

Preparation and characterization of biobased microspheres from lignin sources



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ABSTRACT

Lignin microspheres of uniform spherical shape and narrow size distribution were successfully prepared from a number of different lignins using emulsion solvent evaporation (ESE) technique. Four lignins were examined in this study include; lignin isolated from non-wood/hardwood biorefinery residue (L1), isolated lignin from hardwood kraft black liquor (L2), technical kraft softwood lignin (L3) and technical soda non-wood lignin (L4). Lignin microspheres were prepared from acetyl derivatized lignin and from a solubilized lignin fraction. Dynamic light scattering (DLS) was used to determine particle diameter, size distribution and polydispersity of lignin microspheres. Scanning electron microscopy (SEM) was used to determine morphology of the lignin microspheres. Uniform lignin acetate microspheres were successfully produced from the four lignins in a size range of 1280–1349 nm in dichloromethane and 1313–2545 nm in ethyl acetate. The ethyl acetate soluble fraction of L2 and L4 was formed into spherical shape with the size of 1152 nm and 875 nm, respectively.

1. Introduction

Over 70 million tons per year of lignin is produced as by-product from biomass utilization (Doherty et al., 2011; Lievonen et al., 2016). The majority (~95%) is burned directly to produce energy, and only a small portion (~5%) is used for value added products. The largely unknown molecular structure, variable molecular weight and variable functionality have been roadblocks to higher value uses (Lievonen et al., 2016; Lora and Glasser, 2002). However, the growing interest in sustainable chemicals has led to lignin's use in phenol formaldehyde resin (Mankar et al., 2012; Zhang et al., 2013), polymer blends and composites (Reza Barzegari et al., 2012; Schorr et al., 2014; Thakur et al., 2014), polyurethane (Arshanitsa et al., 2016; Griffini et al., 2015; Li et al., 2017; Nacas et al., 2017; Wang et al., 2017) and polyurethane foam (Cateto, 2008; Huang and Zhang, 2002). To date, lignin nano- and micro-particles have been studied as agricultural active controlled release (Asrar and Ding, 2010; Fernandez-Perez et al., 2011), nano-sized coatings (Popa et al., 2011), filler in composites (Garcia Gonzalez et al., 2017; Jiang et al., 2013; Nair et al., 2014; Yang et al., 2015), controlled drug release (Chen et al., 2016; Chowdhury, 2014), food industry fat mimetics (Stewart et al., 2014), bio-based adhesives, stabilizers, crop additives (Lievonen et al., 2016) and sorbents for heavy metal ions and other environmental pollutants (Frangville et al., 2012).

Spherical lignin microparticles (lignin microspheres) have potential

to be used for controlled release of agricultural actives (i.e. fertilizers, herbicides and pesticides). It is important to note that lignin as a bio-based matrix in such formulations is safer for the environment in comparison with synthetic polymers because it is applied directly into the soil (Dubey et al., 2011; Wilkins, 1983). In addition, uniform spherical shapes of the microparticles provide a steadier release of the actives than the particles which are irregular in shape (Asrar and Ding, 2010). Furthermore, lignin-based microparticles make the formulation economically viable due to dual function as soil stabilizer and carrier for the agricultural actives. It should also be noted that the manufacturing of lignin-based microspheres is feasible with conventional equipments (Asrar and Ding, 2010).

Polymer microspheres can be prepared through emulsion solvent evaporation (ESE) (Ansari et al., 2012; Freiberg and Zhu, 2004; Ravi et al., 2008). The ESE method is based on the emulsification of two phases; an organic phase (water-immiscible organic solvent and solubilized polymer) and an aqueous phase (surfactant and water). Fig. 1 shows the steps in ESE method; (A) phase preparation (B) intermix, (C) solvent removal, and (D) solidification. In the mixing step, an emulsion of oil droplets which contain the polymer and the organic solvent is formed by agitating the mixture at high share rate. Then the organic solvent is evaporated from the system using low share mixing. The microparticles are formed in the solidification step as the organic solvent is completely removed from the system.

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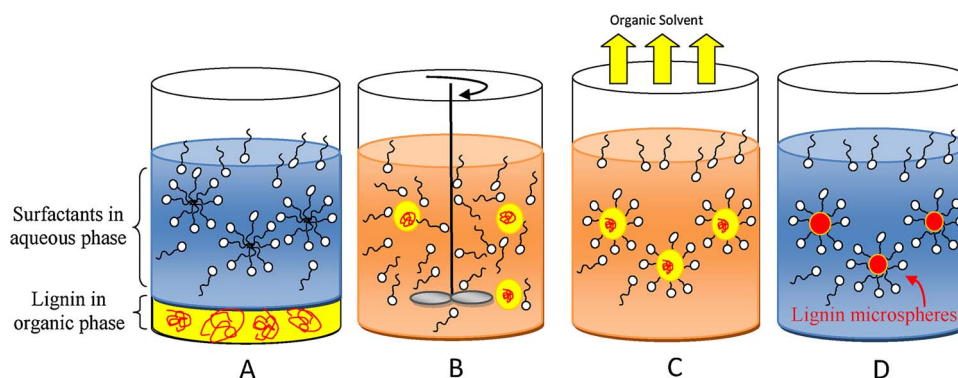


Fig. 1. Preparation of lignin microspheres A) phase preparation, lignin in organic phase and surfactant in aqueous phase, B) intermix, C) solvent evaporation D) solidification.

