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A formaldehyde carbonyl groups-modified self-crosslinked polystyrene resin: Synthesis, adsorption and separation properties

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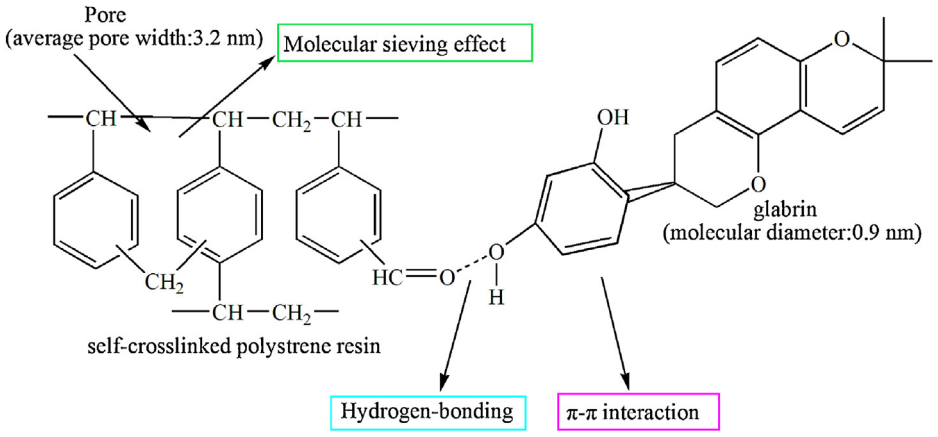
HIGHLIGHTS

- Novel formaldehyde carbonyl modified self-crosslinked polystyrene resins were synthesized and employed to adsorb glabridin.
- The molecular structure and diameter of glabridin were optimized by Gaussian 09D01.
- The resins have much improved adsorption properties for glabridin than the BMKB-1.
- Detailed comparative studies on adsorption equilibrium and kinetics of glabridin with BMKB-1.
- The adsorption mechanism mainly ascribed to a synergistic effect of molecular sieving effect and multiple interactions.

GRAPHICAL ABSTRACT



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ABSTRACT

Based on our previous work and calculational chemistry, the pore-size distribution is the key factor which influences glabridin uptakes on resins. In addition, micropores and mesopores in the range of 1.8–5.4 nm are proper for glabridin adsorption. Based on this, a series of novel microporous and mesoporous self-crosslinked polystyrene resins (named as XT2) were synthesized by Friedel–Crafts reaction after different reaction time and utilized to adsorb glabridin in aqueous solution. The adsorption behaviors of the synthetic resins were studied systematically in terms of adsorption capacity, equilibrium time, isotherm adsorption and regeneration properties and compared with a commercial adsorbent (BMKB-1) which was screened out as the optimal macroporous adsorption resin (MAR) for glabridin based on our previous work. The characteristic methods of BET surface area, pore size distribution, Fourier transform infrared spectroscopy and scanning electron microscopy were investigated to analyze the resins and adsorption process. The glabridin uptakes on XT2-10 were remarkably larger than those of macroporous adsorption resin BMKB-1. The maximum adsorption capacity of XT2-10 is up to 43.69 mg/g for glabridin. The adsorption isotherms could be well described by the Freundlich model, and the adsorption kinetics

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were fitted by both pseudo-second-order kinetic equation and intra-particle diffusion model. The adsorption mechanism was a synergistic effect of specific surface area, molecular sieving effect, and multiple adsorption interactions including hydrogen bonding and π–π stacking. The glabridin uptakes decreased to approximately 93.23% after five cycles of adsorption–desorption, exhibiting an excellent reusability and remarkable regeneration. Based on these results, this research not only opens up the possibility of synthesizing microporous and mesoporous self-crosslinked polystyrene resins, but also provides guidance for understanding the adsorption mechanism of purification of flavones from herbal plants.

1. Introduction

Glabridin is an isoflavonoid originally isolated from the roots of *Glycyrrhiza glabra* L. Glabridin is widely considered to be a phytoestrogen and has been associated with numerous biological properties ranging from anti-atherogenic effects, anti-inflammatory, neuroprotective, antioxidant, to the regulation of energy metabolism, but also including anti-tumorigenic, anti-nephritic, antibacterial and skin-whitening activities [1]. Glabridin and, to a lesser extent, have a growing impact not only on cosmetics but also on the food and dietary supplements (DSs) market.

