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Production of highly uniform Pickering emulsions by novel high-intensity ultrasonic tubular reactor (HUTR)



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ABSTRACT

The current work proposed an alternative ultrasound (US) technology, namely the high-intensity ultrasonic tubular reactor (HUTR) for preparing Pickering emulsions. Using the non-toxic and environmentally friendly cellulose nanocrystal (CNC) as a solid stabilizer, Pickering emulsions were produced using the HUTR and the results showed that Pickering emulsions as small as 1.5 µm can be produced using HUTR at the US power and sonication time of 300 W and 15 min respectively. Additionally, the sizes of Pickering emulsion obtained are found to remain the same upon 30 days of storage. The performance of HUTR in emulsion preparation is compared to conventional US horn system at the same US power. It was observed that the use of HUTR allowed generation of Pickering emulsion that is significantly smaller (around 7.40 µm) and with better droplet size distribution (Coefficient of variation, CV = 31%) as compared to those prepared with US horn method $(12.75 \,\mu\text{m}, \text{CV} = 36\%)$. This is owing to the better distribution of cavitation activity in the treatment chamber of HUTR as compared to those in the horn, according to the sonochemiluminescence (SCL) study. From the 30-days storage stability analysis, the CNC-PE prepared using HUTR was found to more stable against droplet coalescence in comparison to those prepared using US horn. Our findings suggested that the HUTR possessed superior Pickering emulsification capacity when compared to conventional US horn. Further work will be necessary to evaluate the feasibility of such intensifying tubular reactor technology for larger scale emulsification and other process intensification applications.

1. Introduction

Power ultrasound (US) is widely used in many applications including cleaning [1], wastewater treatment [2], emulsion preparation [3] etc. The power US systems utilize the continuous phenomenon of bubble formation, growth and implosive collapse of the bubbles in a liquid medium. The collapse of bubbles generates localized hot spots with temperature up to 5000 K, pressure of 1000 bar and heating/ cooling rates above 10^{10} K/s [4]. In past decades, the lab-scale US technology has been long recognized as powerful and effective tool in numerous applications [1,3,5]. However, conventional lab-scale US equipment (i.e. US horn) often suffers the disadvantages such as low processing volume and probe tip erosion [6]. Although the other US equipment such as ultrasonic bath can allow a larger processing volume as well as avoiding the US transducer erosion, the US intensity induced by the US bath (range around 0.55 W/cm^2) is, unfortunately, too weak for an effective US irradiation as compared to the horn system (> 5 W/cm²) [7]. This highly restrained the employment of US technology in the industry for larger scale processes, particularly for the preparation of emulsion.

An emulsion is a system of dispersed droplets of one immiscible liquid in another. They are present in a wide range of foods including milk, margarine, salad dressing and ice cream. These systems are generally prepared via continuous implication of shear force to the system that results in the dispersion of one of the phases into the other in droplet form [8]. An emulsion system is normally thermodynamically

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Abbreviations: CV, coefficient of variation; CNC, cellulose nanocrystal; CNC-PE, CNC-stabilized Pickering emulsion; SCL, sonochemiluminescence; HUTR, highintensity ultrasonic tubular reactor; US, ultrasound

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unstable owing to the high surface energy between the immiscible liquids. As a result, low molar mass surfactants or surface-active polymers are usually incorporated in the formulations to decrease the interfacial tensions between the phases [9,10]. Since the pioneering work of Ramsden [11] and Pickering [12], alternative way for stabilizing the emulsion droplets had been revealed, i.e. by the use of solid colloidal particles that can be partially wetted and adsorbed at fluid interfaces. The irreversible adsorption of particles onto the liquid interfaces promoted the generation of the particle-stabilized emulsions (or Pickering emulsions) that has extraordinary coalescence inhibition properties [13,14].

