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# Enhanced binding capacity of boronate affinity adsorbent via surface modification of silica by combination of atom transfer radical polymerization and chain-end functionalization for high-efficiency enrichment of cis-diol molecules



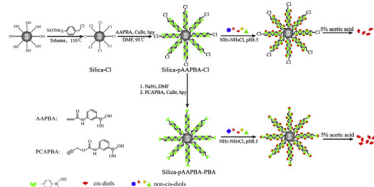
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## HIGHLIGHTS

- Boronate adsorbent is prepared via ATRP and chain-end functionalization.
- The adsorbent has quite high binding capacity for cis-diols.
- Binding capacity is easily manipulated by ATRP condition.
- Chain-end functionalization can improve binding capacity significantly.
- Reduced adsorbent is consumed in dispersed solid-phase extraction of cis-diols.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Boronate affinity materials have been widely used for specific separation and preconcentration of cis-diol molecules, but most do not have sufficient capacity due to limited binding sites on the material surface. In this work, we prepared a phenylboronic acid-functionalized adsorbent with a high binding capacity via the combination of surface-initiated atom transfer radical polymerization (SI-ATRP) and chain-end functionalization. With this method, the terminal chlorides of the polymer chains were used fully, and the proposed adsorbent contains dense boronic acid polymers chain with boronic acid on the chain end. Consequently, the proposed adsorbent possesses excellent selectivity and a high binding capacity of  $513.6 \mu\text{mol g}^{-1}$  for catechol and  $736.8 \mu\text{mol g}^{-1}$  for fructose, which are much higher than those of other reported adsorbents. The dispersed solid-phase extraction (dSPE) based on the prepared adsorbent was used for extraction of three cis-diol drugs (i.e., epinephrine, isoprenaline and caffeic acid isopropyl ester) from plasma; the eluates were analyzed by HPLC-UV. The reduced amount of adsorbent (i.e., 2.0 mg) could still eliminate interferences efficiently and yielded a recovery range of 85.6–101.1% with relative standard deviations ranging from 2.5 to 9.7% ( $n = 5$ ). The results indicated that the proposed strategy could serve as a promising alternative to increase the density of surface functional groups on the adsorbent; thus, the prepared adsorbent has the potential to effectively enrich cis-diol substances in real samples.

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## 1. Introduction

Boronate affinity materials have been widely used in the selective separation and enrichment of cis-diol molecules, such as catecholamine, nucleosides, antioxidant compounds, saccharides, glycoprotein and glycopeptides [1–3]. This selectivity comes from the formation of reversible pH-dependent cyclic esters between cis-diol molecules and boronic acids on the surface of the adsorbent. In an alkaline solution, cis-diols are selectively adsorbed by an adsorbent to generate five- or six-member cyclic esters with boronic acids, while these cyclic esters could disassociate under acidic conditions, resulting in the release of cis-diol molecules into solution [4–6]. Therefore, boronate affinity materials are capable of possessing high selectivity and are attractive in the separation and enrichment of cis-diol molecules from complex biological samples.

Like other types of adsorbents, selectivity and binding capacity are two important characteristics in the evaluation of boronate affinity materials. Accordingly, many studies investigated the improvement of selectivity and binding capacity [7,8]. Binding selectivity essentially arises from the interaction between adsorbates and boronic acids on the surface of adsorbents and thus is related to the types of boronic acid molecules present. Usually, phenylboronic acid is used as a ligand, with which the resulting varieties of adsorbents have similar selectivity [9,10]. To improve selectivity, varieties of substitute phenylboronic acids [7,11] or pyridine boronic acids [12] were used, and the concept of a neighboring amino group capable of B–N coordination was proposed by Zhen Liu [13]. The binding capacity depends on the density of the functional groups of a given material. Traditionally, adsorbents are prepared via the activation of materials with a double active-group molecule followed by bonding with phenylboronic acids; however, the binding capacity of the resulting materials is not satisfactory due to the limited binding sites on the material surface [14–17], which affect the enrichment efficiency of cis-diol molecules. This problem has researched significantly, and recently, the modification of materials with functional polymers has been developed to improve binding capacity. Liu et al. demonstrated that the bonded hyperbranched polymer was able to improve binding strength and binding capacity [18]; Lei Ye and coworkers grafted a fluorescent boronic acid polymer onto a silica surface with 3-(2-azido-acetylamino)phenylboronic acid as monomer via surface-initiated atom transfer radical polymerization (SI-ATRP), producing an adsorbent that exhibited a high binding capacity [19]. Despite these studies, significant effort is still being made to increase binding capacity.

