscopy

A Shimadzu IR Prestige-21 Infrared spectrophotometer was used to obtain spectra for the CC and CNCs. The KBr disk (ultra-thin pellets) method was used in taking the IR spectra. Samples were ground and mixed with KBr (sample/KBr ratio, 1/100) to prepare pastilles. The experiments were carried out in the range of 399–4000 cm^{-1} with a resolution of 2 cm^{-1} and a total of 32 scans for each sample.

2.2.4. Size distribution and zeta-potential measurements

All experiments were carried out in dilute CNC suspension (0.2% w/w) where CNC particles randomly oriented. The dynamic light scattering (DLS, Zeta sizer Nano ZS, Malvern instrument) was used to evaluate the size and zeta potential of CNC suspensions as functions of ionic concentration and pH. This method provided indirect information for the nanoparticle size of CNCs. Samples were measured in deionized water. CNCs particle sizes were measured after 5 min equilibration at 25 °C and results are reported as the average of 3 measurements. The intensity average cellulose nanocrystals diameter, and polydispersity of each sample was obtained from the Cumulant analysis of each sample's correlation function. The distribution of sizes was obtained using the CONTIN analysis of each samples correlation function.

The zeta potential CNC particles in ionic solutions were measured over a range of NaCl concentration (0–100 mM) at 25 °C. The influence of pH (4.2–7.8) of CNC suspension was also investigated. The CNC dispersion was mixed with appropriate quantities of NaOH solutions to achieve a required pH. All suspensions were prepared

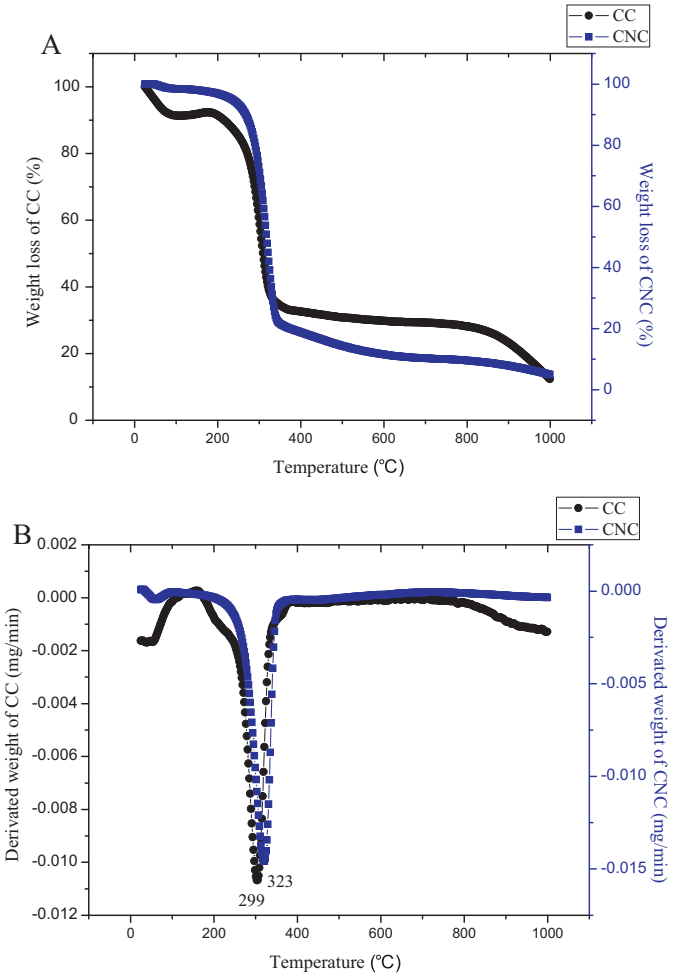

Fig. 4. (A) TG of CC and CNCs; (B) DTG of CC and CNCs.