The particles used to stabilize Pickering emulsions can be categorized into organic and inorganic types. For food and pharmaceutical fields, organic-based particle is generally more preferred as they are able to minimise the toxicity imparted by the solid particles into human body and the environment. Among the organic particles available, cellulose can be considered as one of the best candidate because of its sustainability, biodegradability, nontoxicity, and anti-oxidative properties [15–19]. Subsequently, recent analysis has shown a promising performance of cellulose derivatives such as cellulose nanocrystals, cellulose microfibril and others in Pickering-type stabilization of oil-inwater emulsions [15,20,21].

Cellulose is a linear homopolymer, in which D-glucopyranose rings are linked to each other with β -(1–4)-glyosidic bonds [22]. It exists in nature as highly resistant fibres. There is considerable energy within the cellulose network attributed to the van der Waals forces and hydrogen bonding between hydroxyl groups located at equatorial positions of the glucopyranose rings [22]. Based on previous report, the available types of cellulose can be divided into three categories, namely microfibrillated cellulose (MFC), cellulose nanocrystal (CNC) and bacterial nanocellulose (BNC) [23]. Among the three classes of cellulose, cellulose nanocrystal is more favoured due to its comparatively shorter length and smaller diameter. These features allowed CNC to produce a smaller emulsion in comparison to those produced by other cellulose [20,23]. Hence, CNC will be focused in this work to produce a Pickering emulsion with smallest possible sizes.

The preparation of Pickering emulsions via US irradiation has been well established in the literature [3,15,16,20,24–29]. Li and Fogler [24,25] reported the two-stage emulsification mechanism induced by US. The first stage involved the generation of primary droplets by the acoustically produced interfacial waves, which caused eruption of oil phase into water in the form of droplets. The primary droplets are then broken-up during the second stage and causes localized intense turbulence and shear forces that produce violently imploding bubbles and microjets to effectively breaking the primarily generated droplets of dispersed oil into finer droplets [24,25]. The limiting sizes of emulsion are dependent upon the size, wettability and concentration of adsorbed particles as well as the mixing intensity [30,31].

Studies have been conducted and concluded, that usage of some US system such as the US horn is comparatively more energy-efficient than the conventionally used homogenizer [32,33]. However, the studies were performed mostly by horn system, which often suffers from the probe erosion and thus products contamination. Herein, a new US emulsification tool named high-intensity ultrasonic tubular reactor (HUTR) has been proposed to prepare Pickering emulsion. The HUTR is used to prepare Pickering emulsion stabilized by CNC and its performance was evaluated by comparing the size and stability of the CNC-stabilized Pickering emulsions (CNC-PE) with those prepared by the US horn system. Additionally, luminol photography was used to characterize the cavitation activities in the HUTR to further support the outcomes obtained from CNC-PE production.

2. Materials and methods

2.1. Materials

Cellulose nanocrystals (CNCs) (freeze dried, 0.96 wt% sulfur content) was procured from University of Maine. Red palm superolein (275 ppm β -carotene, melting point: 19 °C) was received from Sime Darby Jomalina Sdn Bhd (Malaysia). Luminol (97%), ethylenediaminetetraacetic acid (EDTA), hydrogen peroxide (30%, H₂O₂), sodium carbonate (Na₂CO₃), and iron(II) sulphate heptahydrate (\geq 99%, FeSO₄) were purchased from Sigma-Aldrich Chemicals Company (Malaysia). Sulphuric acid (95–98%, H₂SO₄), sodium chloride (NaCl) and sodium hydroxide (NaOH) was obtained from R & M Chemical (Syarikat Saintifik Jaya, Malaysia). All water used in this experiment are ultrapure water obtained from Milli-Q[®] Plus apparatus (Millipore, Billerica, USA). All chemicals used in this study were of analytical grade.

2.2. Characterization of CNC fibre

Size and morphology of the CNC was analysed using Hitachi SU8010 field emission scanning electron microscope (FE-SEM) (Hitachi, Japan) under scanning transmission electron microscopy (STEM) mode at 15 kV. The wetting contact angle of water is measured using a contact angle goniometer (Rame-hart, USA). Zeta-potential of CNC was measured using Zetasizer Nano ZS 90 (Malvern instruments, UK) at 25 $^{\circ}$ C.

