



Research Paper

Preparation of an organic–inorganic hybrid molecularly imprinted polymer for effective removal of albendazole sulfoxide enantiomers from aqueous medium

Sara da Silva Anacleto, Hanna Leijoto de Oliveira, Anny Talita Maria da Silva, Tienne Aparecida do Nascimento, Keyller Bastos Borges*

Departamento de Ciências Naturais, Universidade Federal de São João del-Rei, Campus Dom Bosco, Praça Dom Helvécio 74, Fábricas, 36301-160, São João del-Rei, Minas Gerais, Brazil

ARTICLE INFO

Keywords:

Adsorption studies
albendazole sulfoxide enantiomers
organic–inorganic hybrid molecularly imprinted polymer
sample preparation

ABSTRACT

An efficient adsorbent using an organic–inorganic hybrid molecularly imprinted polymer (MIP) based on poly (methacrylic acid)–silica, named MIP-poly(MAA)–SiO₂, was prepared for removal of albendazole sulfoxide (ABZSO) enantiomers from contaminated water. Sorption behaviors of MIP-poly(MAA)–SiO₂ and nonimprinted polymer (NIP) for ABZSO enantiomers including sorption kinetics, isotherms and effect of pH were investigated in detail. The pH 9.0 was the best for adsorption of ABZSO enantiomers and the time necessary to reaching equilibrium of adsorption was 20 min. The kinetic data were analyzed using four models, but the adsorption kinetics were best described by the pseudo-second-order model with $R^2 = 0.999$ for both materials, indicating that adsorption processes occur more effectively on external sites of MIP-poly(MAA)–SiO₂ and NIP-poly(MAA)–SiO₂, and at equilibrium the MIP adsorbed more than 70% and NIP no more than 50% of ABZSO enantiomers. These results agree with the Langmuir isotherm model, which assumes that the adsorption process occurs in a homogeneous way, in a monolayer surface. This model provided for both enantiomers employing MIP-poly(MAA)–SiO₂ and NIP-poly(MAA)–SiO₂ an adsorption capacity (Q) of around 140 mg g⁻¹ and 35 mg g⁻¹, respectively. The constants related to the affinity, K_L , for (R)-(+)-ABZSO and (S)-(-)-ABZSO were 0.0064 and 0.0063 L g⁻¹ for MIP-poly(MAA)–SiO₂ and 0.0166 and 0.0255 L g⁻¹ for NIP-poly(MAA)–SiO₂. This adsorbent material showed great potential in separation, sample preparation processes and removal pharmaceuticals from aqueous medium, besides being able to be used several times without significant loss of its adsorption amount.

1. Introduction

Molecularly imprinted polymers (MIP) are synthetic materials with recognition sites generated artificially that can rebind to the target molecule. The components of a molecular imprinting method include template molecule, functional monomer, cross-linking agent, radical initiator and solvent compatible with the template molecule. These materials are obtained by polymerizing the monomers around a template molecule leading to a highly cross-linked three-dimensional network [1]. These materials have advantages such as selectivity, chemical stability, resistance to high temperatures and good adsorption capacity [2]. Molecular imprinting technology is nowadays a well-known area of

research and is being increasingly used for (i) binding assays [3], (ii) separation processes [4,5], (iii) sample preparation [6], (iv) sensing [7], (v) biological tasks [8] and many other applications [9]. The use as an adsorbent material is the most used technique for the application of MIP [1,2,5,9].

The organic–inorganic hybrid molecularly imprinted polymer presents good textural and morphological properties, providing a higher specific surface area and lower swelling effect in organic solvents than conventional organic imprinted polymers, as well as better chemical stability in a wide pH range than inorganic polymers. The sol–gel process has been used to prepare hybrid materials, in which the polymerization reaction occurs in a homogeneous medium between organic

Abbreviations: ABZ, albendazole; ABZSO, albendazole sulfoxide; ACN, acetonitrile; ACPA, 4,4'-azobis(4-cyanovaleic acid); DMSO, dimethylsulfoxide; EtOH, ethanol; MAA, methacrylic acid; FTIR, Fourier transform infrared; MIP, molecularly imprinted polymer; MeOH, methanol; TMSPPMA, 3-(trimethoxysilyl) propylmethacrylate; NIP, nonimprinted polymer; poly(MAA)–SiO₂, poly(methacrylic acid)–silica; SEM, scanning electron microscopy; TEOS, tetraethylorthosilicate; TGA, thermogravimetric analysis

* Corresponding author.