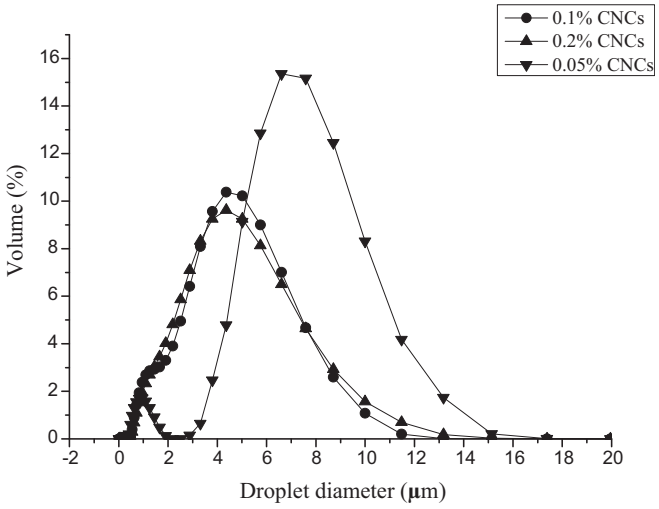

Fig. 6. Emulsion droplet with different CNCs concentration.

in deionized water. Data are representative of at least three experiments varied by less than 5% in all the cases studied.

2.2.5. Thermogravimetric analysis (TGA)

Thermal stabilities of CC and CNC were evaluated by thermogravimetric analysis (TGA). The analysis conditions were: a nitrogen atmosphere with flow 30 mL min^{-1}, heating rate of 5 °C min^{-1}, temperature range from 25 °C to 1000 °C, sample mass between 5 and 7 mg and aluminum pans.

2.3. Preparation and characterization of Pickering emulsions

2.3.1. Preparation of D-limonene Pickering emulsions by CNCs

CNCs suspensions with different content of CNCs were prepared by ultrasonic dispersion method. Practically, different amounts of CNCs powder (5, 10 and 20 mg) were added to 10 g deionized water respectively and sonicated at 0.4 kW power level (3 s sonication, 2 s standby) for 3 min. D-limonene Pickering emulsions were prepared using D-limonene and CNCs aqueous suspension at the required concentrations without further dilution to match an oil/water ratio of 10/90 (Kalashnikova et al., 2011a). Practically, 0.5 g of D-limonene was added to 4.5 g of CNCs aqueous suspension in a plastic vial and sonicated at 0.4 kW power level (3 s soniacation, 2 s standby) for 1 min.

2.3.2. Morphology of D-limonene Pickering emulsion

Emulsion droplets were visualized using optical micrograph. The CNCs-stabilized Pickering emulsions were captured by an Olympus BX 51 optical microscope fitted with a digital camera (Olympus, DP50). Emulsion droplets were placed directly onto a glass microscope slide and viewed under 4–40× magnification.

2.3.3. Droplet diameters measure

Droplet diameters were measured by laser light diffraction using a Malvern 2000 granulometer apparatus equipped with a He–Ne laser (Malvern Instruments, U.K.) with Fraunhofer diffraction.

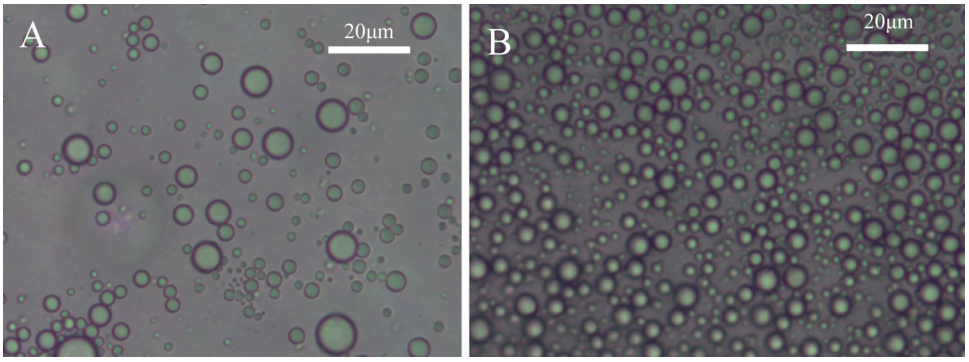

Fig. 5. Optical microscopy images of D-limonene Pickering emulsions prepared with 0.05% (A) and 0.20% (B) CNCs (oil to water ratio of 1:9).

