



Sol-gel based biogenic silica composite as green nanosorbent for chemometric optimization of micro-solid-phase extraction of beta blockers[☆]

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ARTICLE INFO

Article history:

Received 26 December 2017

Received in revised form 3 April 2018

Accepted 18 April 2018

Available online 21 April 2018

Keywords:

Micro-solid-phase extraction

Liquid chromatography–tandem mass spectrometry

Biogenic silica composite sorbent

Chemometric optimization

Beta-blockers

ABSTRACT

An environmentally friendly micro-solid phase extraction (μ -SPE) method utilizing a plant based nanocomposite as a sorbent for determination of trace level beta blockers (β -blockers) in hospital wastewater prior to Liquid chromatography–tandem mass spectrometry (LC–MS/MS) analysis. μ -SPE extraction conditions were evaluated using a multivariate chemometric approach. Rice husk silica-carbon nanocomposite (5–20 Wt.% Fe) in glycerol were synthesized via hydrolytic sol-gel method. The nanosorbent were fully characterized and then evaluated for μ -SPE of trace level β -blockers in hospital wastewater. To establish the best extraction conditions at minimal experimental cost, multivariate techniques based on fractional factorial (FFD) and central composite designs (CCD) with desirability function (DF) were used to optimize the extraction conditions. Experimental results showed good agreement with predicted values and logical DF was realized at relatively low extraction time. Under optimized conditions, good linearity ranges (0.02–5.0 $\mu\text{g L}^{-1}$) with correlation of determinations higher than 0.9954 were obtained. The limits of detection and quantitation for the five β -blockers (atenolol, alprenolol, pindolol, acebutolol and propranolol) ranged from 4.0–6.4 and 13.0–19.0 ng L^{-1} , respectively. Inter-day and intra-day precision (percent relative standard deviations, $n = 5$) were lower than 8.3% while relative recoveries for hospital wastewater samples (80.6–105.1%) were in satisfactory ranges. This experimental approach therefore, demonstrated simplicity, reduction in the experimental runs, effectively increased sensitivity of LC–MS/MS and was hence suitable for complex matrix sample analysis.

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1. Introduction

The recent trend in environmental analysis is geared towards new approaches that simplify sample preparation procedures and make them green, cheaper, safer, faster and easier so as to generate precise results with low detection limits [1]. For the past few decades, there have been a multiplex increase in the effect of environmental chemical contamination due to worldwide use of pharmaceutically active compounds [2]. Among these compounds, the global presence of beta blockers (β -blockers) as emerging contaminants in aquatic environments have aroused scientific interest

in regard to their ambiguity in the environment and their adverse effects on non-target organisms (aquatic fauna and flora); even at trace level concentrations [3,4]. β -blockers are commonly used drugs by clinician to treat myocardial infarctions [5]. They act by relaxing muscles thus directly slowing down the heart rate and as such, they have been abused by athletes that require high levels of mental endurance. Hence, have now been forbidden by the World Anti-Doping Agency [6]. Research has highlighted the ecotoxicity and undesirable effects associated with mixed β -blockers on organisms even at low concentrations [7]. Hospitals are considered as an incontestable hot spot and point source for some β -blockers contamination [8–10]. Hospital wastewater (HWW) represents a complex matrix composed of contagious excretions, microorganisms, detergents, disinfectants, biological fluids, heavy metals and pharmaceutical compounds [9]. Owing to the poor degradability of β -blockers, they escape treatment and end up in both surface and drinking water [8]. To date, there are many opportunities

[☆] Selected paper from the 46th International Symposium on High Performance Liquid Phase Separations and Related Techniques (HPLC 2017 Jeju), 5–9 November 2017, Jeju, Republic of Korea.

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for screening various ultra-trace level analytes in complex matrices with highly sensitive and selective analytical instruments, but however, all require valid sample preparation protocols [10]. Sample preparation is aimed at elimination of sample interference effects, increasing the method's selectivity factor and thus leads to improved analyte enrichment [11]. In particular, the ability of liquid chromatography methods to avoid extra derivatization steps have been explored for sensitive environmental analysis of trace β -blockers. However, their sensitivities are greatly compromised by matrix effects and hence require clean extracts [2]. In an effort to enhance sample throughput, recent research trend has focused on miniaturization and automation [12].

As such, numerous miniaturized extraction techniques have been reported for trace level determination of β -blockers in aqueous matrices and these include dispersive micro-solid phase extraction [15,16], microextraction by packed sorbent [17,18], electrically enhanced microextraction [14], microwave assisted-solid phase extraction [15], stir bar sportive extraction [16], hollow fibre-protected liquid-phase microextraction [17] and electromembrane coupled with solid phase microextraction [18]. Micro-solid phase extraction (μ -SPE) method is miniaturized preparation technique that is applicable to different complex matrices analysis such as bioanalysis, wastewater, food analysis, and sewage sludge [17,24]. The efficiency of the μ -SPE method depends on the wise choice of sorbent [20]. Nano-composite sorbents offer unique extraction phase qualities through their high functionalities that enhance numerous interactions of target analytes via electrostatic interactions [21]. Recently, silica-based mesoporous materials (MCM-14 and UVM-7) have widely been investigated as effective sorbents in trace preconcentration studies [22], however, their synthesis involve expensive and environmentally unappealing approach. Hydrolytic sol-gel modification of biogenic raw materials with metals offers tremendous opportunities in the design and fabrication of inexpensive and selective sorbents for adsorptive removal of organic pollutant [25,28,29]. Rice husk ash (RHA) is a cheap source of amorphous silica composite that provides sufficient support/surface area and naturally endowed functionalities for dispersion of any metal [23–25]. Additionally, RHA offers an excellent source of mesoporous silica (rice husk silica, RHS), hydroxyl-group-rich surface for anchoring metals, improving chemical stability and enhancing remarkable textural characteristics during synthesis of sorbents [30,31]. Iron functionalized green nanosilica composite materials show great promise in adsorption of low level pollutants in environmental waters. It is asserted that, the selectivity and improved extraction efficiency of iron supported RHS sorbents is enhanced by iron oxide [25–27].

