Journal of Cleaner Production 113 (2016) 919–924

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Note from the field

Microwave-assisted hydrothermal extraction of natural malic acid for the synthesis of low transition temperature mixtures

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A R T I C L E I N F O

Article history:
Received 14 July 2015
Received in revised form
9 December 2015
Accepted 15 December 2015
Available online 23 December 2015

Keywords:
Microwave-assisted hydrothermal extraction
Malic acid
Kinetic modelling
Synthesis
Low transition temperature mixture
Delignification

A B S T R A C T

This work describes the utilization of microwave hydrothermal extracted malic acid from cactus, lophatherum herb, papaya and *Luffa cylindrica* as hydrogen bond donor for the synthesis of natural low transition temperature mixtures (LTTMs) with sucrose as hydrogen bond acceptor. The effects of parameters including reaction temperature, extraction time, mass of sample and oxidant, H_2O_2 were discussed. The saturation equation was used to fit with the experimental data, observing only a slight loss of the goodness of fit. The optimum conditions for microwave hydrothermal extraction were found to be at 1 g of sample, 200 °C and 45 min in the presence of hydrogen peroxide (H_2O_2) as oxidant. Consequently, the proposed method was successfully applied to extract malic acid from plants and fruits for the synthesis of LTTMs. The LTTMs prepared from the extracted malic acid have identical physicochemical properties with the LTTMs derived from commercial malic acid due to the existence of hydrogen bond and the ability to dissolve lignin.

1. Introduction

Conventional extraction techniques such as soaking, maceration, water percolation and solvent extraction for natural products normally require long extraction time and large volume of organic solvents. These also result into degradation of active compounds obtaining relatively lower extraction efficiency of the target compounds (Moltó-Puigmartí et al., 2011; Chan et al., 2011; Wu et al., 2012). Hydrothermal extraction using water is a natural and green alternative for natural product extraction at high temperature and pressure condition. This method has been used to extract polar organic compounds or to decompose lignocellulosic materials to produce valuable compounds such as saccharides and aromatic acids (Kitada et al., 2009; Matsunaga et al., 2013).

Microwave possesses many advantages for the extraction of bioactive compounds (Sanchez-Aldana et al., 2013) such as reduced processing time, higher extraction rates and more accurate control of reaction conditions (Tsubaki et al., 2012; Yemis and Mazza, 2012). Microwave-assisted extraction has been proven to be a promising technique for the extraction of phytochemicals from botanical plants and food samples (Xiao et al., 2012; Quitain et al., 2013). Direct interaction of microwaves helps to heat up the solvent and also lead to a tremendous increase in internal pressure, rupture of plant tissue and release of active compounds into the solvent (Dhobi et al., 2009; Mandal et al., 2007).

Francisco et al., 2012 introduced 26 types of natural low transition temperature mixtures (LTTMs) from environmentally benign starting materials which show glass transition points instead of eutectic melting points. LTTMs can be prepared from cheap, readily available and toxicologically well characterized starting materials (Francisco et al., 2013). Preparation of LTTMs is in vicinity to the synthesis of deep eutectic solvents (Cvjetko Bubalo et al., 2014). The hydrogen bonding interactions of LTTMs lead to some of the promising characteristics of ionic liquids as solvents and shared by deep eutectic solvents (Francisco et al., 2012). The potentials of LTTMs to degrade the lignocellulosic biomass structure were

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http://dx.doi.org/10.1016/j.jclepro.2015.12.053
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evaluated and less biomass particles could be noticed after the pretreatment with the mixtures derived from malic acid (Francisco et al., 2012). Thus, natural abundant resources such as plants and fruits which contain high malic acid content have high potential to be used for the synthesis of LTTMs.

The aim of the present work was to utilize the malic acid obtained from papaya, cactus, *Luffa cylindrica* and lophatherum herb via microwave-assisted hydrothermal extraction for the synthesis of natural LTTMs. The influencing parameters including extraction temperature, reaction time, mass of sample and oxidant, H_2O_2 were investigated. The extraction kinetics were modelled using saturation equation and compared with experimental results. The comparative study of the LTTMs prepared from commercial malic acid and microwave hydrothermal extracted malic acid in terms of hydrogen bonding and lignin solubility was also conducted.

2. Materials and methods

2.1. Raw materials and chemicals

The plants and fruits with high content of malic acid such as papaya, cactus, *L. cylindrica* and lophatherum herb were used as the source of hydrogen bond donor for the synthesis of LTTMs. All these samples were ground using a blender with the power rating of 300 W for 20 min and dried completely in an oven at 50 °C for 7 days. The sucrose (>97%) was obtained from Wako Pure Chemical Industries Ltd as the source of hydrogen bond acceptor. On the other hand, the lignin (96%, alkali lignin) was obtained from Tokyo Kasei Kogyo Co., Ltd.