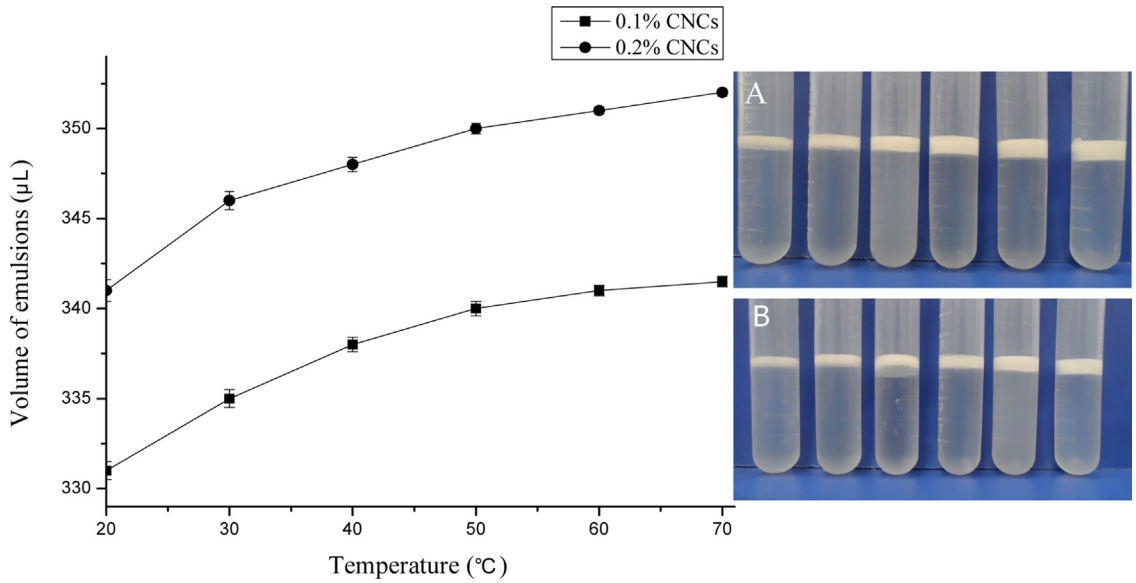

Fig. 7. Effect of temperature on volume of emulsion with (A) 0.2% w/w CNCs and (B) 0.1% w/w CNCs.

2.3.4. Zeta potential measurements of emulsions

The zeta potential of CNCs stabilized emulsion was measured using a particle electrophoresis instrument (Zetasizer Nano ZS, Malvern Instruments Ltd., Malvern, and Worcestershire, UK). Immediately prior to measurements, the samples were diluted to a concentration of approximately 0.05% w/w using deionized water to avoid multiple scattering effects. The zeta-potential was reported as the average and standard deviation of measurements made on three freshly prepared samples, with three readings taken per sample.

2.3.5. Test of emulsion stability to creaming

The stability to creaming of the generated emulsions was checked by centrifugation for 10 min at 4000 rpm and the thickness of the creaming layer was measured with a digital caliper and converted to volume (Kalashnikova et al., 2011a). Different factors that may influence the stability of emulsions to creaming were also studied. The emulsions were prepared as described above using 0.5 g D-limonene and 4.5 g CNCs suspensions with various concentrations, i.e. 0.05%, 0.10%, 0.20% w/w CNCs. These emulsions were then used to different pH and temperature and NaCl solutions for the stability tests to creaming. For the thermal stability test, the diluted emulsions were incubated in a water bath for 30 min at 20, 30, 40, 50, 60 and 70 °C. The pH stability test was performed by adjusting pH of the emulsions to 4.2, 4.8, 5.5, 6.2, 7.0 and 7.8 using 0.1 M NaOH solution. For the stability tests to ionic strength, the emulsions were diluted using NaCl solutions to a final concentration of 0–100 mM NaCl. After each treatment, the treated emulsions were centrifuged and the thickness of the creaming layer was measured with a digital caliper and converted to volume.

