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Graphene oxide based molecularly imprinted polymers with double recognition abilities: The combination of covalent boronic acid and traditional non-covalent monomers

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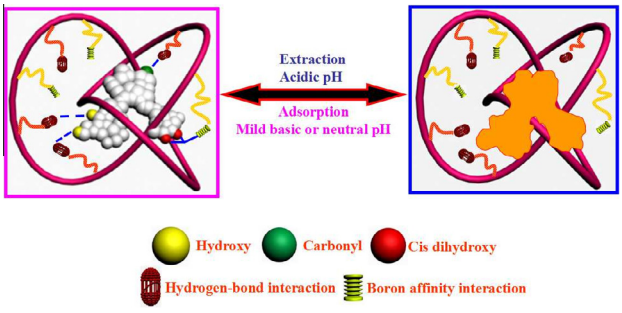
HIGHLIGHTS

- DR-MIPs were successfully fabricated by a binary complex imprinting approach.
- DR-MIPs possessed reversible "pH response" effect and with double recognition abilities.
- DR-MIPs possessed a specific affinity for luteolin.
- Purified luteolin exhibited a good antibacterial effect.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, graphene oxide (GO) based molecularly imprinted polymers with double recognition abilities (DR-MIPs) were prepared and considered as adsorbent for the specific recognition and capture of luteolin (LTL). To exhibit the tightest binding hosts for LTL, the double recognition abilities were achieved by adopting 4-vinylphenyl boronic acid (BA) and methacrylic acid (MAA) to be the covalent and non-covalent imprinted monomers, respectively. Then, their functional groups and shape of imprinted sites endowed DR-MIPs with a specific affinity for cis-diol-containing structure, hydroxyl and carbonyl groups of LTL. The results of batch mode experiments indicated kinetic equilibrium time and binding capacity of DR-MIPs were 30 min and 56.27 mg g^{-1} at 298 K, respectively. The Langmuir isotherm and pseudo-second-order kinetic models were the main adsorption mechanisms for DR-MIPs, and the fast adsorption and large binding amount were resulted from the two-dimensional (2D) structure of GO and enough imprinted sites with double recognition abilities. DR-MIPs also showed excellent recognition ability, and the estimated relative selectivity coefficients (k') for structural analog quercetin (QRT), hydroquinone (HDQ) and p-nitrophenol (P-NP) were 13.73, 18.62 and 19.95, respectively. In addition, DR-MIPs possessed outstanding reusability and enhanced purification property for 85% raw LTL. The purified LTL products achieved approximately 93.47%, and they exhibited the obvious antibacterial performance.

1. Introduction

Luteolin (3′,4′,5,7-tetrahydroxyflavone) is one of the ubiquitous flavonoids distributed in various types of vegetables, fruits and

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natural herbal drugs [1]. Luteolin has been proved to display a wide range of hygienical function and pharmacological prosperities, including antibacterial, anti-oxidant, anti-inflammatory, anti-cancer, antidiabetics, enhance immunity ability and anti-viral properties [2,3]. So far, several methods have been applied for separation and purification of luteolin from extract, such as acid sinking method, thin layer chromatography, column chromatography, lead salt deposition and macroporous resin adsorption and so on [4–7]. Although the methods mentioned above have unique advantages, they also require time-consuming pre-treatment steps, complex operation process and especially for poor selectivity. Therefore, highly selective separation and sensitive recognition of luteolin from complex samples are in great demand.

Molecular imprinting technology, as most promising methodologies for producing molecular imprinted polymer (MIPs), is a classic strategy to obtain synthetic receptors in molecular recognition [8]. In the process of synthesizing MIPs, functional monomers are primarily preassembly in the vicinity of a template molecule, copolymerized with cross-linking monomers and initiator, and after removal of the template molecules, the memory cavities contains complementary binding sites rebinding the template molecules with high specificity [9]. In the recent years, many significant works about MIPs for separation and purification of flavones have been reviewed to have obvious advantages, such as more accessible sites, fast mass transfer and specific selectivity [10–12]. O'Mahony et al. used 4-vinylpyridine as functional monomer to recognize quercetin by molecular imprinting technology [13]. McArdle et al. utilized chalcone isomerase (CHI) as monomer based on biosynthetic enzymes via imprinted process to recognize flavonoid-based natural products [14]. For the first time, Zhang's group synthesized imprinted porous materials by the sol–gel method for selective separation Luteolin [15]. Then they reported their continuous work about molecularly imprinted membrane adopting (3-aminopropyl)trimethoxysilane as functional monomer to recognize luteolin [16]. These efforts have been made not only provided several feasible ways for designing MIPs, but also demonstrated the ability of MIPs for specific targeting of flavonoids. Moreover, non-covalent interaction between functional monomers and imprinted molecule were involved prior to highly cross-linked polymeric process. However, detailed investigations have shown that a part of imprinted binding sites in the imprinted polymers through non-covalent interaction were easy to irreversibly shrink, which had negative effects for selectivity [17]. Accordingly, employing the covalent interaction for the production of MIPs would be preferable, due to their homogeneous binding sites and better selectivity [18].

