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The potential of Kraft black liquor to produce bio-based emulsion-templated porous materials

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ABSTRACT

Emulsion-templated porous monoliths based on castor oil-in-black liquor and on 1,2-dichloroethane-in-black liquor medium internal phase emulsions have been prepared in order to evaluate a possible valorisation of that undervalued by-product of the paper mill Kraft process. The cross-linking behaviour of the different polymers originally contained in the black liquor was investigated. It appears that both lignin and hemicellulose fragments are involved. Characterisation of the monoliths by scanning electronic microscopy and mercury intrusion porosimetry showed that using either castor oil or 1,2-dichloroethane allowed to obtain macrocellular morphology along with a high porosity. However, higher concentration of the internal phase is possible in emulsions prepared with 1,2-dichloroethane than with castor oil, leading to more attractive materials from both chemical and environmental aspects.

1. Introduction

The principle of preparation of porous polymers through concentrated emulsions lies on the mixing of two non-miscible fluids, leading to the formation of a HIPE (high internal phase emulsion) or a MIPE (medium internal phase emulsion) from which the external (continuous) phase is converted into a polymeric structure and the internal phase is removed leaving behind voids often called cavities. These cavities are generally interconnected by circular holes often called windows. The materials presents an open porous structure and are generally referred as polyHIPEs (polymerized high internal phase emulsion) when the internal phase (dispersed droplets) constitutes more than 74% of the volume, and as polyMIPEs (polymerized medium internal phase emulsion) when it comes down to 54% [1]. Poly(M)HIPEs based on poly(styrene–divinylbenzene) copolymers are the most widely studied systems. However, the use of bio-polymers as starting material would be of great interest in a Green Chemistry approach. The dissolution of wood by alkali media during the preparation of paper pulp in the Kraft process leads to the production of a by-product called black liquor. Its production is up to 1.5 tons for 1 ton of paper pulp. Black liquor is an aqueous alkaline mixture containing dissolved degraded lignin and hemicellulose fragments coming from the wood that is digested during the Kraft process [2]. Those bio-polymers composed approximately 70% w/w of the solid matter of black liquor [3]. Therefore, black liquor can be considered as a renewable feedstock. Due to the supply of bio-polymers that Kraft black liquor can represent, it deserves more valorisation than its present use as low-grade fuel. The original purpose of our study was to prepare efficient and sustainable porous materials by taking into account the Green Chemistry principles [4]. The large variety of preparation techniques used to synthesize these materials has allowed researchers to obtain a collection of porous monoliths exhibiting different properties which render them suitable to a wide range of applications. These materials act as candidates as adsorbents [5], catalyst supports [6–8], electrodes for batteries [9–11], or double-layer capacitors [12,13]. We have recently developed an original approach allowing the preparation of macroporous interconnected monolithic materials with Kraft black liquor as main raw material [14]. The process involves the formulation of an oil-in-water MIPE as soft templating medium. The oil (internal or dispersed phase) used is a non-edible vegetable oil, whereas the continuous phase is constituted of black liquor containing a hydrophilic surfactant and epichlorohydrin as crosslinking agent. We have shown in previous studies [15] that epichlorohydrin reacts totally with the polymers in black liquor, therefore the problem of its potential toxicity seems to be largely solved. The use of castor oil as disperse phase allows the formulation of stable MIPEs, leading to macrocellular biopolymers

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(polyMIPE) and contributes to the "greenness" approach of this study as castor oil can be considered as a renewable feedstock [16]. However, the very high viscosity rapidly reached by the emulsion limits the maximum volume fraction of internal phase inserted to a value of about $\phi = 0.54$, even when using an efficient emulsification technique. This behaviour prevents to the preparation of highly porous and highly interconnected monoliths and hence limits the potential applications of the process. More recently, we have shown that application of the Life Cycle Assessment (LCA) methodology to the replacement of castor oil by 1,2-dichloroethane (DCE) in the preparation of polyMIPE from black liquor indicates unexpected important environmental benefits when using the latter [17]. The present paper reports a comparative description of the morphology of the materials obtained using both castor oil and 1,2-dichloroethane as the internal phase in oil-in black liquor emulsions to prepare porous materials. Moreover the cross-linking behaviour of the black liquor components has been investigated.

2. Experimental

2.1. Materials

Crude Kraft black liquor collected from a local paper mill (Smurfit Kappa Cellulose du Pin Kraft paper mill, Facture, France) was used as received. Castor oil, epichlorohydrin, DCE, Kolliphor® EL, sulphuric acid, sodium hydroxide pellets, ethanol and propan-1-ol were purchased from Sigma–Aldrich and used as received. The densities of DCE and castor oil are 1.25 g cm^{-3} and 0.95 g cm^{-3} respectively and their viscosities are 0.84 mPa s and 950 mPa s at 20 °C, respectively.

The as-received Kraft black liquor comes as a viscous, black liquid. Its major physico-chemical properties are: dynamic viscosity $\mu = 7000$ mPa s at 23 °C; pH = 14 (solution diluted to 5% dry matter); density $\rho = 1.3$ g mL^{-1}; dry matter amount = 50 wt.%. Phenol group content (0.5 mmol g^{-1}) and total hydroxyl group content (0.8 mmol g^{-1}) of black liquor were determined according to a published procedure [14].