3. Results and discussion

3.1. Preparation and characterization of cellulose nanocrystals

CNCs were obtained from CC with a novel one-step procedure using APS. The yield of CNCs, under the condition of reaction to 16 h, with respect to the initial amount of dried CC was 50%. APS reaction leads to stable aqueous suspensions of CNCs which are negatively charged, thus, are very stable (Boluk, Lahiji, Zhao, & McDermott, 2011). During the APS oxidation process, carboxylic acid groups are presented. The reaction conditions used led to homogeneous and stable aqueous suspensions. The size distribution of CNCs by intensity was shown in Fig. 1, and mean size of CNCs was 363 nm, which showed that CNCs were obtained by APS hydrolysis. The X-ray diffraction patterns of CC and CNCs were shown in Fig. 2. In CC diffractogram, there was a predominance of type I cellulose, verified by the presence of peaks at $2\theta = 16.4°$, 22.5°, and 34°, and the amorphous background was characterized by the low diffracted intensity at around 18°. The CNC diffractogram exhibited the most intense peak (0 0 2) with a shoulder (1 0 1) and one lower peak (0 0 4). Such features resembled the diffraction pattern of cellulose I (Borysiak & Garbarczyk, 2003; Flauzino Neto, Silvério, Dantas, & Pasquini, 2013) and confirmed the integrity of the material during the course of treatment with APS. The crystallinity index (CrI) of CC and CNCs were 63.6% and 67.2%. From FTIR of CC and CNCs (Fig. 3), it can be found that CC and CNCs all showed adsorption bands at 3500 cm^{-1}, which was the signal of alcoholic hydroxyl groups. The IR spectra of CNCs displayed a signal at 1735 cm^{-1}, which is attributed to C=O. The presence of signals at 1429, 1161, 1110, and 897 cm^{-1} indicated that the CNCs were primarily in the form of cellulose I, and the absence of OH stretching and out-of-plane bending at 3240 and 750 cm^{-1} characteristic of cellulose I_α confirmed the cellulose was I_β structure (Jiang, Han, & Hsieh, 2013; Leung et al., 2011), indicating no significant changes of the cellulose structure and mercerization did not occur (Leung et al., 2011). Thermal decomposition parameters were determined from the TG, DTG curves as described below at a heating rate of 5 °C min^{-1}. The TG and DTG curves of CC and CNCs powder are shown in Fig. 4A and B respectively. For two samples, the weight loss profiles exhibited essentially two events. The first was related to the evaporation of water-adsorbed materials. Here a small weight loss was found in the range of 30–140 °C. The second event corresponded to the process of cellulose degradation. In the present study, the decomposition of the CC showed a main stage, indicating that the composition of material was main cellulose and lignin. The DTG curve of CC showed a main peak, which accounted for the pyrolysis of cellulose (about 299 °C). But CNCs has an increased thermal stability. The thermal degradation of CNCs shows an increased value of 323 °C than CC of 299 °C. As the result, nanocellulose obtained from corncob cellulose has higher thermal stability than CC. The small amount of hemicelluloses and lignin existing in CC were removed by the oxidation of APS, and the stability of CNCs with high crystalline might be improved.