E-mail address: keyller@ufsj.edu.br (K.B. Borges).

<https://doi.org/10.1016/j.jece.2017.11.049>

Received 2 October 2017; Received in revised form 7 November 2017; Accepted 16 November 2017

Available online 20 November 2017

2213-3437/ © 2017 Elsevier Ltd. All rights reserved.

and inorganic precursors. A survey of the literature demonstrates that few attempts have been made for the preparation of hybrid materials for selective extraction or preconcentration of veterinary pharmaceuticals [10–12].

The use of the adsorption process for the determination of analytes in different matrices is a good advance in sample preparation due to the availability of a large range of adsorbents as well as their properties, including high surface area, good adsorption capacity and reusability [13,14]. In recent works, MIP have shown varying adsorptive capacities from high values such as 378.6 mg g⁻¹ [15] to low values, 0.35 mg g⁻¹ [16], with a wide range of adsorption equilibrium times, for example, times equal to 10 [17] and 20 [18] min, which entails a rapid adsorption.

Because of human and veterinary applications of pharmaceutical compounds, the aquatic environment has become an emerging area of research [19]. The presence of pharmaceutically active compounds in the aquatic environment can alter the normal endocrine function and physiological status of animals and humans [20]. To date, only limited investigations have been conducted on the ecotoxicological effects of veterinary drugs [19]. In this context, benzimidazoles are a class of compounds used in the prevention and treatment of parasitosis, within this class can be mentioned albendazole (ABZ). One of its metabolites is albendazole sulfoxide (ABZSO), which is formed by oxidation [21]. ABZSO is used directly as a broad spectrum anthelmintic and acts on the parasites by means of two mechanisms: inhibition of the energy metabolism and polymerization of tubulin, which is a subunit of protein present in the microtubules of the cells of parasites. It is active against nematodes, cestodes and trematodes, showing good activity in both adult and larval forms [22]. ABZSO has one asymmetric center at the position of the sulfur atom, which gives rise to the existence of two enantiomers, (R)-(+)-ABZSO and (S)-(-)-ABZSO, with different pharmacological behaviors [23–25]. After administered as a racemic mixture, the ABZSO undergoes stereoselective metabolism, being the (R)-(+)-ABZSO enantiomer predominant in human plasma [26].

To our knowledge, no studies on the development of molecularly imprinted hybrid materials (organic and inorganic) based on the use of 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) as a single cross-linking agent have been carried out for ABZSO enantiomers' adsorption. According to the aforementioned, we have synthesized an organic-inorganic hybrid MIP based on poly(methacrylic acid)-silica named poly(MAA)-SiO₂ [27] to (i) evaluate the adsorption of ABZSO enantiomers from aqueous medium, (ii) assess the experimental variables affecting optimal adsorption of ABZSO enantiomers, (iii) explore adsorption isotherms and kinetic models to identify the possible mechanism of ABZSO adsorption and (iv) perform desorption studies and evaluate the reusability of MIP-poly(MAA)-SiO₂ and nonimprinted polymer (NIP)-poly(MAA)-SiO₂. This is the first work that hybrid materials, synthesized by reactions of coupling free radical addition and sol-gel processing, has been used as adsorbents, which in contact with the solution containing the ABZSO enantiomers presented high adsorption capacity.

2. Experimental

2.1. Solvents, reagents and standard solutions

Ethanol (EtOH), methanol (MeOH) and acetonitrile (ACN) HPLC grade were purchased from JT Baker (Mexico City, MX, Mexico) and chloroform from Tedia (Fairfield, CA, USA). Water was distilled and purified using a Millipore Milli-Q Plus system (Bedford, MA, USA). Tetraethylorthosilicate (TEOS) was purchased from Merck (Berlin, Germany) and dimethylsulfoxide (DMSO) and acetic acid from Vetec (Duque de Caxias, RJ, Brazil). Methacrylic acid (MAA), 3-(trimethoxysilyl) propyl methacrylate (TMSPMA) and acetic acid were obtained from Sigma-Aldrich (São Paulo, SP, Brazil) and 4,4'-azobis(4-cyanovaleic acid) (ACPA) from Santa Cruz Biotechnology (Santa Cruz, CA, USA). Hydrochloric acid and sodium hydroxide were purchased from

Synth (Diadema, SP, Brazil). The reference standard of ABZSO was obtained from United States Pharmacopeia- USP 98.0% (w/w). ABZSO solution was prepared by weighing 10.2 mg and dissolving in 10 mL of MeOH to obtain a concentration of 1 mg mL⁻¹ for subsequent dilution during the development work. The prepared solutions were stored at -20 °C in the absence of light.