2.3. Preparation of coarse CNC-stabilized Pickering emulsion

Pickering emulsions were prepared by using CNC as solid particle stabilizers and red palm olein as oil phase. First, 300 mL of coarse emulsions were prepared with a fixed oil content (10 wt%), CNC particle concentrations (0.5 wt%) and NaCl (30 mM) using a high-speed homogenizer (Model Ultra-Turrax T-25, IKA, Germany) at 9000 rpm for 5 min prior to ultrasound treatment. Subsequently, the coarse emulsion is either sonicated using the HUTR (22 kHz, Lab750, Sinaptec, France) or US horn. It should be noticed that the US power is referred to the constant output power from the US generator. Detail procedures are as follow:

2.3.1. Pickering emulsions prepared using HUTR

The coarse Pickering emulsion was sonicated for a designated time (1, 3, 5, 7, 10, 13 and 15 min) at various ultrasound powers of 100, 200 and 300 W to prepare fine Pickering emulsions. The resultant emulsion sample was collected in glass vials and stored at room temperature for further characterization.

2.3.2. Pickering emulsion prepared using US horn system

The coarse emulsion medium was sonicated for 1, 3, 5, 7, 10, 13 and 15 min at 100 W US power to prepare fine Pickering emulsions. The resultant emulsion sample was collected in glass vials and stored at room temperature for further characterization.

2.4. Droplet size, zeta potential and morphology measurement

The mean droplet diameter of the CNC-stabilized Pickering emulsion (CNC-PE) was measured using a Mastersizer (Mastersizer 3000, Malvern Instruments, UK) equipped with a Hydro EV wet dispersion unit. The zeta potential of Pickering emulsion droplet was analyzed via Zetasizer (NanoZS 90, Malvern Instrument, UK). The morphology of Pickering emulsion droplet was observed using an inverted optical microscope (Nikon Eclipse TS100, Nikon Instruments Inc., USA) at $10 \times$ magnification. The emulsion was diluted for $50 \times$ using water prior to optical microscopy. The coefficient of variation (CV) was calculated from the standard deviation (σ) and the mean droplet diameter ($D_{4,3}$):

$$CV(\%) = \sigma/D_{4,3} \times 100$$

2.5. Luminol photography

Luminol photography was performed to map the areas of cavitation activities by analysing the sonochemiluminescence (SCL) intensities produced. The luminol solution was prepared by mixing 1 mM luminol, 0.1 mM EDTA and 0.1 mM H_2O_2 in 0.1 M of Na₂CO₃. Subsequently, the pH of the luminol solution is tuned to 12 using NaOH. The SCL images were captured from the top of the reactor using a digital single lens reflex camera (Mirrorless Digital System, Sony A6000) mounted with a Sony macro lens, with 6400 ISO setting, F3.5 aperture and 30 s of exposure time in a pitch dark environment. A dark frame image without the presence of ultrasound was taken prior to capturing each of the SCL images. The original SCL images were then analysed by subtracting the dark frame image using ImageJ [34].

2.6. Fricke dosimetry

Fricke dosimetry was performed according to Jana and Chatterjee [35] with slight modification to estimate the content of OH radicals. In brief, the Fricke solution was prepared by mixing $FeSO_4$ (1 mM), H_2SO_4 (0.4 M) and NaCl (1 mM) in distilled water, and then sonicated with either US horn (100 W) or HUTR (100, 200 and 300 W) at different sonication time (0, 1, 3, 7, 10 and 15 min) to oxidize the Fe^{2+} to Fe^{3+} . The absorbances of the Fe^{3+} ions were measured using a spectrophotometer (Genesys 10 s UV, Thermo Fisher Scientific, USA) with pure distilled water as blank.

2.7. Statistical analysis

Analysis of variance (ANOVA) were conducted using Prism software and p < 0.05 was considered as statistically significant.