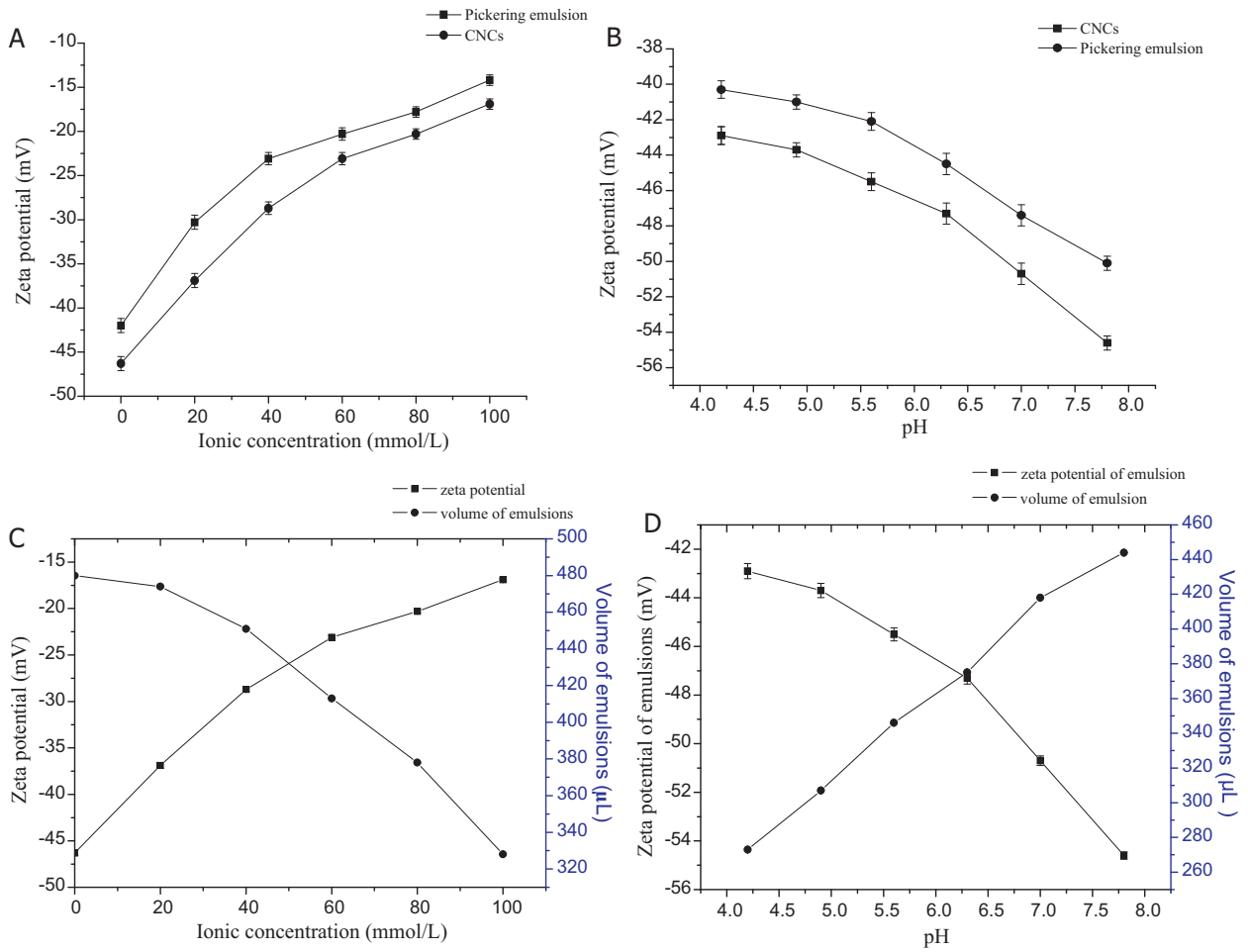

Fig. 8. (A–D) Effect of the ionic strength (with NaCl) and pH (with NaOH) on CNCs suspension and D-limonene Pickering emulsions zeta potential and emulsion volume with increasing ionic concentration and pH.

3.2. Emulsion preparation

The aqueous phase, for all tested emulsions consisted of CNCs dispersed in water at the required concentration without further treatment. D-limonene was added afterward. The biphasic system was then sonicated, resulting in a stable oil–water emulsion. Fig. 5 shows the optical microscopy image of D-limonene Pickering emulsion. Emulsions prepared with 0.05% w/w CNCs yielded large droplets (>5 μm), as shown in Fig. 5A, compared with those made with higher concentrations, as 0.2% w/w in Fig. 5B. Fig. 6 shows droplets of emulsions under different CNCs concentrations. Larger emulsion droplets were much less stable under low shear by mixing compared with the smaller droplets formed at higher nanoparticle concentrations. In the case of 0.05% w/w CNCs, the volume mean particle diameters were about 6.9 μm. When the concentration of CNCs was up to 0.2% w/w, the volume mean particle diameters were 4.2 μm. It was obvious that the concentration of CNCs had a significant impact on the particle size of emulsions.

3.3. Stability of emulsions to creaming under different temperature ionic, concentration and pH

Pickering emulsions were formulated at a 10/90 ratio (o/w), with 0.2% w/w suspension of CNCs in the water phase. And then the prepared emulsions were used to test emulsion to creaming stability under different factors, i.e. temperature, pH and ionic concentration. Temperature is an important factor that could influence the stability of Pickering emulsions. Ionic strength and pH also play important roles in regulating the electrostatic interactions that may occur between adjacent nanoparticles at the oil–water interface (Dyab, Binks, & Fletcher, 2012; Zoppe et al., 2012). Therefore, temperature, salt concentration, pH and tests were then carried out to specify stability characteristics.

The influence of temperature on the behavior of CNCs-stabilized emulsions was explored by applying samples under different temperature from 20–70 °C as shown in Fig. 7. Results showed that the emulsions were heated from 20–70 °C, the stability of emulsions to creaming increased. It could be explained by that CNCs were irreversibly adsorbed to cover emulsions droplets and formed 2 D-network, when temperature raised, CNCs tended to give a stronger structure, as a result, the inter-particle distances were decreased and the associative forces among the nanocrystals were enhanced (Tzoumaki, Moschakis, & Biliaderis, 2009; Tzoumaki, Moschakis, Kiosseoglou, & Biliaderis, 2011). Thus, the stability of emulsions to creaming was enhanced. Besides, it was also indicated that the increase in the stability of emulsions became higher with increasing CNCs concentration. That was because under the condition of low CNCs concentration, the inter-particle of CNCs had weak associative forces, so CNCs formed a weak droplet network. When CNCs concentration increased, the particle could form a stronger network, as a result, the stability of emulsions increased.

