



Experimental investigation of a natural favonoid adsorption on macroporous polymers with intrinsic *cis*-diol moieties recognition function: Static and dynamic methods



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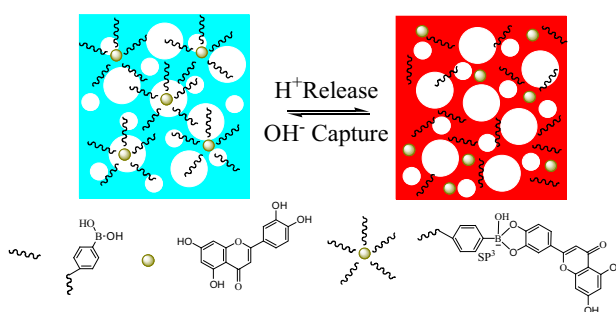
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HIGHLIGHTS

- MPs-BA-1 possessed macroporous polymer network and accessible binding sites for *cis*-diols.
- MPs-BA-1 has excellent adsorption capacity, binding kinetics, specific affinity, and reusability.
- Dynamic adsorption incorporated with analysis of RSM determined the optimal conditions.
- The results could be facily adopted to predict and design optimal conditions in the scale-up.

GRAPHICAL ABSTRACT



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ABSTRACT

Macroporous polymers with boronate affinity ability (MPs-BA-1) were prepared via high internal phase emulsions (HIPES) template and then applied to selective adsorption a natural favonoid luteolin (LTL). As-prepared MPs-BA-1 possessed macroporous polymer network and accessible binding sites for *cis*-diols, and its adsorption behaviors were studied using static and dynamic methods. In static conditions, adsorption amount of LTL increased rapidly in the first 30 min and reached to equilibrium in approximately 2.0 h. Superior conformity of the second-order model confirmed the chemical nature of the interaction between the LTL and binding sites. The fitting adsorption isotherm was a Langmuir type, and the maximum monolayer adsorption amounts at 298 K, 308 K and 318 K were 60.97 $\mu\text{mol g}^{-1}$, 70.10 $\mu\text{mol g}^{-1}$, and 55.03 $\mu\text{mol g}^{-1}$, respectively. Dynamic adsorption incorporated with the analysis of response surface methodology (RSM) suggested that the optimal adsorption amount (73.47 $\mu\text{mol g}^{-1}$) achieved when the flow rate of LTL solution was 3.0 mL min^{-1} , temperature was 28.28 °C and concentration of LTL solution was 30 mg L^{-1} . MPs-BA-1 served the specific adsorption towards LTL, and the recognition mechanism based on borate affinity was also described. MPs-BA-1 retained the adsorption amounts for successive cycles, but the loss using dynamic method was larger than in the batch method.

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1. Introduction

Luteolin (LTL), as one of the more common flavonoids, possesses remarkable natural pharmacological activities, including antioxidation, anti-inflammatory, antitumor, and so on [1]. In recent years, LTL was found to be widely existed in the vegetables, fruits,

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Chinese traditional herb medicine and peanut shell [2]. Nowadays, organic solvent extraction is the basic method for extracting LTL, but the selective separation and further purification is also a great challenge to us [3]. At present, macroporous adsorption resin is attracting increasing attention, especially in the field of separation science, owing to convenient operation, easy regeneration, and low expense [4,5]. However, it still has considerable drawbacks, such as difficulties in control of pore sizes and poor selectivity etc [6].

In recent decades, boronate affinity has aroused more and more interest due to its unique reversible covalent bonding with *cis*-diol containing compounds [7]. With this well-known property, boronic acid derivatives have been employed in the fields of carbohydrate recognition, creating self-healing materials, molecular sensors, and cancer cell sweepers [8–10]. Particularly, the recognition and selective separation of biological macromolecule, such as the polysaccharide, glycoprotein and insulin, are widely researched [11]. LTL, as one kind of flavonoids with medical value, also has the *cis*-diol groups. Considering this typical structure, boronic acid-based macroporous adsorption resin, provide quick, efficient, and specific adsorption of LTL, could be developed based on the boronate affinity strategy.

High internal phase emulsions (HIPEs)-templating technique is versatile and facile for the preparation of well-designed and controlled porous polymers [12]. This technique involves the preparation of one emulsion system, in which the disperse phase accounts for more than 74% [13,14]. In this case, the droplets change their spherical shapes into the form of polyhedrons, which is same as the typical structure of foam [15]. Thus, the resulting macroporous polymers possess good permeability and high mass transfer efficiency, which are considered to be an important tool as adsorbents [16,17]. In recent years, our group prepared the macroporous polymers via HIPE templating technique to capture λ -cyhalothrin and copper ions [18,19]. However, it should be noted that in order to use macroporous resin as separators to selectively capture LTL, the boronate affinity had to be combined with the HIPEs-templating technique.

