International Journal of Biological Macromolecules 94 (2017) 309–318

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

Brönsted acidic ionic liquid based ultrasound-microwave synergistic extraction of pectin from pomelo peels

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ARTICLE INFO

Article history:
Received 23 June 2016
Received in revised form
24 September 2016
Accepted 11 October 2016

Keywords:
Brönsted acidic ionic liquid
Pectin
Pomelo
Ultrasound-microwave synergistic extraction
Response surface methodology

ABSTRACT

3-Methyl-1-(4-sulfonylbutyl) imidazolium hydrogensulfate, $[HO_3S(CH_2)_4mim]HSO_4$, was applied as an extractant in an ultrasound-microwave synergistic extraction approach to substitute conventional solvent for the extraction of pectin from the albedo part of pomelo peels. The analysis of variance (ANOVA) test and response surface method were employed for the optimization of the extraction conditions. A pectin yield of 328.64 ± 4.19 mg/g was achieved using the obtained optimal conditions, which was significantly higher than yields of conventional methods with reference solvents. Pectin samples extracted with $[HO_3S(CH_2)_4mim]HSO_4$ and hydrochloric acid solutions were tested by ANOVA and showed no significant differences in total carbohydrate content and degree of esterification; while galacturonic acid content was significantly different for the pectin from each extraction solvents. The differences revealed from images of atomic force microscopy and scanning electron microscope, Fourier transform infrared spectroscopy, and thermogravimetric analysis suggested the physiochemical properties of pectin could be affected by the extraction solvent. The $[HO_3S(CH_2)_4mim]HSO_4$ proved to be a promising alternative to conventional solvents and the proposed method is efficient for the extraction of pectin from the albedo of pomelo peels.

1. Introduction

Ionic liquids are a group of non-molecular ionic chemicals and are comprising organic and inorganic ions [1]. Ionic liquids have attracted increasing attention for a variety of processes because of their excellent physicochemical parameters [2,3]. Ionic liquids have been successfully used to dissolve cellulose effectively [4]. Meanwhile, their extensive applications are also reflected in natural products separation science, including the extraction of flavonoids [5], volatile components [6], and coumarins [7]. Task-specific Brönsted acidic imidazole ionic liquids, such as 3-methyl-1-(4-sulfonylbutyl) imidazolium hydrogen sulfate ($[HO_3S(CH_2)_4mim]HSO_4$) with two acidic sites, have been designed primary as an alternative to traditional mineral acids (e.g. H_2SO_4 and HCl) for catalytic applications [8,9]. Very recently, $[HO_3S(CH_2)_4mim]HSO_4$ has been demonstrated as an excellent solvent with good acidic effects with a promising future for the preparation of natural products, such as flavonoid glycosides [10] and phenolic acids [11].

Pomelo (belonging to Rutaceae family) is a native citrus species of Southeast Asia that has great economic value and is cultivated and consumed worldwide [12]. Large amounts of waste products (albedo and flavedo) are produced every year because of high consumption of pomelo. The albedo part of pomelo peel has been regarded as a potential source of soluble dietary fibres as it is rich in pectin [13,14].

Pectin is a complex polysaccharide primary contained in the cell walls of many fruits and vegetables. Pectin has gelling and stabilizing characteristics and is used commercially as a food additive for the following applications: thickener (for jams, jellies and confectionery production), emulsifier, and stabilizing agent (in acidified milk beverages) [15]. Pectin also possesses a variety of health benefits, such as cholesterol-lowering properties [16], immunostimulating activity [17], and antipancreatic cancer activity [18].

Industrial extraction techniques for the production of pectin are generally carried out using acidic conditions (inorganic acids solution, pH 1.5–3.0) at high temperature [19], which can give rise to negative environmental impacts and high corrosion damage to equipment. Enzymolysis seems to be a good alternative to traditional extraction methods [20]. However, this approach has some limitations because enzymatic specificity is a disadvantageous factor and could increase the cost of large-scale industrial production.

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http://dx.doi.org/10.1016/j.ijbiomac.2016.10.028
0141-8130/

To our best knowledge, there is only one reported application of nonacidic ionic liquids to extract pectin from lemon peels [21]. Extraction solvents with low pH are indispensable for the extraction of pectin [22]. The insoluble pectin constituents can be directly contacted and hydrolyzed into soluble pectin under acidic conditions and thus released and dissolved from plant tissues [22–24]. We were interested in the potential of $[HO_3S(CH_2)_4mim]HSO_4$ as solvent to extract pectin from the albedo part of pomelo peels and intended to take advantage of the good solvent effect and intrinsic acidic property of this SO3H-functionalized ionic liquid.

Ultrasound-microwave synergistic extraction (UME) processing has developed as a novel technique in the field of separation science in recent years [25,26]. The outstanding performance of UME is mainly ascribed to the benefits of both microwave and ultrasonic irradiation. The benefits of microwave irradiation are: first, microwave energy can accelerate water permeability to capillaries and the water absorption ability of the plant material, thus improving extraction efficiency [27]; second, the special heating mechanism heats the entire material simultaneously in a short time; third, microwaves can induce dipole rotation of molecules and migration of dissolved ions, which is considered to be responsible for the disruption of hydrogen bonds and thus break down of the plant cell walls [28]. A previous study has reported microwave energy can be efficiently absorbed and transferred by ionic liquids [29]. Ultrasonication provides three beneficial aspects, cavitation, the mechanical function, and thermal effect, which are maximally utilized in the extraction process and giving rise to relatively high extraction efficiency.