3. Results and discussion

3.1. Structure and configuration of the HUTR

Fig. 1 shows the side, top and diagonal views of the high-intensity ultrasonic tubular reactor (HUTR) drawn using AutoCAD 2013. The sonication chamber is located in the center of the HUTR system to provide uniform US treatment (see Fig. 1a–c). This can increase the possibility of promoting a radial propagation of acoustic waves with high energy level across the axis of tube [36]. The sonication compartment is able to hold up to 600 mL of liquid. It should be stressed that the operating processor of the current US reactor is sync to computer software. This promotes the on-site monitoring of various operating conditions of the HUTR during the sonication process, including the temperature of sonication medium, frequency variation, as well as the electrical input and US power to the sonication medium. In current



report, to evaluate the potential of HUTR as an alternative technique for industrial applications involving acoustic waves, the performance of HUTR in preparing Pickering emulsion stabilized by non-toxic food grade CNC has been carried out to act as a practical example for application involving ultrasound cavitation and the outcomes are further related to the active cavitation zones analysis using sonochemiluminescence (SCL) imaging.

3.2. Characteristics of cellulose nanocrystal

(1)

Prior to emulsion preparation, the characteristics of the CNC is first determined. The surface properties, including the wettability and colloidal stability of a particle are the main features that determined the Pickering stabilizing performance of the solid particles. Here, the surface morphology of the purchased CNC was determined via FESEM imaging under STEM mode. The STEM image revealed that CNC has a rod-like structure with diameter of 5–7 nm and length ranging from 150 to 250 nm (Fig. 2a). On the other hand, the surface wettability of CNC was determined by measuring the contact angle of a water droplet when in contact with a CNC-coated glass slide. From Fig. 2b, it was clear that the deposition of CNC on the glass slide results in a small but significant rise in the contact angle, indicating the increased hydrophobicity of the glass slide upon coating with CNC. Lastly, the surface charge of CNC was measured in term of zeta potential using a zetasizer to determine its colloidal stability. It should be stressed that sulphuric acid-hydrolysed CNC contained a certain concentration of sulphate half-ester groups on its surfaces. This results in high surface charges, and therefore a high electrostatic repulsion between the CNC particles at the interface that eventually affected their ordering at the oil-water interfaces [37]. Thus, it is not possible to form stable Pickering emulsion without the addition of NaCl. As expected, the CNC exhibits a high zeta-potential (-70 mV) without the presence of salt for charge screening (Fig. 2c). The measured zeta-potential values then progressively reduced with addition of salt, and subsequently entered a low charge domain with a zeta potential value of -25 mV with NaCl content of 30 mM onwards (Fig. 2c). Thus, the salt concentration of 30 mM is used for all the following Pickering emulsion preparation.

3.3. Preparation of Pickering emulsion using HUTR

Emulsions prepared at different US power using the HUTR are compared at different sonication time. To illustrate these comparisons, Fig. 3 shows the droplet size obtained by sonicating the emulsions containing 0.5 wt% CNC, 30 mM NaCl and 10 wt% red palm oil at 100, 200 and 300 W. It is clear from Fig. 3a that the increase in both US power and sonication time resulted in smaller oil globule. Pickering emulsions with smallest size (1.5 µm) were obtained under 300 W and 15 min sonication time. This can be explained where the increase in both US power and sonication time caused higher cavitation activity in the reactor and thus higher shear applied to droplets. As a result, the oil globule experienced a more violence microjet shearing from the cavitation bubbles that further breaking the coarse emulsion droplets into finer ones [38,39]. To verify the above-mentioned claims, we determined the cavitation activity in the HUTR via SCL photography. SCL is one of the commonly utilized methods to characterize the cavitation activity in US equipment [40]. Fig. 4a(iii)-(v) shows the SCL images from the top view of the HUTR upon sonication at different power modes. It can be noticed that the "hot spots" generated from SCL has covered the entire processing medium of the reactor. The SCL intensity has escalated gradually from 43.55 \pm 3.58 to 72.76 \pm 2.77 unit as the US power increased from 100 to 300 W (Fig. 4b). This indicates an increment in the amount of hydroxyl radicals generated in the HUTR as the US power increased, suggesting that a more uniformly distributing cavitation profile could be attained at higher US power. The Fricke dosimetry results showed the increase of hydroxyl radicals from 0.012 to 0.051 mmol/dm³ at increasing US power increased from 100 to