Most practical research reports involving μ -SPE optimization rely on systematic study of one-factor-at-a-time in which all the factors are kept constant save the one being studied [15,25,32]. Such univariate approaches generate incomplete conclusions due to their failure to determine accurately, the interaction between variables [28]. Multivariate techniques based on design of experiments (DOE) are fast and efficient optimization approach. This is because they can potentially reduce the number of experimental runs, allow simultaneous optimization, and explain correctly the interaction effects [26,34]. Out of these multivariate optimization techniques, FFD and CCD approaches, are more efficient towards judicious selection and optimization of the most significant parameters [29]. Usually, a desirability/derringer function (DF) within CCD model is employed as a multi-criteria strategy to establish more accurately the numerical optimized values [30]. The aim of this study is to investigate the synergistic contribution of biogenic silica nanocomposite nanosorbent based μ -SPE technique with chemometric optimization of trace level β -blockers in hospital wastewater. Fractional factorial design was used to screen the most significant parameters while central composite design with

a desirability function was used as a multi response optimization strategy to achieve the best optimized experimental variables.

2. Materials and methods

2.1. Materials

All chemicals and reagents used in this experiment were of better analytical grade unless otherwise stated. All standards had a purity grade of more than 97%, adequate to LC-MS/MS analyses. Ferric nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.5%) was used as the iron precursor, sodium hydroxide, nitric acid, sulfuric acid, hydrochloric acid, sodium chloride, glycerol, acetone and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich (St. Louis, USA). Formic acid, methanol, and acetonitrile (LCMS grade) were secured from Fisher Scientific (Schwerte, Germany). Alprenolol hydrochloride (ALP), ($\geq 95\%$) atenolol (ATE), (99%), acebutolol hydrochloride (ACE) ($\geq 98\%$), propranolol hydrochloride (PROP) ($\geq 99\%$) and Pindolol (TLC powder, PIN) ($\geq 98\%$), were purchased from Sigma-Aldrich (Deisenhofen, Germany) and used as received. Accurel (Q3/2, R/P) polypropylene sheet membranes (0.2- μm pore size, 157- μm thickness) were purchased from Membrana (Wuppertal, Germany). Rice husk was secured from a rice mill (Kerala, India) was used as biogenic silica precursor. Commercial sorbents: activated carbon, C₁₈, Porapak, Silica, C₁₈-porasil, Polysep- 4% divinylbenzene and Polysep- 12% divinylbenzene, were bought from Alltech (Deerfield, IL) and used without modification for μ -SPE comparison study. Plastic crimper vials, 0.2-mL (Landgraaf, The Netherlands) were used during ultrasonication. Ultrapure water obtained from Milli-Q system (Milford, MA, USA) was used throughout the experiments. Polyether sulfone syringe filters (pore size, 0.2 μm) were obtained from Sigma Aldrich. β -blockers standard stock solutions (1000 mg L^{-1}) were each prepared in methanol while mixed drug working solutions were prepared weekly by appropriate dilutions of a series of low concentrations of standard solutions in MilliQ water. They were then stored at a temperatures of 4 °C and were always brought to ambient temperature before use.

2.2. Instrumentation

All experiments were performed using a Shimadzu Nexera ultra high-performance liquid chromatograph coupled to a Triple Quadrupole Mass Spectrometer LCMS-8050 (Shimadzu). For data handling and quantification, Labsolutions (Shimadzu Corporation) was used. The liquid chromatography (LC) instrument included two pumps, Shimadzu (Kyoto, Japan), an auto sampler, CTC-Pal (Analytics AG, Zwingen, Switzerland) and a 50 μL sample loop. Chromatographic separation of the analytes was carried out on an Ultra IBD column (100 \times 2.1 mm \times 3 μm particle size; Restek, Bellefonte, PA, USA). The injection volume was 10 μL . Gradient elution with solvent A (0.03% formic acid) and solvent B (methanol/acetonitrile, 25:75) at a flow rate of 0.3 mL/min was applied. The starting gradient was 10.0% of mobile phase B with a hold of 0.5 min and then increased to 25% at 3.0 min, then to 30% at 3.5 min at a hold time of 0.5 min. From there, it was increased to 90% for another 0.5 min then again to 10% in another 0.5 min and 0.5 min was used for column equilibration and stability. The total run time was 6 min. The column oven temperature was set at 40 °C and the CTC-Pal tray temperature was set at 12 °C. Nitrogen was used as both drying and nebulizing gas and argon was used as collision gas. A neat β -blockers mixed standard was directly infused in to the ion source to establish the precursor to product transitions for the target analyte. Electrospray LC-MS/MS technique in multiple reaction monitoring (MRM) in positive ionization mode

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