The main objective of the current study is to investigate the formation of macroporous polymers incorporated with boronate affinity (MPs-BA), by templating in water-in-oil (W/O) HIPEs. For this purpose, an appropriate control of emulsion stability was achieved, and then the 4-vinylphenylboronic acid (VPBA) was introduced into the continuous phase, allowing us to obtain the final porous foams. By batch and dynamic adsorption process, the selective capture ability of MPs-BA towards LTL was evaluated.

2. Experimental section

2.1. Materials

4-vinylphenylboronic acid (VPBA), ethylene glycol dimethacrylate (EGDMA), butyl acrylate, thymol, *p*-nitrophenol (pNP), 4-chloro-3-hydroxytoluene (4C3H) and alizarin red S (ARS) were supplied by Aladdin Industrial Corporation (Shanghai, China). Hypermer 2296 were kindly supplied by Foshan Excel Chemical Co., Ltd. (Fujian, China). Luteolin (LTL) was provided by Kan Sheng Co., Ltd (Shangxi, China). 2,2'-Azobisisobutyronitrile (AIBN), potassium sulphate (K_2SO_4), and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China).

2.2. Instruments

The photograph of emulsion droplet was observed by an EV5680 optical microscope. The morphology of (MPs-BA) was observed by scanning electron microscopy (SEM, JSM-7001F; JEOL Ltd., Japan). Fourier transform infrared (4000 – 400 cm^{-1}) spectra

were recorded on a Nicolet Nexus 470 FTIR apparatus (U.S.A.). Elemental compositions of (MPs-BA) were also investigated by X-ray photoelectron spectroscopy (XPS). Fluorescent light analysis of ARS combining with MPs-BA was detected by laser scanning confocal microscope (LSCM) around 480 nm solid state laser light source. Ultraviolet (UV-Vis) absorption spectra were obtained by TU-1810 UV visible spectrophotometer (Beijing Purkinje General Instrument Co. Ltd., Beijing, China). High performance liquid phase (HPLC) analysis was carried out on an agilent system (Agilent, 1200, Germany) equipped with a UV-Vis detector.

2.3. Synthesis of macroporous polymers with boronate affinity ability (MPs-BA)

Firstly, 3.0 mL of butyl acrylate and 0.5 mL of EGDMA were transferred into two round-bottom flasks with three necks (100 mL), then different amounts of VPBA (0 g, 0.1 g) and 0.01 g of AIBN were also put into the flasks. The mixture as the continuous phase was dispersed homogeneously with ultrasonic dispersion for five minutes. Next, 0.5 mL of surfactant hypermer 2296 and 16 mL of K_2SO_4 solution (0.2 M) served as dispersed phase were added drop-wise into the continuous phase under a constant stirring at 800 rpm. After 5.0 min, a stable W/O HIPEs system was formed, and then the obtained emulsion was transferred into the glass ampoule. The glass mold was sealed and heated in the thermostat water bath at 70 °C for 12 h. Subsequently, achieved MPs-BA was purified by soxhlet extraction in a certain number of acetone for one day, in order to remove the dispersed phase and other residuum. Finally, MPs-BA samples were dried in a vacuum oven at 50 °C for 24 h. In this work, MPs-BA samples prepared with 0 g and 0.1 g of VPBA were named as MPs-BA-0 and MPs-BA-1, respectively.

2.4. Study on boronate affinity ability

Boronate affinity ability of MPs-BA was investigated by ARS based fluorimetric assay [20]. Briefly, MPs-BA particles (5.0 mg) were added to 0.02 mM ARS solution (100 mM phosphate buffer, pH 8.5, 10 mL). After reacting for 6.0 h at room temperature avoiding the light, the mixture was centrifuged and the supernatant was decanted. And then the sediment was washed repeatedly with the phosphate buffer (100 mM, pH = 8.5) to remove the residual ARS. Finally, the resulting MPs-BA particles were re-dispersed in the same phosphate buffer and visualized by LSCM with a 476 nm solid state laser light source. For comparison, the resulting MPs-BA particles were washed by phosphate buffer (pH = 5.0) to evaluate the pH sensitive release performance of boronic acid groups, and visualized by LSCM [21].

2.5. Batch mode adsorption experiments

In the static adsorption experiments, adsorption kinetics and adsorption isotherm were included to study the adsorption ability of MPs-BA. In the experiments of adsorption equilibrium, 10 mg of MPs-BA-1 particles were put into the centrifuge tube, and LTL solutions (100 mM phosphate buffer, pH 8.5, 10 mL) with different concentrations (from 5.0 mg L⁻¹ to 25 mg L⁻¹) were prepared. Then LTL testing solutions were added into centrifuge tube, and the mixtures were transferred into the temperature-controlling bath at 25 °C. After incubating for 4.0 h, MPs-BA-1 particles captured LTL were collected by centrifugation, and the supernatant solution was filtered through a microporous polyvinylidene (PVDF, aperture was 0.45 μm) membrane to remove suspended particles. The obtained filtrate was measured by UV-Vis spectrophotometer to measure the concentration of LTL at 351 nm. What's more, the whole process should repeat at least three times and the operation

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