(c)

NaCl Content (mM)

Fig. 2. (a) Surface morphology of CNC. (b) Wetting behaviours of plain (i) glass slide and (ii) CNC with their respective contact angle values. (c) Surface zeta potential of CNC as a function of NaCl concentration, red dotted line indicates the boundary magnitude between high and low zeta potential value. Error bar represents standard error in measurement. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. Mean droplet diameter of CNC-stabilized Pickering emulsions prepared respectively using US horn and HUTR at different sonication time at designated US power. Error bar represents standard error in measurement.

300 W (15 min sonication time) (Fig. A1).

For comparison purposes, CNC-PEs were also prepared using US horn system. From Fig. 3, it is clear that the mean diameter of Pickering

emulsions prepared by US horn were larger than those prepared by HUTR, with recorded mean emulsion diameter of 12.75 vs 7.40 μ m for US horn vs HUTR respectively even though the operating US powers are identical. The observed outcome is plausible because the active cavitation areas of US horn are limited to the area below the probe tip (see Fig. 4a(ii)). In comparison, the HUTR is able to provide a homogeneous cavitation medium (see sonochemiluminescence images from Fig. 4a (iii)–(v)) with higher SCL intensities as compared to those obtained using US horn (43.55 \pm 3.58 vs 33.42 \pm 3.12 arb. unit). The results showed that the Pickering emulsions in the reactor can be effectively processed even at large scale and thus demonstrated the practicality of the pilot-scale HUTR as effective US equipment for emulsion preparation.

To further analyse the emulsion produced using the HUTR, the evaluation was related to the distribution of emulsions droplets as function of power and time. Fig. 5a–c displayed the droplet size distribution of samples at 1, 7 and 15 min, correspondingly for the US horn- and HUTR-induced Pickering emulsion at 100, 200 and 300 W US power while their respective coefficient of variation (CV) was calculated using Eq. (1) and plotted in Fig. 6. For HUTR, it can be observed that the initial distribution of emulsion droplets was a single peak with located around 50 μ m (Fig. 5a), with low CV (30% < , Fig. 6). The droplet distribution then turned highly polydispersed (CV \approx 36%) when the emulsions were sonicated to 7 min regardless of the applied US power (Fig. 5b). Further increasing the US power and sonication





time to 15 min results in the reduction of CV (\approx 32%) and the shifting of the highest peak towards the smaller droplet diameter ranges (Figs. 5c and 6). This indicated the reduction of mean diameter of the Pickering emulsion and it is most likely due to the reduced viscosity of the emulsion medium at long sonication time. The temperature increment during sonication is a well-known phenomenon, and since viscosity reduced with increasing temperature [41], prolonged US cavitation

results in reducing viscosity of the sonication medium. At lower viscosity, the energy threshold for cavitation induced by US decreased [42]. This facilitates a more violent cavitation effects and thus resulting in easier formation of Pickering droplets with smaller diameter.

For US horn-induced CNC-PEs, although the volume density of the peak located around $1 \,\mu m$ gradually increased at higher sonication time, the dual peaks were still observed around 1 and 100 μm at 15 min



Fig. 4. (a) Sonochemiluminescence images obtained from US Horn and HUTR sonication at different US power: (i) no US (control), (ii) US Horn 100 W, (iii) HUTR 100 W, (iv) HUTR 200 W and (v) HUTR 300 W. (b) SCL emission upon sonication using US horn and HUTR at different US power. Error bar represents standard error in measurement. Different alphabetic letters were significantly different at $P \le 0.05$ by Bonferroni's Multiple Comparison Test.

Fig. 5. Droplet size distribution data of CNC-PE prepared respectively using US horn and HUTR at (a) 1, (b) 7 and (c) 15 min sonication time at designated US power.



