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The preparation of high-capacity boronate affinity adsorbents by surface initiated reversible addition fragmentation chain transfer polymerization for the enrichment of ribonucleosides in serum

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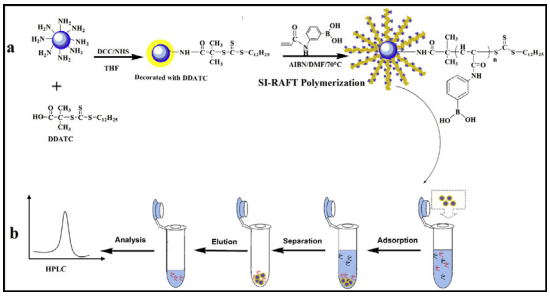
HIGHLIGHTS

- High capacity boronate affinity adsorbents were prepared via SI-RAFT.
- The adsorbents possess high adsorption capacity and good selectivity to ribonucleosides.
- The adsorbents exhibit faster adsorption and desorption speed towards ribonucleosides.
- The adsorbents were used to selectively enrich ribonuclosides from calf serum.

GRAPHICAL ABSTRACT



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ABSTRACT

Boronate affinity adsorption is uniquely selective for cis-diol-containing molecules. The preparation and application of boronate affinity materials has attracted much attention in recent years. In this work, a high-capacity boronate affinity adsorbent was prepared by surface-initiated reversible addition–fragmentation chain transfer polymerization (SI-RAFT). Commercial aminated poly(glycidyl methacrylate) (PGMA) microspheres were modified with the chain transfer agent (CTA) S-1-dodecyl-S-(α,α-dimethyl-α-acetic acid)trithiocarbonate (DDATC). Boronate-affinity adsorbents were then prepared via SI-RAFT polymerization employing 3-acrylamidophenylboronic acid (AAPBA) as the monomer. The Fourier transform infrared spectroscopy (FT-IR), nitrogen adsorption and desorption measurements have proven the successful grafting of AAPBA on PGMA microspheres surface. The boronate affinity adsorbents thus prepared possess much higher adsorption capacity (99.2 μmol/g of adenosine) and both faster adsorption and desorption speed towards ribonucleosides, the adsorption and desorption could be completed in 2 min. The high selectivity of the adsorbents to ribonucleosides was verified in the presence of a large excess of deoxynucleosides. The boronate affinity adsorbents were then employed for sample pretreatment before HPLC analysis of ribonucleosides in serum. The ribonucleosides were effectively enriched by boronate affinity dispersive solid-phase extraction (BA-DSPE), with high mass recoveries and good precision. The simultaneous determination of uridine and guanosine in calf serum was achieved by utilizing the standard addition method, their contents were determined to be 170 ± 11.6 ng/mL and 39.6 ± 4.4 ng/mL respectively. The results proved that the prepared boronate affinity materials could be applied for sample pretreatment of cis-diol containing molecules in biological samples.

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1. Introduction

Biological molecules that contain a *cis*-diol group are important types of compounds that include, but are not limited to, carbohydrates, glycoproteins, RNA, nucleosides and some active ingredients in traditional Chinese medicine. Cis-diol containing biomolecules are a special class of compounds among which many are analytes of interest in the research frontiers of life science [1–3]. Therefore accurate detection concentrations of these cis-diol-containing biomolecules are very significant in theory and in practice. However, it is very hard to achieve this purpose because cis-diol-containing biomolecules are typically present at very low levels and the matrix interferences are usually very serious. Therefore, high efficiency isolation and enrichment of the cis-diol-containing biomolecules are critical for their analysis. At present, the most efficient and facile isolation and enrichment method for cis-diol-containing biomolecules is boronate affinity solid-phase extraction (SPE). The basic principle of boronate affinity extraction relies on the formation of five- or six-membered cyclic esters with bonds between the cis-diols and boronic acid ligands under alkaline conditions. The formation of the boronate ester bond is reversible and can be hydrolyzed under acidic conditions to release the target molecules. This technique can achieve the isolation and enrichment of cis-diol-containing biomolecules from complex biological samples [4,5].