In the present study, a Brönsted acidic ionic liquid based ultrasound-microwave synergistic extraction (BUME) technique was proposed for the extraction of pectin from the albedo part of pomelo peels. The response surface method (RSM) was used to evaluate the importance of three major variables to optimize the extraction conditions of pectin. Conventional heat reflux extraction (HRE) method and traditional solvents were investigated and compared with BUME. In addition, the physicochemical properties of the pectin samples that were extracted with $HO_3S(CH_2)_4mim]HSO_4$ aqueous solution and hydrochloric acid solution using UME were investigated.

2. Experimental

2.1. Plant material

Fresh pomelo fruit were purchased from Hada fruit market (Harbin, China) in November 2015. The pomelo were cultivated in Guanxi (Fujian province, China), and authenticated by Prof. Baojiang Zheng of the College of Life Science, Northeast Forestry University, China. Fresh samples of albedo were cut into lumps with a knife, dried in a shaded place at 25 °C for 7 days, then powered into a 40–60 mesh and stored in a desiccator for the future experiments.

2.2. Solvents and chemicals

$[HO_3S(CH_2)_4mim]HSO_4$ and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) were bought from Chengjie Chemical Co. Ltd. (Shanghai, China) and used without purification. Other chemicals were of analytical grade. Water applied in the experiments was purified by a reverse osmosis Milli-Q (Millipore, Bedford, MA, USA) instrument.

2.3. Apparatus

An UWave-1000 ultrasound-microwave synergy extraction system (XTrust, Shanghai, China) laboratory-scale apparatus operating at a frequency of 2450 Hz was employed in BUME, UME and microwave assisted extraction (MAE) procedures for the extraction of pectin from the albedo part of pomelo peels. Microwave energy transmitted to the reactor could be adjusted through a power feedback/control. Maximum microwave irradiation power output was 700 W. Ultrasonic power was uncontrolled and fixed at 50 W (40 kHz). An infrared temperature sensor was used to detect the temperature of the reaction cavity (57 cm × 51 cm × 52 cm).

2.4. BUME procedure

The extraction procedure is presented in Fig. 1. Dried albedo powder 1 g and a proper volume of $[HO_3S(CH_2)_4mim]HSO_4$ aqueous solution were mixed in a flask and then treated in the extraction system. The supernatant was isolated from insoluble residue after extraction using four-layer filter paper and then cooled to 25 °C. Crude extracts were precipitated by adding ethanol to a proportion of 80% (v/v) and standing overnight at 4 °C. Floccus precipitates were gathered by centrifugation (8000 × g for 30 min at 20 °C), washed three times with dehydrated alcohol and dried in a freezer dryer. Gravimetric analysis was carried out to calculate pectin yield. Dried pectin samples were redissolved in pure water and detected by a UV–vis Spectra (UV-2550; Shimadzu, Kyoto, Japan) to evaluate the amount of residual $[HO_3S(CH_2)_4mim]HSO_4$ [30]. No absorbance at 211 nm was detected in pectin samples, demonstrating the improved extraction method is reliable. Concentrations of $[HO_3S(CH_2)_4mim]HSO_4$, liquid–solid ratio, microwave irradiation power, and extraction time were investigated with single factor experiments for selecting suitable ranges for subsequent optimization experiments.

2.5. Optimization of BUME procedure with RSM

A Box–Behnken design of RSM was employed to predict the optimal pectin extraction conditions in regard to three factors, which include extraction time, liquid–solid ratio, and microwave irradiation power. The factorial design is composed of 17 runs (12 factorial runs and 5 center runs). Pectin yield was set for the response to combine the independent factors (Table 1). Experiments were performed at random to minimize the impacts of unforeseen variability in the determined responses. Each factorial run was conducted in triplicate and the average values were presented as actual values. The interactions between the responses and the three independent variables were evaluated by the generalized form of a quadratic equation as following:

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+i}^{3} \beta_{ij} X_i X_j \quad (1)$$

where Y is the estimated response; the regression coefficients for the intercept, square, linearity and interaction are expressed as β_0, β_{i}, β_{ii}, and β_{ij}, respectively; and the three independent factors are presented as X_1, X_2, and X_3.

2.6. Comparison of BUME with reference method and solvents

HRE was investigated as the reference pectin extraction method. Conditions for HRE were: hydrochloric acid solution (pH 2.5), 1000 W of heating power, 180 min of extraction time, and a liquid–solid ratio of 27 mL/g. Pure water, hydrochloric acid solution, and Na_2SO_4 (10 mM) were used as reference extraction solvents with UME under the optimal conditions obtained for the experimental design to identify the prominently effect of an $[HO_3S(CH_2)_4mim]HSO_4$ aqueous solution on the extraction of pectin. MAE was performed with 1.0 M [Bmim]Cl as described in previous study [21] to compare with the improved method.