Effects of pH and ionic concentration on stabilizing emulsions were examined by measuring the zeta-potential of the droplets. The dependence of zeta-potential of the droplets in 0.2% w/w CNCs stabilized emulsion on the ionic environment (NaCl concentration) were similar to that of the 0.2 wt% CNCs suspension, and the

results are shown in Fig. 8A and C. Aqueous solutions with 0, 20, 40, 60, 80 and 100 mM NaCl concentrations were added to aqueous dispersions of CNCs and emulsions. As the salt concentration increased, there was a greater tendency for CNCs to aggregate, since the stabilizing repulsive forces were weakened by the increase in electrolyte concentration (Tzoumaki et al., 2011). When NaCl concentrations reached 100 mM, a small amount of CNCs aggregated in the CNCs suspension, and zeta potential of CNCs suspension and emulsion entered the domain of low-charged surfaces below 20 mV. It was observed that the absolute value of the zeta-potential of the emulsion droplets across the whole ranges of NaCl concentration remained relatively lower than those of the CNCs particles. The low net charge on the droplets could be explained in terms of the relatively low surface load of CNCs and/or because of ionic impurities in the samples that adsorbed to the surface of the oil droplets and changed their electrical charge (Surh, Decker, & McClements, 2006). The magnitude of zeta-potential of the emulsion droplets decreased with increasing the concentration of NaCl from 46.3 mV with no added salt to16.7 mV at 100 mM NaCl due to the electrostatic screening of the charged (—COO—) groups by the counter-ions (Na^+). It is conventionally recognized that the larger the absolute magnitude of zeta-potential, the greater is the electrostatic repulsion between droplets, and therefore the better the stability to their surface charge. Similar responses to those obtained by varying the ionic strength were also noted by changing the pH. As can be seen in Fig. 8B and D, the trends of zeta-potential of the droplets in 0.2% w/w CNCs stabilized emulsion on different pH environment were similar to that of the 0.2 wt% CNCs suspension, and the zeta potential of CNCs suspension and emulsion were both increased when pH increasing. The 0.20% w/w CNCs-stabilized emulsion volume was increased with increasing of pH value from 4.2 to 7.8. The magnitude of zeta-potential increased when 0.1 M NaOH was added, and the zeta-potential of the emulsion droplets and CNCs remained negative at all pH values, possibly because of the negatively charged —COO— groups on CNC particles. The CNCs has no cationic groups and therefore did not become positively charged at any pH. An increase in pH from 4.2 to 7.8 caused an increase in the magnitude of negative charge on the droplets from −32.9 to −46.3 mV, which was probably due to deprotonation of some of the protonated carboxyl groups ($COOH \rightarrow COO^- + H^+$) (Winuprasith & Suphantharika, 2013). It is conventionally recognized that increasing of the surface charge can improve the stability of emulsions because of the increasing repulsive forces between droplets against flocculation and coalescence. In our study, when the pH of the system was increased from 4.2 to 7.8, the surface charge decreased from −42.9 mV to −54.5 mV. So the larger the absolute magnitude of zeta-potential, the greater is the electrostatic repulsion between droplets, and therefore the better the stability (Dickinson, 2009).

4. Conclusion

In this study, cellulose nanocrystals were prepared from corncob cellulose by one step with ammonium persulfate hydrolysis. The degree of cellulose crystallinity increased during ammonium persulfate hydrolysis, which could be explained by the degradation of the amorphous cellulose during reaction process. Besides, the hydrolysis conditions used led to obtain stable aqueous suspensions of CNC which are negatively charged, due to the presence of carboxyl groups. D-Limonene Pickering emulsions were prepared by CNCs at high sonication power and long time with 0.2% (w/w) CNCs exhibited satisfactory size and high stability to creaming. Furthermore, the stability of the CNCs-stabilized emulsions was decreased at low pH or high salt concentration due to the electrostatic screening effect. In addition, the stability of emulsion increased when temperature increased from 20 °C to 70 °C, during the thermal treatment. The possible reason may be that CNCs were irreversibly adsorbed to cover emulsions droplets and formed 2D-network. Thus, CNCs from corncob cellulose are useful stabilizer for preparing D-limonene Pickering emulsion.

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