Excellent microsphere formation is highly dependent on the right choice of organic solvent. A suitable organic solvent will have a low boiling point and low miscibility in water and is capable of solubilizing the lignin polymer (Li et al., 2008; Soppimath and Aminabhavi, 2002). Dichloromethane (DCM), ethyl acetate (EA) and chloroform are suitable solvents for ESE because they have the capacity to dissolve polymers, do not have high solubility in water and their boiling point is lower than the boiling point of water. Among these organic solvents DCM is a commonly used solvent for formation of microsphere due to its low boiling point, low miscibility with water and dissolves most polymers. However, lignin has a very low solubility in DCM and is also relatively insoluble in most common organic solvents because of its hydrophilic functional groups (i.e. aliphatic hydroxyl) (Sameni et al., 2017; Shukry et al., 2008). In order to improve lignin solubility in organic solvents, acetylation, substitution of the hydroxyl groups with acetyl, can be employed (Olarte, 2011). It is also important to note that DCM is a carcinogen according to the environmental protection agency (EPA), and therefore it is important to identify a solvent which does not have negative environmental and health impacts for the ESE method (Birnbaum et al., 2000; Sah, 1997; Soppimath and Aminabhavi, 2002).

Evaluation of the lignin microspheres is based on the microsphere size, size distribution, uniformity and morphology. Dynamic light scattering (DLS) and scanning electron microscopy (SEM) were used for the evaluation. The theory of solvent diffusion/evaporation is reviewed in order to elucidate the mechanism of lignin microspheres formation by the ESE method. In addition, EA soluble lignin was evaluated for its ability to form lignin microspheres. The objective of this study is to identify the effect of lignin's molecular weight, the type of organic solvents (i.e. DCM and EA) and the degree of solubility of lignin in organic solvents on the formation of lignin microspheres.

2. Experimental

2.1. Materials

There were four lignins used in this study. L1 lignin was isolated from industrial residue generated at a bioethanol plant in United States. This plant uses hardwood and non-wood species in their process. L2 lignin was isolated from the black liquor of a kraft pulp mill located in Botucatu, Brazil where the predominant species was eucalyptus. The lignin extraction method used to derive L1 and L2 was described in a previous paper (Sameni et al., 2016). L3 is a technical softwood kraft lignin (Indulin AT) produced by MeadWestvaco Corporation, Charleston, SC, USA. L4 is a technical non-wood soda lignin (Protobind 2000) produced in ALM, Chandigarh, India. The lignin content of L1, L2, L3 and L4 samples was reported 90.5, 92.3, 93.1 and 95.1, respectively (Sameni et al., 2016).

The organic solvents were purchased as follow: Dichloromethane (DCM) (Caledon, Georgetown, Canada), ethyl acetate (EA) (Caledon, Georgetown, Canada), Pyridine (Caledon, Georgetown, Canada),

polyvinyl alcohol (PVA) (Sigma-Aldrich, Oakville, Canada), acetic anhydride (Caledon, Georgetown, Canada).

2.2. Acetylation

Acetylation of lignin was carried out by method described by Olarte (2011). Briefly, 2.0 g oven-dried lignin was added to 80 mL of pyridine-acetic anhydride (1:1) mixture. After 24 h mixing in a sealed container, the solids were precipitated with 300 mL of 0.1N HCl solution. The solid was filtered and washed with 0.1N HCl solution and 2–3 times with deionized water. The solid was collected and dried at 40 °C overnight and sealed in an air tight vial for further study.

2.3. Preparation of lignin and lignin acetate microspheres

Lignin acetate microspheres were produced following the method described in a previous study, Sameni et al. (2015). Briefly, 20 mg lignin acetate was dissolved in 2 mL of either DCM or EA. The organic phase was homogenized (10,000 rpm for 30 s) with 20 mL polyvinyl alcohol (0.2% w/v). One hundred mLs of water was added to the emulsion and stirred for 3 h with magnetic stirrer in an open beaker to remove the solvent. Next, the mixture was centrifuged for 10 min at 9000 rpm, and twice washed with deionized water. The solids were freeze-dried and sealed in air tight vial for further study.

Lignin microspheres were prepared from the ethyl acetate solubilized lignin. The soluble portion was collected after filtration of the ethyl acetate solution using a 10–15 μm pore-size filter crucible. The solvent from the soluble part was removed by using a rotary evaporator and was dried at 50 °C overnight. The soluble portion of lignin was found to be 23.7, 42.7, 8.8 and 60.6%w/w for L1, L2, L3 and L4, respectively. The lignin microspheres were prepared in the same manner as the acetylated lignins. The emulsion was prepared by homogenizing a mixture of organic phase (20 mg of solubilized lignin in 2 mL of EA) and aqueous phase (20 mL polyvinyl alcohol with concentration of 0.2% w/v) at 10,000 rpm for 30 s. Next 100 mL distilled water was added to the emulsion and the organic solvent was removed through magnetically stirring for 3 h in an open beaker. After formation of the particles and solvent removal, the colloid was centrifuged for 10 min at 9000 rpm and twice washed with deionized water. Finally, the microspheres were freeze dried and stored in air tight glass vials.

The yield was determined by measuring the mass of freeze-dried microspheres divided by the mass of the starting lignin or lignin acetate. Table 1 indicates the naming protocol for the lignin and lignin acetate microspheres that were prepared with DCM and EA.

2.4. Particle size determination

The average microsphere diameter (Z-Ave), size distribution and polydispersity index (PDI) of the samples were analyzed using Zetasizer (Nano ZS, Malvern Instrument, UK). Note that particle size in the text

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