Recent studies have showed that SI-ATRP can control the polymer chain and endow the adsorbent with high binding capacity due to the presence of accessibly high-density functional groups on the surface of the adsorbents [20,21]; however, there are few reports on the preparation of boronate affinity materials by SI-ATRP. Although Lei Ye and coworkers grafted a fluorescent 3-(2-azido-acetylamino)phenylboronic acid monomer onto silica using SI-ATRP, the study focused on the fluorescent response of the material and did not investigate the relationship between the binding property and the polymer brush [19]. However, this relationship is critical to design the structure and properties of an adsorbent. Therefore, it is still necessary to investigate the preparation of a boronate affinity adsorbent by SI-ATRP in detail, also the advantages of this adsorbent in the enrichment of cis-diol molecules. From the principle of ATRP, well-defined polymers with dense functional group units on solid materials can be created and a halogen atom which can serve as a reactive site for further functionalization still exists at the end of a polymer chain [22]. Previous study has demonstrated that the end groups in the polymer significantly affect the properties of the resulting polymer [23], but this end effect has not been used to

manipulate the binding properties of the adsorbent. With chain-end functionalization technology, it should be possible to bond functional groups onto the end of a polymer chain. According to chromatographic theory [24], the end-group in a polymer chain might favor the accessibility of the analyte for the functional groups.

In this work, we prepared a high-capacity boronate affinity adsorbent grafted with boronic acid end-functional boronic acid polymer chain via the combination of SI-ATRP using 3-acrylamidophenylboronic acid as monomer with end-capped technology by “click chemistry”. And the relationship between the binding capacity and the ATRP condition was investigated. Based on the enrichment of three cis-diol drugs (i.e., epinephrine, isoprenaline and caffeic acid isopropyl ester) in plasma samples, the advantage of this high-capacity boronate affinity adsorbent was shown in the analysis of cis-diol molecules.

## 2. Experimental

### 2.1. Preparation of boronate affinity adsorbent

#### 2.1.1. Immobilization of initiator onto silica

Under nitrogen, silica (5.0 g) was dispersed in dried toluene (100 mL) and then 4-(chloromethyl) phenyltrimethoxysilane (4-CPTS; 2.20 mL, 9.98 mmol) was added; the reaction mixture was then stirred at 110 °C for 12 h. The initiator grafting density was calculated from a mass balance based on the difference between the initial and final concentrations of 4-CPTS in the solution. The final concentrations of 4-CPTS were determined by HPLC using an Inertsil ODS column (5 µm, 4.6 × 250 mm). Mobile phases was acetonitrile-water solution (1:1, v/v), and the UV wavelength was 254 nm. The final unknown concentrations of 4-CPTS were calculated from the calibration curve. The resulting initiator-modified silica was filtered out, washed with toluene and methanol, and dried at 50 °C for 4 h under vacuum.

#### 2.1.2. Grafting of 3-acrylamidophenylboronic acid (AAPBA) on silica by SI-ATRP

A typical polymerization procedure was as follows: initiator-modified silica (1.0 g) was used as an initiator dispersed in N,N-dimethyl formamide (DMF), to which AAPBA (1.6 g, 8.12 mmol; it was made according to the reference [25] and the details in Supporting Data), 2, 2'-bipyridyl (0.20 g, 1.28 mmol) were added. After the mixture was deoxygenated via three freeze–pump–thaw cycles, CuBr (0.10 g, 0.64 mmol) was quickly added to the flask under a nitrogen atmosphere. The polymerization proceeded at 90 °C for a given time during continuous stirring. The resulting beads were washed with methanol, water and methanol in sequence. To separate the residual catalyst completely, the obtained beads were re-dispersed into the mixture of methanol and 0.25 M EDTAN<sub>2</sub> solution, and the mixture was stirred at 40 °C for 4 h. After filtration, the silica (silica-pAAPBA-Cl) was washed with water, methanol and acetone, and dried at 50 °C for 4 h under vacuum.

#### 2.1.3. End-functionalization of polymer chain on the surface of silica

Silica-pAAPBA-Cl (0.50 g) and NaN<sub>3</sub> (0.160 g, 2.46 mmol) were added into 20 mL DMF. The mixture was stirred at 80 °C for 16 h. The silica (silica-pAAPBA-N<sub>3</sub>) were washed with water, methanol and acetone, and dried at 50 °C for 4 h under vacuum.

Silica-pAAPBA-N<sub>3</sub> (0.50 g), 25 mL tetrahydrofuran, 3-(prop-2-ynyloxycarbonylamino)phenylboronic acid (PCAPBA; 0.38 g, 1.6 mmol; it was made according to the reference [26] and the details in Supporting Data) and CuBr (0.072 g, 0.5 mmol) were added into a flask. The reaction mixture was degassed by two freeze pump–thaw cycles and left under N<sub>2</sub>; then 2, 2'-bipyridyl (0.156 g,

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