In recent years, many new boronate affinity materials have been reported [4–7]. Many of these boronate affinity materials have already been employed to selectively extract various cis-diol containing molecules, such as glycoproteins [8], ribonucleosides [9], stevioside [10], ribavirin [11], bacteria [12] and saccharides [13] from complex biological samples. However, in current reports of boronate affinity adsorbents, small organic molecules bearing a boronic acid moiety were covalently bonded to the surfaces of solid supports or were introduced into scaffolds of monoliths via boronic acid-containing monomers. In these cases only a monolayer boronic acid groups were capable of bonding with the cis-diols, thus resulting in very limited adsorption capacities [14,15]. To improve the adsorption capacity, Xu and co-workers [9] synthesized a boronate-decorated polyethyleneimine (PEI) with grafted hybrid magnetic nanoparticles for the highly selective enrichment of modified ribonucleosides. The thicker grafting layer of the PEI brushes supplied a large number of anchor sites for boronate groups. Meanwhile Liu et al. [16] prepared a boronate affinity material by introducing dendrimeric polymers on the magnetic particles. This introduced a high density of boronate affinity sites, resulting in a high adsorption capacity. These works showed that polymers with multiple active groups could be utilized to increase the ligand density of boronic acids. However, in the above methods, polymer chains were covalently grafted to solid supports. This resulted in a limited grafting density due to the significant steric hindrance of large molecular polymers that limited further improvement in the adsorption capacity. Therefore, it is important to explore a more applicable and practical strategy for the preparation of high-capacity boronate affinity adsorbents.

"Grafting to" and "grafting from" are the two typical methods for surface modification with polymers. Compared to the "grafting to" method, "grafting from" is capable of grafting polymer chains on a solid support with a high grafting density because the monomers diffuse into the active sites [17]. Therefore, a higher polymer-grafting density could be obtained by the "grafting from" method. As one of the types of newly developed synthetic methods in macromolecular chemistry, controlled/living radical polymerization (CRP) has drawn much attention in the field of surface modification by the "grafting from" method. Generally, CRP possesses the advantages of generating polymers with low polydispersities, homogeneous structures and desirable architectures [18]. In the surface-initiated CRP method, the grafted polymer was propagated from the surface radical that was produced by the decomposition of initiators immobilized on the surface of a solid support, so a high polymer grafting density could be achieved. The most frequently used CRP methods in recently years include atom-transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer polymerization (RAFT). Comparing to ATRP, the RAFT reactions does not need strictly anaerobic conditions and a cuprous ion catalyst is not involved, avoiding the laborious copper-removing step. Meanwhile, RAFT polymerization is the most flexible polymerization technique with respect to monomer choice and functional group tolerance and allows for the preparation of separation materials with complex/advanced architectures [19,20]. In recent years, people have utilized the RAFT polymerization technology for the preparation of separation materials with great success. For instance, Xu et al. [21] proposed a facile route to the synthesis of spherical polyacrylic acid (PAA) brushes via RAFT polymerization for high-capacity protein immobilization; an ultra-high protein immobilization capacity of 2600 μg streptavidin/mg adsorbent was realized by virtue of its richness in carboxyl groups. Sellergren and coworkers [22] synthesized a molecularly imprinted membrane (MIM) via RAFT polymerization. Chiral molecules were separated by MIM within a few minutes, which was more efficient than traditional methods. Zhao et al. [23] prepared magnetic-surface molecularly imprinted nanoparticles via SI-RAFT polymerization for highly separation of fluoroquinolones (FQs) in human urine. The highly uniform nanoscale MIP layer was homogeneously grafted on the surface, which favored fast mass transfer and rapid binding kinetics, which were observed.

Ribonucleosides are the basic unit in ribonucleotides in living organisms. They belong to the cis-diol-containing compounds. Ribonucleosides are mainly produced in the process of RNA transcription. Normal ribonucleosides, such as cytidine, uridine, guanosine, and adenosine, have shown many types of biological activities that possess very important physiological significance and influence. These include the growth and development of organisms and their genetics, controlling the various nutrient factors in the body's metabolic regulation [4]. When the body develops cancer or other diseases, normal ribonucleosides are chemically modified at the post-transcriptional stage, forming modified ribonucleosides, such as 1-methylguanosine, N2-methylguanosine, and 3-methyluridine, which have been suggested as potential diagnostic markers of cancer-related diseases [24,25]. At present, the analysis of ribonucleosides mainly depends on HPLC [4,26] and CE [27], in which the sample pretreatment is a critical process for obtaining accurate results. To date, boronate affinity-based SPE is the most widely applied method for the isolation and enrichment of ribonucleosides [9,27].

In this work, we successfully developed a novel synthetic route for preparing boronate affinity adsorbents for SPE via SI-RAFT. The performance of the boronate affinity adsorbents for the adsorption of ribonucleosides was evaluated. Additionally, a dispersive SPE (DSPE) method has been proposed for sample pretreatment of ribonucleosides in serum.

2. Material and methods

2.1. Materials and reagents

Aminated poly(glycidyl methacrylate) (PGMA) microspheres (specific surface area is 110 m^2/g, particle diameter is 150–300 μm) were provided by Xi'an Sunresin New Materials Co., Ltd. (Xi'an, China); 3-aminophenylboronic acid and acryloyl chloride were obtained from J&K technology Co., Ltd. 2,2-azobis(2-methylpropionitrile) (AIBN) was obtained from Tianjin Chemicals Co. Ltd. (Tianjin, China). N,N-dimethylformamide (DMF),

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