2.2. Synthesis

2.2.1. Formulation of stable castor oil-in-black liquor MIPEs

Synthesis of medium internal phase emulsion from black liquor using castor oil as dispersed phase has been previously reported [14,16]. Briefly, a mixture of black liquor (25 g), epichlorohydrin (2.77 g), castor oil (23.67 g) and Kolliphor® EL (1.1 g) was placed into a double syringe-pump device [18]. Backwards and forwards movements of the plungers were induced by an electric motor and a rod. The rate of passage of the whole emulsion through the connecting tube was adjusted to 10 round-trip per minute. The emulsification time was 80 min.

2.2.2. Formulation of stable DCE-in-black liquor (M/H)IPEs

Due to the low viscosity of DCE compared with castor oil, a different emulsification device was used allowing the gradual adding of the solvent, but requiring scaled-up quantities of chemicals. In a typical experiment, a mixture of black liquor (82.5 g), epichlorohydrin (8.8 g) and Kolliphor® EL (18.7 g) was placed in a cylindrical, round-bottomed reactor thermostated at 50 °C. The reactor was then sealed to avoid solvent evaporation. The mixture was stirred at approximately 300 rpm with a rod fitted with one radial and one axial six blades impellers, connected to an overhead stirrer motor. Together, DCE was added dropwise at a rate of 1.0 mL min^{-1}, until no more organic solvent insertion was visually observed. Concentrated emulsions presenting a maximum internal phase volume fraction of $\phi = 0.74$ were thus prepared.

2.2.3. Preparation of Kraft lignin HIPEs

Lignin was precipitated from black liquor by acidification using sulphuric acid (ca. 96% in water). The acid was added dropwise to the black liquor under stirring until pH = 1. A brown precipitate appeared that was filtered, washed with distilled water until pH = 5–6 and then eventually isolated by centrifugation. 23.94 g of dried lignin was dissolved in 23.94 g of an aqueous solution of sodium hydroxide (30 wt.%) to obtain an alkali solution of precipitated Kraft lignin. To compose the continuous phase, 10.85 g of Kolliphor® EL and 5.11 g of epichlorohydrin were added to the lignin solution and the resulting mixture was placed in a cylindrical, sealed, round-bottomed reactor thermostated at 50 °C. The mixture was stirred at approximately 300 rpm with a rod fitted with one radial and one axial six blades impellers, connected to an overhead stirrer motor. DCE (181.67 g) was then added dropwise at a rate of 1.0 mL min^{-1} using a syringe pump under constant mechanical stirring, leading to an emulsion with an internal phase volume fraction of $\phi = 0.74$.

2.2.4. Preparation of the monoliths

The obtained thick black emulsions were placed in tightly closed polytetrafluoroethylene cylindrical moulds ($\varnothing = 4.5$ cm, $h = 1.5$ cm), and heated for 24 h at 60 °C in an oven for crosslinking.

2.2.5. Monoliths drying and solvent recovery

The dispersed phase and the residual water coming from black liquor have to be removed preferentially at the same time for sake of simplicity of the drying process. Furthermore, all organic solvent involved have to be recycled as efficiently as possible. An exhaustive washing of the liquid-filled monoliths with a short chain alcohol such as methanol or ethanol followed by drying of the monolith is usually the preferred method. Therefore, castor oil-containing monoliths were extracted with ethanol in a Soxhlet apparatus (48 h). The monoliths were finally dried under a hood to constant weight. Ethanol was recovered by distillation under reduced pressure using a rotary evaporator and reused without further purification. Castor oil could not be recycled as it was degraded during the monolith synthesis, probably through saponification by the high soda level of black liquor. In the case of DCE, the existence of DCE/methanol (40/60 w/w, boiling point = 60 °C) and DCE/ethanol (50/50 w/w, boiling point = 70.5 °C) azeotropes precludes this route if the recycling of DCE is expected to be performed. For that reason, propan-1-ol was chosen as extracting solvent as no azeotropic composition appears to exist with DCE. DCE-containing monoliths were then extracted by immersion in a bath of propan-1-ol at room temperature (48 h). The monoliths were then dried in a vacuum oven at 60 °C to constant weight. Propan-1-ol and DCE were separated by fractional distillation over a spinning band column working at atmospheric pressure. The spinning band distillation column used for solvent recycling was a double-walled PROLABO (50 × 0.8 cm) glass column equipped with a polytetrafluoroethylene helical band stirred at 1000 rpm. The number of theoretical plates was estimated to 15–20. The holdup ratio was about 1/5. All solvents, except castor oil, were recovered with losses of approximately 2% and reused without further purification. The recovered DCE showed no hindrance to stability in further black liquor emulsifications.

In the following, castor oil-based and DCE-based monoliths have been abbreviated COM_x and $DCEM_x$, respectively, where x represents the volume fraction of the dispersed phase of the emulsion.