2.2. Microwave-assisted hydrothermal extraction experiments

The microwave used for the extraction of malic acid was CEM MARS 5 microwave digester. In each experimental run, a 50 mL of distilled water and dried sample were charged into the reactor. The microwave power of 600 W and pressure of 50 bar were chosen in this study (Zohourian et al., 2011). The solvent was centrifuged after the process of extraction. The supernatant was separated from the residue through filtration using an Advantec ashless quantitative filter paper (Grade 5C, <5 μm). The microwave-hydrothermal extraction was conducted at extraction temperatures of 140, 160, 180 or 200 °C and reaction time at 15, 30, 45 or 60 min. The experiment was repeated with increasing mass of sample (0.1, 0.5, 0.75 and 1 g) and in the presence of oxidant, H_2O_2 solution (35 wt% H_2O_2) at equal proportion with the sample in a reactor (XP-1500 Plus).

2.3. High performance liquid chromatography (HPLC) analysis

The percentages of malic acid extracted from the samples were analyzed by using JASCO high performance liquid chromatography (HPLC). HPLC analysis was conducted by using potassium dihydrogen phosphate buffer as a mobile phase with UV detection at $\lambda = 210$ nm. The pH value of mobile phase was adjusted to pH 2.8 by using 10 mM of phosphoric acid. The column used was Wakosil-II 5C18 HG Prep. The flow rate of the mobile phase was fixed at 0.5 mL/min and 20 μL as injection volume.

2.4. Mathematical model

The overall kinetic data based on the yield of malic acid by microwave hydrothermal extraction were modelled using the saturation equation (Wong-Paz et al., 2014). The equation used was:

$$\frac{1}{C_t} = \frac{k}{C_{eq}}\left(\frac{1}{t}\right) + \frac{1}{C_{eq}} \qquad (1)$$

where C_t, C_{eq} and k represents solute concentration in liquid phase at any time, the equilibrium solute concentration and the constant that describes the released fraction, respectively. The concordance between experimental data and calculated value is established by the correlation coefficient (R^2).

2.5. Synthesis and analysis of LTTMs

LTTMs were synthesized by adding sucrose into microwave-hydrothermal extracted malic acid and heated up slowly in an oil bath with the molar ratio of malic acid-sucrose-water (MSW 1:3:10) until all the sucrose was dissolved. The excessive water content in the LTTMs was removed by freeze-drying (EYELA FDU-1200) at −45 °C, and stopped once the samples showed constant weight (Yiin et al., 2016).

The hydrogen bonding of LTTMs was evidenced using Frontier FT-IR Spectrometer (PerkinElmer) equipped with attenuated total reflectance (ATR). The water content of freeze dried LTTMs was measured by using the Metrohm 870 Karl Fischer Titrino Plus. The solubility of lignin was determined using cloud point method (Francisco et al., 2012).

3. Results and discussion

The malic acid is present in the plant materials being investigated such as papaya (Morais et al., 2015), cactus (Moßhammer et al., 2006), *L. cylindrica* (Chang et al., 2007) and lophatherum herb (Kozukue, 1986). Nevertheless, the extraction of malic acid under microwave-assisted hydrothermal conditions and specific quantifications of malic acid content of plant materials have not been reported.

Thus, the spectra obtained from fruits and plants were compared with the standard in order to investigate the total area of peak for extracted malic acid at respective retention time. In this context, a calibration curve of L-malic acid's concentration (ppm) against peak area (ƒÊV.sec) was plotted for four working aqueous solutions ranging from 250 to 1000 ppm. The linear equation for the calibration curve is shown below:

$$y = 10^{-6}x + 60.674 \quad \left(R^2 = 0.9997\right) \qquad (2)$$

where x is frequency of output voltage/amplitude of spontaneous signals (ƒÊV.sec) and y is concentration of extracted malic acid (ppm). The results indicated that the malic acid in fruits and plants had been extracted by the proposed microwave-hydrothermal approach.

3.1. Influence of reaction temperature and extraction time on the malic acid yield

It can be seen in Fig. 1 that the malic acid yield increased with increasing temperature and time up to 200 °C and 45 min, respectively. Equilibrium was reached at temperature above 180–200 °C. The results were comparable with the works of Zohourian et al. (2011) in which the extraction yield increased with increasing temperature and the yield decreased as a result of further degradation of target compounds above the optimum temperature. The solvent power increased at higher temperature due to the drop in viscosity and surface tension, facilitating the solvent to solubilize solutes and further improving matrix wetting