Boron affinity (boronic acid affinity) refers to its unique reversible interaction of covalent bonding between boronic acid and cis-diol-containing compounds (CDCCs) [19–21]. The excellent covalent affinity of boronic acids toward CDCCs relies on the property that they could form stable cyclic esters with cis-diol moieties in mild basic or neutral aqueous solution, while the cyclic esters dissociate once switching the medium to acidic pH [22]. Considerable efforts have been devoted to constructing boronate-functionalized materials, especially boronate affinity molecular imprinting, for the specific recognition and subsequent isolation of CDCCs. For instance, Li et al. [23] and Zhang et al. [24] selected boronic acid as functional monomer to prepare the MIPs of glycoprotein directly. Gu et al. fabricated MIPs that using boric acid as function monomer to graft on the surface of the carrier for the selective recognition of dopamine [25]. Thus, combining boron affinity with the covalent interaction of MIPs significantly improved the "capture" ability among MIPs and CDCCs, which based on specific boronic acid groups contained in the MIPs and their shapes of the imprinted cavities. Nevertheless, a universal and simple approach for separation luteolin, which was one of the typical CDCCs, via boronate affinity molecular imprinting has not been reported.

In recent years, several different monomers were optimized and used simultaneously to prepare MIPs favoring the improvement of selectivity, and the basic mechanism stemmed from antibodies in nature, which recognizing target molecules by a combination of multiple weak electrostatic, hydrophobic, and hydrogen-bonding interactions between complementary three-dimensional surfaces [26]. Subhra Mohapatra's group designed molecularly imprinted polymeric nanoparticles using methacrylic acid (MAA), ethyl alcohol and N-isopropylacrylamide (NIPAm) as hydrogen-bonding, negatively charged and hydrophobic functional monomers for atrial natriuretic peptide [27]. Shea et al. prepared peptide imprinted polymer nanoparticles, and the functional monomers included NIPAm as the backbone monomer in combination with acrylamide (AAm), acrylic acid (AAc), N-(3-aminopropyl) methacrylamide hydrochloride (APS), and N-tert-butylacrylamide (TBAm), as hydrogen-bonding, negative-charged, positive-charged, and hydrophobic functional monomers, respectively [28]. Gong et al. developed a pH-sensitive molecularly imprinted nano spheres/hydrogel composite utilizing 2-hydroxyethyl methacrylate (HEMA) and 2-(diethylamino)ethyl methacrylate (DEAEMA) as monomers for controlling release of dexamethasone-21 phosphate disodium [29]. To mimic these interactions, MIPs with multi recognition resulted from several monomers may be promising approach for separation of luteolin. Surprisingly, luteolin themselves not only possess the cis-diol-containing structure served as the binding sites that can form the covalent interaction with boronic acid, but also it equipped with hydroxyl groups and carbonyl group can be employed to form the hydrogen bonding with traditional non-covalent monomers. To the best of our knowledge, such a possibility by introducing covalent boric acid and traditional non-covalent monomers for recognition luteolin has never been well explored. Therefore, it is highly desirable to develop MIPs with double recognition (DR) ability combination of non-covalent and covalent imprinted sites, and then clarify their recognition mechanism. This will be very helpful to design highly efficient MIPs for their applications of selective recognition target molecules.

Graphene oxide (GO), as a novel two-dimensional (2D) honeycomb lattice carbon nanomaterial with a monolayer structure, is a promising candidate for MIPs supports, especially because of their huge surface area and potential chemical modification [30–37]. Enlightened by the information mentioned above, a binary complex imprinting approach via the combination of covalent boronic acid and traditional non-covalent monomers was carried out, and prepared graphene oxide based MIPs with double recognition abilities (DR-MIPs) for enhanced recognition and selective separation of luteolin. In this work, 4-vinylphenyl boronic acid (BA) and methacrylic acid (MAA) were firstly employed as functional monomers, ensuring the interaction with luteolin via covalent boron affinity and non-covalent hydrogen bonding, respectively. Then atom transfer radical precipitation polymerization (ATRPP) was conduced to control template-imprinting sites to situate at the surface or in the proximity of the GO surface, which providing more binding sites, outstanding adsorption performances and fast association kinetics [38–41]. Furthermore, double recognition ability derived from non-covalent and covalent imprinted sites presented enhanced recognition and high selectivity toward luteolin, and the possible DR mechanism was described in Scheme 1.