2.2. Instrumentation and conditions

All analyses were performed on an Agilent chromatograph (Santa Clara, CA, USA) model 1260 with quaternary pump (G1311 B), thermostat (G1330 B), automatic injector model 1260 Hip ALS (G1367 E) and a diode array detector (DAD) model 1260 VL+ (G1315C). Data were collected and analyzed using AgilentOpenLABChromatography Data System software (Santa Clara, CA, USA). For the enantioselective separation of ABZSO, Chiralpak IA-3 column (100 mm × 4.6 mm, 3 μm), protected with a guard column C12 Phenomenex AJP-6074 (4 mm × 3.0 mm) was employed. The infrared spectra of the MIP-poly(MAA)-SiO₂ and NIP-poly(MAA)-SiO₂ were obtained in the 4000–400 cm⁻¹, resolution 4.0 cm⁻¹, region by means of a Fourier Transform Infrared (FTIR) spectrometer (Spectrum GX PerkinElmer, Wellesley, MA, USA) using the KBr pellet method. The thermogravimetric analysis (TGA) was performed in a thermobalance (2950 Thermal Analysis Instrument, New Castle, DE, USA) with a heating rate of 10 °C min⁻¹, under flowing nitrogen (50 mL min⁻¹) from 25 to 600 °C. The morphology of the materials was evaluated by scanning electron microscopy (SEM) using a Hitachi Analytical Table Top Microscope TM3000 (Tarrytown, NY, USA) with an acceleration voltage of 15 kV and magnifications of 500 × and 2000 × for each synthesized adsorbent material.

2.3. Synthesis of MIP-poly(MAA)-SiO₂ and NIP-poly(MAA)-SiO₂

The synthesis of MIP-poly(MAA)-SiO₂ was based on the precipitation method, involving reactions of coupling free radical addition and sol-gel processing, with some modification according to literature data [13,14]. Initially, 22.0 mg of ABZSO was weighed, which was subsequently transferred to a suitable bottle and a mixture of 5.25 mL of chloroform and 1.75 mL of DMSO (3:1, v/v) added. This mixture was sonicated for 1 min. Afterward, 5.0 mL of MAA was added to the flask and the solution was subjected to ultrasound for 10 min. Then, 1 mL of TMSPMA and 2.0 g of ACPA were also added to the mixture. A chain structure prepolymer was formed by copolymerization of MAA and TMSPMA in the presence of ACPA and ABZSO. Finally, a solution composed of 2 mL of TEOS, 7 mL of chloroform:DMSO (3:1, v/v) solution and 2 mL of 3% HCl was added to the flask dropwise and subjected to ultrasound for 25 min. The flask was sealed, maintained in an oven at 80 °C and the reaction proceeded for 24 h. Fig. S1 shows a scheme of synthesis of MIP-poly(MAA)-SiO₂ hybrid material. After polymerization, MIP-poly(MAA)-SiO₂ was removed from the flask, crushed and washed with a solution of MeOH:acetic acid (9:1, v/v) exhaustively for removal of the ABZSO. Then, MeOH was used to remove the acetic acid. On the other hand, NIP-poly(MAA)-SiO₂, which did not contain the template, was also prepared using the same synthetic protocol, but without the template. Finally, the polymers were sieved to obtain regularly sized particles between 106 and 63 μm.

2.4. Adsorption studies

Ultra-pure water samples were spiked with ABZSO enantiomers in different concentrations, and then 5 mL were added to 50 mL Falcon tubes containing 20 mg of MIP-poly(MAA)-SiO₂ or NIP-poly(MAA)-SiO₂, separately. The mixture was stirred at 250 rpm for 30 min in a horizontal shaker and, subsequently, the supernatant was centrifuged for 2 min at 1500 rpm, filtered using Millipore Millex-GV hydrophilic filter PVDF 0.45 μm and analyzed using HPLC-DAD. All

Download English Version:

<https://daneshyari.com/en/article/6664247>

Download Persian Version:

<https://daneshyari.com/article/6664247>

[Daneshyari.com](https://daneshyari.com)