

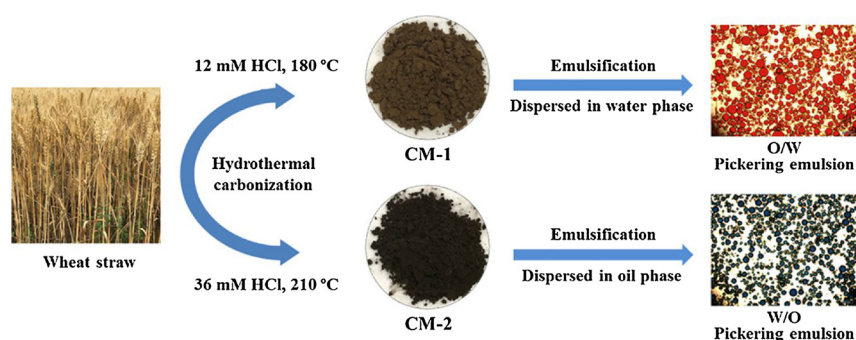
Pickering emulsions stabilized by amphiphilic carbonaceous materials derived from wheat straw

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GRAPHICAL ABSTRACT



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ABSTRACT

Amphiphilic carbonaceous materials CM-1 and CM-2 were synthesized through the hydrothermal carbonization (HTC) of wheat straw powder. The samples were examined by scanning electron microscopy, Fourier–transform infrared spectroscopy and elemental analysis. The results showed that acid concentration and temperature greatly affected the surface properties and wettability of the carbonaceous materials during hydrothermal carbonization. The carbonaceous materials were then used to stabilize Pickering emulsions. CM-1 generated oil-in-water (O/W) Pickering emulsions, while CM-2 generated water-in-oil (W/O) Pickering emulsions. The effects of homogenization speed, particle concentration, dispersed phase to continuous phase volume ratio, pH, and oil type on the morphology, droplet size, size distribution, and stability of the emulsions were investigated. The obtained emulsions exhibited remarkable stability and were easily separated by filtration. This novel strategy for preparing emulsions using CM-1 and CM-2 was highly advantageous for the recovery and reuse of stabilizers.

1. Introduction

Recently, Pickering emulsions have received extensive attention in food science [1], drug delivery [2], biphasic catalysis [3], and the preparation of porous materials [4]. Pickering emulsions are emulsions stabilized by solid particles [5,6]. By employing appropriate particles,

common oil-in-water (O/W) and water-in-oil (W/O) type emulsions, as well as complex multiple emulsions, can be formed [5]. Compared with traditional surfactants, solid particles have many advantages as stabilizers, including environmental friendliness, low cost, and recyclability [7]. Most importantly, solid particles can adsorb irreversibly at oil–water interfaces [8], forming extremely stable emulsions.

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The characteristics, namely type and stability, of a Pickering emulsion are thought to be determined by the nature of solid particles, such as size, shape, and, particularly, wettability [9,10]. To adsorb at biphasic interfaces, solid particles must be partly wetted by the oil and water phases [11]. Therefore, particles with extreme hydrophilic or hydrophobic surfaces cannot form Pickering emulsions [9,12,13]. Accordingly, most solid particles must be modified to obtain a specific surface polarity for efficient emulsification. As the modification procedures are usually tedious and time-consuming, the development of more cost-effective and generally available solid particles as efficient stabilizers is important [14,15].

In the past decade, the hydrothermal carbonization (HTC) process has been successfully used to transform biomass into carbonaceous materials [16–18]. For example, we have produced carbonaceous microspheres from the direct hydrothermal treatment of yeast cells, whose cell walls consist mainly of glucan [19]. Interestingly, such carbonaceous materials have been found to display amphiphilic property without any post-modification, allowing stable dispersion in both water and nonpolar organic solvents. These carbonaceous materials have subsequently been demonstrated as effective stabilizers of Pickering emulsions [3].

Straw is among the most abundantly available biomasses in the world. HTC can convert straw into carbon-rich solid particles known as hydrochar [20]. Hydrochars exhibit large surface areas and high contents of oxygen-containing functional groups. Extensive effort has been directed toward the beneficial use of hydrochars as adsorbents [21], catalysts [22], CO₂ sequestration substrates [23] and fuels [24,25]. However, the application of hydrochars as stabilizers in Pickering emulsions has yet to be reported. This study is focused on investigating the feasibility of using amphiphilic carbonaceous materials (CMs) obtained by the HTC of wheat straw powder as stabilizers in Pickering emulsions. The results showed that the wettability of CMs could be adjusted by varying the hydrothermal conditions. As a result, both O/W and W/O type Pickering emulsions were obtained with high long-term stability. Furthermore, the stabilizers were easily recovered and reused.

2. Materials and methods

2.1. Materials

Wheat straw powder was crushed and passed through 200-mesh sieve. HCl, NaOH, styrene, cyclohexane, isooctane, *n*-heptane, toluene, ethanol, and methylene blue (MB) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sudan III was obtained from Sigma-Aldrich. All chemicals above were of analytical grade and used directly without further treatment.