Fig. 6. Coefficient of variation for CNC-stabilized Pickering emulsions prepared respectively using US horn and HUTR at different sonication time at designated US power.

of sonication time (Fig. 5a–c), with a comparatively higher CV (36%) as compared to those prepared using HUTR at 100 W power (31%) (Fig. 6). This suggested that some CNC-PEs were possibly not treated uniformly even at longer sonication time due to the poor cavitation distribution ability of US horn (Fig. 4).

A quick examination on coalescence stability of CNC-PE sonicated for 15 min at different US power for both the US horn and HUTR was carried out over a storage period of 30 days. The coalescence stability of the Pickering emulsions has been evaluated by studying the evolution of mean emulsion diameter and zeta potential upon storage for 30 days. One could observe that the mean emulsion droplet size of CNC-PE prepared using HUTR respectively at 200 and 300 W US power remained the same over the designated 1-month storage period. On the other hand, the US horn-induced CNC-PE droplet size experienced a gradual increment in mean droplet size from day 0 to day 20 (Fig. 7). The observed phenomena are likely to be contributed by the stabilizing behaviours of CNC onto the interfaces between oil and water. As shown in Eq. (2), an amount of energy is required for attachment/detachment of a single particle onto the interface between two immiscible liquids. Hence low energy input may result in an incomplete attachment of



Fig. 7. Changes in mean emulsion diameter of CNC-PE prepared at different US power using US horn and HUTR upon 30 days of storage. Error bar represents standard error in measurement.



Fig. 8. Changes in zeta potential of CNC-PE prepared at different US power using US horn and HUTR upon 30 days of storage. Error bar represents standard error in measurement.

particles onto the interfaces, which thus caused the resultant Pickering emulsion with only temporal stability to coalesce into larger droplets. Based our fluorescent microscopic images, some dispersed CNC were found to be unabsorbed or unattached to the oil globules (yellow-circled region) after subjected to 100 W HUTR sonication (Fig. A2).

$$\Delta E = \pi r^2 \gamma_{ow} (1 - \cos \theta_{ow})^2 \tag{2}$$

where E is the attachment/detachment energy, r is the radius of emulsion droplets, γ_{ow} is the interfacial tension and θ_{ow} is the interfacial contact angle.

Based on our zeta potential measurement data, the net negative surface charge of the emulsion droplets prepared by US horn was found to decrease slightly after 2 weeks of storage at room temperature. All the HUTR-induced emulsions appeared to be relatively stable with an average zeta potential of about – 40 mV during 1-month storage period (Fig. 8). The results further demonstrated the better storage stability of the HUTR-induced CNC-PE as compared to those prepared by US horn.

4. Conclusion

In this work, a high-intensity ultrasonic tubular reactor (HUTR) was utilized to prepare palm olein Pickering emulsion stabilized by CNC. The results showed that the sizes of Pickering emulsions reduced with increasing US power and US irradiation time owing to the improved uniformity of cavitation activity in the HUTR. The cavitation activities of HUTR have been identified by sonochemiluminescence. The outcomes showed that HUTR can provide a more uniform cavitation activity in the sonication medium as compared to conventional US horn system. The CNC-PEs with smallest size of 1.5 µm were successfully produced under the US power and sonication time of 300 W and 15 min respectively and its size remained almost unchanged up to 30 days storage. In comparison to US horn system, the mean diameter of emulsions prepared using the HUTR at 100 W is found to be smaller $(7.40 \,\mu\text{m})$ with narrower distribution (CV = 31%) than those prepared using US probe sonicator (12.75 μ m, CV = 36%). This is mainly attributed to its unique tubular reactor design configuration that promotes effective cavitational activity within the emulsification chamber. The current investigation on the HUTR offers an alternative strategy for industrial processing of Pickering emulsions.

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Appendix

See Figs. A1 and A2.



Fig. A1. OH radicals generated upon US horn and HUTR sonication at different time. Error bar represents standard error in measurement.



Fig. A2. Fluorescent micrographs of CNC-PE prepared by HUTR at (a) 100 W and (b) 300 W. The yellow-circled region indicated the location of unabsorbed CNC particles (blue halo). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2019.02.008.

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