Industrial Crops & Products 121 (2018) 236–240

Contents lists available at ScienceDirect

Industrial Crops & Products

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

Silica microspheres from rice husk: A good opportunity for chromatography stationary phase

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ARTICLE INFO

Keywords:
Rice husk ash
Sodium silicate
Mesoporous silica microsphere
HPLC column
Natural compounds analysis

ABSTRACT

The aim of this research is to produce spherical and porous silica particles from rice husk for chromatographic applications in HPLC columns. After complete combustion of rice husk, white powder of silica was obtained which was dissolved in NaOH and subsequently heated to produce sodium silicate solution. Spherical porous silica gel was synthesized from the prepared sodium silicate in the presence of Pluronic P123 as the surfactant, under acidic solution. Different porosities were prepared by applying various factors including different vacuums, temperatures and reaction times in order to obtain the optimum conditions for particle aging. An analytical column was packed with the prepared silica microspheres and evaluated for the separation of 10-deacetylbaccatin III and rutin from taxol and hesperidin, respectively.

1. Introduction

Rice husk (RH) is an agricultural residue which is abundantly produced in rice industry. Silica is the major element of rice husk ash (Chawla et al., 1983). Nowadays, some countries must spend high costs to get rid of RH, due to its disposal and environmental problems (Sun and Gong, 2001). Therefore, extraction of silica from RH would be considered as a new challenge in order to produce a valuable material from a waste product, and the process is cost-effective because of the high amount of RH as waste product and large content of silica in RH ash. There are many reports on extraction of silica from RH (Liou and Wu, 2010; Sun and Gong, 2001; Umeda et al., 2007; Zhang et al., 2010). After complete combustion of RH, approximately 20 wt% of dry RH is ash; the ash itself is consisted of about 90–98% of silica (Mittal, 1997), but the silica content in RHs could be different according to plant growth conditions (Liou and Wu, 2010; Sun and Gong, 2001; Umeda et al., 2007; Zhang et al., 2010). Several approaches to extract silica from RHs have been investigated (Sun and Gong, 2001). Purification of the obtained silica is crucial for applications as the HPLC stationary phase, and in this favor various acid leaching procedures have been performed (Hamdan et al., 1997; Kalapathy et al., 2000; Unger, 1979; Witoon et al., 2008). Kalapathy et al. (Kalapathy et al., 2000) scrutinized silica construction using RH as the raw material, dissolved in sodium hydroxide solution. They found that assimilating the initial acid washing of the rice husk ash as well as the final water washing of silica, dramatically intensifies the purity of the silica sample. Following an acid pretreatment step results in a highly pure silica which can be used for preparation of sodium silicate solution via treatment with sodium hydroxide. It's worth noting that the mentioned process does not require very high energy, compared to the production of sodium silicate by liquating the quartz and sodium carbonate at high temperature (1300 °C) (Affandi et al., 2009). Application of extracted silica from RH as a packing for HPLC columns was first introduced by Burns and coworkers, who had prepared C_{18}-modified silica particles (Burns et al., 2006). In another study, Tungkananurak used the extracted silica from RH for preparation of normal-phase HPLC packing (Tungkananurak et al., 2007). They developed a simple method to produce mesoporous silica microspheres using non-ionic surfactants. Mentioned investigations clearly confirm the suitability of the extracted silica from RH for applications as the HPLC stationary phase in different chromatographic modes such as normal and reversed-phase liquid chromatography.

Therefore, we employed this silica for another mode of chromatography, called pre aqueous liquid chromatography (PALC), in which high amount of water as the mobile phase is applied on bare silica stationary phase (Dos Santos Pereira et al., 2009). The aim of the present work was to prepare silica microspheres with different porosities. The obtained silica was characterized using several analytical techniques such as scanning electron microscopy (SEM), energy-dispersive X-

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https://doi.org/10.1016/j.indcrop.2018.05.023
Received 15 April 2018; Received in revised form 18 April 2018; Accepted 9 May 2018

ray spectroscopy, Fourier transform infrared spectroscopy (FTIR), and N_2 adsorption-desorption measurements.

2. Materials and methods

RH sample used in this study was obtained from Mazandaran lands. HCl and NaOH were purchased from Merck Chemical Company (Darmshdt, Germany). Pluronic P123 (M_{aver} = 5800), taxol, 10-deacetylbaccatin III, rutin and hesperidin were obtained from Sigma-Aldrich (St. Louis, USA). Silica microsphere 10 µm, 100 Å was purchased from YMC Company. Deionized water from Millipore Direct-Q was used throughout the experiments.