2.2. Synthesis and characterization of CMs

CMs were synthesized by mild hydrothermal treatment of wheat straw powder. Typically, straw powder (3 g) was dispersed in 0–60 mM HCl solution (30 mL), transferred to a 40 mL Teflon-sealed autoclave, and heated. After 12 h, the resulting slurry was isolated by centrifugation and washed to neutrality using deionized water and ethanol. After drying and grinding, the CMs samples were obtained. The sample properties depended on the HCl concentration and hydrothermal temperature. CM-1 was obtained using 12 mM HCl at 180 °C, while CM-2 was obtained using 36 mM HCl at 210 °C.

The sample morphologies and sizes were analyzed by SU8010 scanning electron microscopy (SEM; Hitachi, Honshu, Japan). The sample surface properties were analyzed by Magna 750 Fourier-transform infrared spectroscopy (FTIR; Nicolet, Wisconsin, USA) in the spectral region 4500–500 cm⁻¹. The C, H, N, and O contents of the samples were measured using a Flash 2000 elemental analyzer (Thermo, Wisconsin, USA). Atomic ratios (O + N)/C, O/C, and H/C were calculated from the elemental contents. Sample contact

Table 1
Pickering emulsion formulations.

Factors	O/W Pickering emulsion	W/O Pickering emulsion
Homogenization speed	2 wt% CM-1, 1:2 R_{dc} , 3000–6000 rpm	4 wt% CM-2, 1:1 R_{dc} , 3000–6000 rpm
Particle concentration	1:2 R_{dc} , 1–5 wt% CM-1	1:1 R_{dc} , 3–7 wt% CM-2
Volume ratio of dispersed phase to continuous phase (R_{dc})	3 wt% CM-1, 3:1–1:5 R_{dc}	6 wt% CM-2, 3:1–2:3 R_{dc}

angles were measured by a direct compression method using a JC2000C optical contact angle-measuring device (Zhongchen, Shanghai, China). Sample compression was measured using an FW-4 powder pressing machine (Tuopu, Tianjin, China).

2.3. Preparation and characterization of Pickering emulsions

Typically, solid particles were dispersed in the continuous phase with ultrasonication for 10 min. The dispersed phase was then added to the suspension and the mixture was emulsified for 2 min using Tube Drive Control Workstation (IKA, Staufen, Germany). The Pickering emulsion formulations are shown in Table 1, where R_{dc} is the volume ratio of dispersed phase to continuous phase.

Optical micrographs of Pickering emulsions were obtained using a Motic B Series microscope (Motic, Fujian, China). Emulsion droplet diameters were measured using Motic Images Plus 3.0 software. Pickering emulsion stability was investigated by comparing the initial morphology of the Pickering emulsion with that after allowing to stand at room temperature for a period of time.

The total volume of the two phases was fixed at 6 mL. Aqueous and oil phases were deionized water and styrene, respectively.

3. Results and discussion

3.1. Characterization of CMs

CM-1 and CM-2 were fabricated through the hydrothermal carbonization of raw wheat straw powder. CM-1 retained the fibrous structure and smooth surfaces of the wheat straw, but with the length decreased from 60–90 μm to 40–70 μm (Fig. 1b). In contrast, CM-2 mainly comprised small blocks of smaller particles, with only a few retaining the fibrous structure with lengths of 20–50 μm (Fig. 1c and d). These results suggested that CM-2 underwent dramatic collapse during the hydrothermal carbonization process.

The FTIR spectrum (Fig. 2) showed that aliphatic CH₂ units on the surface of wheat straw (bands at 2987.83, 2933.49, 2901.04, and 2895.81 cm⁻¹ attributed to aliphatic CH₂ units) were not destroyed in the hydrothermal carbonization process [26]. The peaks at 1113.81, 1105.25, 1055.94, 1034.26, and 1031.69 cm⁻¹ represented aliphatic C–O and alcohol O–H stretching vibrations [23,27,28]. The intensities of these bands decreased in the order straw > CM-1 > CM-2, which indicated that the amount of oxygen groups on the straw surface was reduced during hydrothermal carbonization, with the CM-2 surface having fewer oxygen groups than the CM-1 surface. Bands at 1594.00, 1511.30, 1509.94, and 1457.80 cm⁻¹ were assigned to C=C framework vibrations in the aromatic ring [27]. The intensities of these bands increased in the order straw < CM-1 < CM-2. Furthermore, new bands were observed on the surface of CM-2, including aromatic C=O stretching vibrations at 1701.02, 1604.12, and 1603.27 cm⁻¹ [28], C–O and phenolic O–H stretching vibrations of aromatic rings at 1208.64 cm⁻¹ [27], and aromatic C–H out-of-plane bending vibrations at 838.25 cm⁻¹ [29]. These results suggested that the aromaticity of the straw was enhanced by hydrothermal carbonization.

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