Materials Science & Engineering C 94 (2019) 684–693

Contents lists available at ScienceDirect

Materials Science & Engineering C

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

Modification of mesoporous silica with molecular imprinting technology: A facile strategy for achieving rapid and specific adsorption

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ARTICLE INFO

Keywords:
Mesoporous silica
SBA-15
Molecular imprinting
Click reaction
2,4-Dichlorophenoxyacetic acid

ABSTRACT

In order to improve the diffusion kinetics of molecularly imprinted materials (MIMs), applying imprinting technology to mesoporous materials is a promising strategy. In the present study, an imprinting approach based on the combination of mesoporous silica materials and molecular imprinting technology is reported. Molecularly imprinted material (MIM) for 2,4-dichlorophenoxyacetic acid (2,4-D) was prepared by using 2,4-D as the template molecule, alkyne-modified β-cyclodextrin and propargyl amine as the combinatorial functional monomers and SBA-15 as the supporter. The functional monomers were anchored to the azide-modified SBA-15 by azide–alkyne Click reaction. The synthesized MIM was characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), elemental analysis (EA), thermal gravimetric analysis (TGA), low-angle X-ray diffraction (XRD) and N_2 adsorption–desorption analysis. The interactions between template and functional monomers were studied by proton NMR analysis and UV–vis experiments. The results of the equilibrium binding experiments and selective tests showed that the prepared MIM has binding affinity and specificity for a group of analytes which have similar size and shape to those of template. Binding kinetic experiments demonstrated that the present imprinting approach can effectively enhance the mass transfer rate. The solid phase extraction of 2,4-D using MIM as the adsorbent was investigated. The extraction conditions for the processes of loading, washing and eluting were optimized. The recoveries of the molecularly imprinted solid phase extraction (MISPE) column for 2,4-D were 76.3–88.9% with relative standard deviations (RSD) of 3.48–7.64%.

1. Introduction

Molecular imprinting is a promising technique for the creation of selective recognition sites in synthetic materials [1,2]. With high selectivity and advantages such as easy preparation, chemical and thermal stability and low cost, molecularly imprinted materials (MIMs) have been applied in a wide variety of fields, such as separation [3,4], solid phase extraction (SPE) [5,6], catalysis [7–9], binding assays and sensors [10–19]. The traditional procedures for molecular imprinting involve complexation of functional monomers and target templates, followed by cross-linking of the monomers and subsequent removal of the templates, thus revealing adsorption sites that are complementary in size and shape to the templates. Despite being convenient, the traditional approach shows some shortcomings, including incomplete template removal, small binding capacity, poor sites accessibility, slow mass transfer and so on [20–22]. To overcome such drawbacks, many strategies, such as surface imprinting [23–26], preparing nano-scaled imprinted materials [27–30], and thin films [16,31,32], have been developed. The purpose of these strategies is to control the imprinted sites to be located at or close to the surface of the imprinted materials.

Mesoporous silica, one of typical mesoporous materials, is an inexpensive and robust porous silica-based solid. Mesostructured silicas are particularly ideal candidates to act as hosts for a variety of guest molecules in many applications such as adsorption, separation, chromatography, catalysis, drug delivery carrier and chemo/biosensing, etc. owing to their unique characteristics such as large surface areas, ordered pore systems, and well defined pore radius distributions [33]. However, the practical applications of mesostructured silicas have been greatly limited because of their nonselective sorption behavior. Combining the advantages of selectivity originating from molecular imprinting and the accessibility from mesoporous silica, mesoporous silica based MIMs have gained increasing attentions in recent years [34–36]. It is reasonably believed that the molecular imprinting technique will be a powerful tool to improve the selectivity of the absorption of

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https://doi.org/10.1016/j.msec.2018.10.032
Received 22 February 2018; Received in revised form 23 August 2018; Accepted 5 October 2018
Available online 08 October 2018