2.1. Extraction of silica from RH

RH was gathered from a local rice mill. Undesirable fine dust materials were removed over air-blowing separation technique and the rest was washed throughly to remove the physically adhered impurities using tap water. After consecutive washing, RH was dried in an air-circulated oven at 100 ± 2 °C for 10 h. The cleaned RH was burned at 700 °C for 6 h under air to yield a brownish powder. In order to obtain the impurity-free ash, cleaned RH was treated with 1 N aqueous solution of HCl under boiling condition for 1 h, followed by washing with distilled water. The RH was then dried and burned following the same procedure as specified above. Eventually, the obtained ash was white in color (Fig. 1).

2.2. Preparation of sodium silicate

White ash (5 g) was poured in 500 mL of 1 N NaOH solution and heated at 100 °C for 4 h under efficient stirring to dissolve silica and produce sodium silicate solution. The resulting slurry was filtered and subsequently washed with water to eliminate the residual impurities.

2.3. Preparation of porous spherical silica gel from sodium silicate solution

0.4 g of P123 was dissolved in 50 mL of 2 M HCl solution and 10 mL of sodium silicate solution was added to it under stirring at 250 r.p.m. The resulting mixture was stirred for about 20 min and then, it was transferred into a polyethylene Erlenmeyer and heated overnight at 75 °C. Obtained particles were then filtered and washed with deionized water and were subsequently dried at 80 °C for 24 h. Next, the powder was calcined at 550 °C for 5 h to remove the surfactant and eventually, porous silica microspheres were obtained. For synthesis of silica gels with different pore sizes, various factors including temperature, aging time and vacuum of the oven were controlled (summarized in Table 1).

Table 1
Summary of conditions for production of different porosities.

Pore size (nm)	Oven temperature (°C)	Oven vacuum (m bar)	Aging time (hour)
2.6	80	800	24
6.1	30	200	24
6.4	60	200	24
11.9	60	200	48

2.4. Characterization of silica

Chemical compositions and morphologies of the prepared synthetic silica were checked by scanning electron microscope (SEM) (VEGA3-LMU model) manufactured by TESCAN (Czech Republic) coupled to EDS at 15 KV N_2 adsorption–desorption isotherms were measured at −196 °C over calcined sample using a Belsorp Mini II instrument (Bel Japan). Surface area and pore size were determined from Nitrogen adsorption branch using Brunauer– Emmett–Teller (BET) method. In order to identify the functional groups of silica and their bonding modes, IR spectra were recorded at 5 cm^{-1} resolution with 60 scans, using Bruker Tensor 27 spectrometer (USA).

2.5. High performance liquid chromatography

Chromatographic experiments were performed using a Knauer HPLC system equipped with the pump of model S 1000 and controller, auto-sampler of model S 3900, and the photodiode array detector of model S 2800. Deacetylbaccatin III and taxol were analyzed using solvent mixture of water/methanol as the mobile phase, with the following gradient program: 0–5 min 100% water, 5–15 min 80% water, 15–25 min 70% water, 25–35 min 50% water, 35–45 min 30% water, 45–55 min 20% water. The flow rate was 1 $mLmin^{-1}$ and injection volume was 20 µL.

2.6. Column packing

A stainless-steel column (120 × 4.6 mm) was packed with a column-packing apparatus (Knauer) by means of the slurry technique (2–2.5 g of sample dried at 120 °C and dispersed by ultrasonic stirring in 23 mL of methanol). Methanol was used to push the slurry into the column. The packing pressure was 4500 psig.

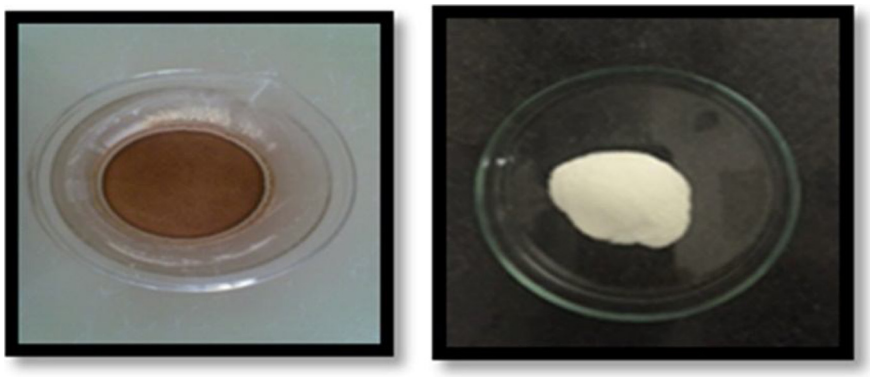

Fig. 1. (a) Burned Rice husk at 700 °C for 6 h (b) Cleaned Rice husk after treatment with 1 N aqueous solution of HCl under boiling condition for 1 h.