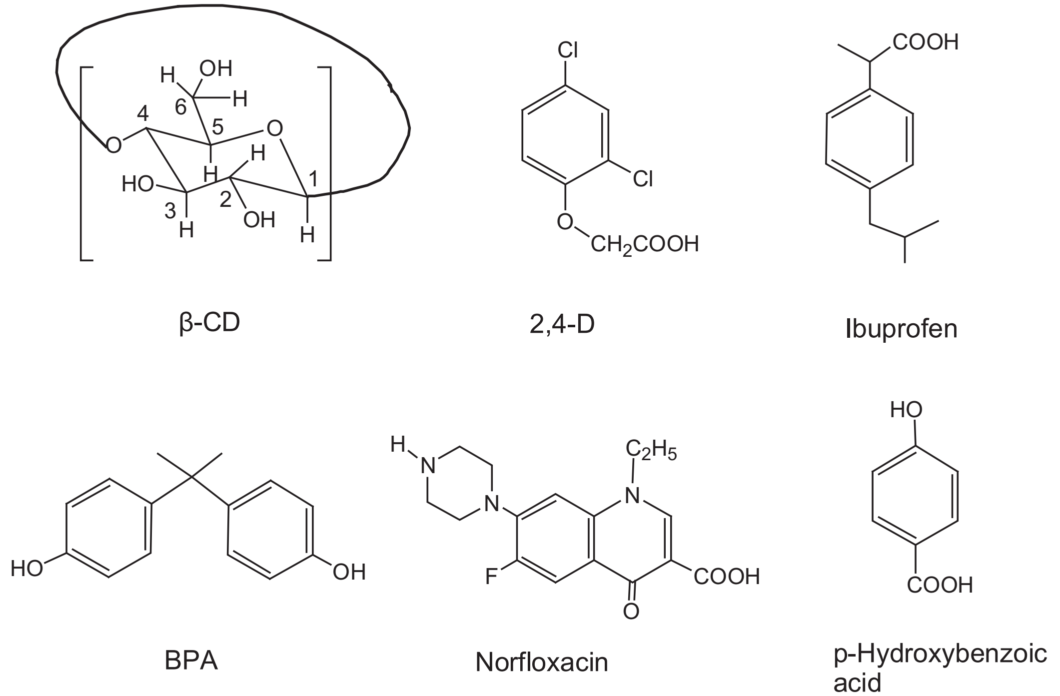

Fig. 1. Structures of β-CD, 2,4-D and related substrates used in this study.

mesostructured silicas.

β-Cyclodextrin (β-CD) is a torus-shaped, cyclic oligosaccharide consisting of seven α-1,4-linked D-glucopyranose units with an internal hydrophobic cavity and a hydrophilic outer surface. β-CD has been shown to form inclusion compounds with a wide variety of suitably sized guest molecules. In the past several years, β-CD and its derivatives have been chosen as functional monomers for making MIMs [37–41]. Two strategies were reported for using β-CD as functional monomers in imprinting. For those comparatively big templates, several β-CD molecules are assembled around the template and each β-CD molecule accommodates a part of the template, so that the assembled β-CD molecules can work as a whole to recognize the template precisely [38,39,41]. When making MIMs for those templates whose main body could be accommodated in the cavity of β-CD, β-CD and another compound are combined to act as functional monomers [40].

2,4-Dichlorophenoxyacetic acid (2,4-D) as a phenoxy herbicide, is used to control the growth of weeds and broadleaf plants. It is one of the oldest and most widely available herbicides in the world. 2,4-D is a moderately toxic, it is reported to have negative effects on the endocrine system (specifically the thyroid and gonads) and immune system [42,43]. On account of its poor biodegradability, it can be detected as a pollutant in aquatic systems. Owing to the low-level concentrations of 2,4-D in environmental matrixes, clean-up and pre-concentration procedures are usually required prior to analysis. SPE is a versatile and reliable technique that is widely used for sample clean-up and pre-concentration. However, most of the traditional SPE material has poor selectivity. Using MIMs as the extraction sorbents is a feasible method to solve this problem [5,6]. Therefore, it is desirable for us to design and synthesis of 2,4-D imprinted materials for analytical applications [44].

The copper-catalyzed azide–alkyne cycloaddition (CuAAC) coupling reaction is a prototypical example of Click reaction that has gained popularity in functionalization of polymeric architectures and bioconjugation for its selectivity, efficiency, and convenience [45,46]. In traditional imprinting technology, MIMs are prepared by free-radical polymerization or sol-gel processes. Recently, Zhao et al. have developed a method for preparation of MIMs through the exploitation of Click reaction [47].

In the present study, the feasibility of fabrication of imprinting sites in the nano-pores of mesoporous silicas by Click reaction was investigated by using 2,4-D as the model template molecule. Molecularly imprinted material (MIM) for 2,4-D was prepared by using alkyne-modified β-cyclodextrin and propargyl amine as the combinatorial functional monomers and azide-modified SBA-15 as the supporter. The functional monomers were conjugated to the mesoporous silicas by azide–alkyne Click reaction. To the best of our knowledge, this is the first time to anchor combinatorial functional monomers to the walls of the nano-pores of mesoporous silicas by Click reaction. The prepared MIM exhibited binding affinity and specificity for the template. The binding kinetics tests demonstrated that the imprinting approach can improve site accessibility for the template effectively. The solid phase extraction (SPE) of 2,4-D using MIM as the adsorbent was further investigated. The results demonstrated that the 2,4-D imprinted SPE column was suitable for the extraction of 2,4-D from water samples.

2. Experimental section

2.1. Materials and characterization

2.1.1. Materials

2,4-D and bisphenol A (BPA) were purchased from Sigma-Aldrich (Shanghai, China). Norloxacin was obtained from Guangzhou South Hospital (Guangzhou, China). Pluronic P_{123} ($EO_{20}PO_{70}EO_{20}$), Ibuprofen, 3-chloropropyltrimethoxysilane and tetraethoxysilane (TEOS) were obtained from Aladdin (Shanghai, China). Sodium azide, $CuSO_4{\cdot}5H_2O$, sodium ascorbate, p-toluenesulfonyl chloride (TsCl) and propargyl amine were purchased from Energy Chemical (Shanghai, China). Dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) were dried with molecular sieve 3A and then distilled under reduced pressure. β-CD was purchased from Shanghai Chemical Plant (Shanghai, China), it was recrystallized from water and dried under vacuum at 110.0 °C for 24 h. Deionized water (18.2 MΩ cm) obtained from a Hitech laboratory water purification system (Hitech Instruments Co. Ltd., Shanghai, China) was used throughout the experiments. All other solvents purchased from commercial resources were of analytical or chromatographic grade and used as received without further