Although high-purity glabridin can be obtained, methods widely used at present are not appropriate for industrial process because of high-cost, time-consuming processing and environmental pollution. Adsorption resins have received considerable attentions due to their excellent performance in isolation and purification of fine chemicals, pharmaceuticals and food additives [2]. The adsorption resins have been widely applied in enriching the glabridin from crude *G. glabra* L. extracts in China, Japan, and other Asia countries. However, the main problem in the attempt to separate specific component is the poor adsorption selectivity of adsorption resins. In order to obtain better adsorption selectivity for a specific compound, chemical modification of ordinary adsorbents is often adopted by introducing some special functional groups onto the adsorbent matrix [3]. Polymeric adsorbents are widely applied in modern adsorption separation technology due to their favorable physicochemical stability, large adsorption capacity, excellent selectivity and structural diversity [4–6]. Their geometric pore structure can be easily regulated by adjusting the crosslinking reagents and porogens and their surface chemistry can be changed with ease by using co-monomers with desired functional groups in copolymerization or by a particular chemical reaction of the synthesized polymer [7,8].

Recently, a new kind of hypercrosslinked polymeric adsorbent (HCP) was found to be very effective for removing aromatic compounds from aqueous solutions [9,10]. This kind of hypercrosslinked polymeric adsorbent was firstly prepared by Davankov and Tsyurupa and is usually synthesized from a linear poly (styrene-co-divinylbenzene) (PS) or a low cross-linked PS by adding bi-functional cross-linking reagents such as monochloromethylether, *p*-dibenzenylchloride and *p*-dichlomethylbenzene, and Friedel–Crafts catalysts including anhydrous zinc chloride, iron(III) chloride and stannic(IV) chloride [11–13]. They can also be prepared from a macroporous low cross-linked chloromethylated PS via its self Friedel–Crafts reaction. The structure characterization of this kind of polymeric adsorbent possessed a high crosslinking degree (40–500%), small average pore diameter (about 3 nm), a high BET surface area (700–1300 m^2/g) and a large pore volume (0.4–0.8 cm^3/g) with a predominant micro/mesopores [12–14]. The adsorption experiments indicate that HCPs have very high capacity toward various substances from gas phase media and aqueous solutions, which are far superior to macroporous polystyrene adsorbents [15,16].

In the present study, a self-crosslinked polymeric adsorbent modified with formaldehyde carbonyl groups, XT2 was synthesized from chloromethylated polystyrene and used as the adsorbent. A kind of natural product, glabridin, as previously mentioned, was chosen as the representative adsorbate. The adsorption characteristics, kinetics and thermodynamics of XT2 for glabridin were elucidated in aqueous solution. The main goal of this report is to compare the adsorption performance of XT2 and BMKB-1 and examine the effects of the pore structure and functional groups of the polymeric adsorbent surface on the adsorption properties.

2. Experimental

2.1. Materials

Glabridin extract with 90% purity used as the adsorbate in this study was purchased from Nanjing Zelang Medical Technology Co., Ltd. (Nanjing, China). Acetonitrile used for HPLC analysis was of chromatographic grade and purchased from Tianjin Chemical Reagent Co., Inc. (Tianjin, China). Acetic acid was purchased from Shandong Yuwang Industrial Co., Ltd. (Shandong, China) and distilled water used was obtained in our laboratory. All solutions prepared for HPLC were subjected to filtration through 0.45 μm nylon membranes before use.

2.2. Synthesis of formaldehyde carbonyl groups-modifed self-crosslinked resins

As described in Fig. 1 , formaldehyde carbonyl groups-modifed self-crosslinked resins were fabricated by one step. 20 g of chloromethylated polystyrene beads was firstly swollen in 75 mL of nitrobenzene at 298 K overnight. Under mild mechanical stirring, 1.875 g of anhydrous zinc chloride was added as the catalysts into the reaction mixture as quickly as possible at 298 K. After the added zinc chloride was completely dissolved, the mixture was evenly heated to 388 K within 1.5 h using linear temperature program with gradients of 1 °C/min. After refluxing reaction mixture at 388 K for 4, 6, 8, 10, and 12 h, respectively, the self-crosslinked polystyrene resin beads labeled as XT2-4, XT2-6, XT2-8, XT2-10, and XT2-12 were obtained. To remove residual nitrobenzene and zinc chloride after the reaction, the polymeric beads were subjected to rinsing with 1% hydrochloric acid solution and ethanol respectively till the effluent was transparent, and finally washed with deionized water until neutral pH. The polymeric beads were extracted with ethanol in Soxhlet apparatus for 10 h and then dried under vacuum at 323 K for 6 h.

2.3. Adsorbent characterization and analytical methods

The chorine content of the resins was measured according to a Volhard method [17]. The specific surface area and pore volume of the resins were determined by nitrogen adsorption–desorption isotherms at 77 K using a Micromeritics ASAP 2020 surface area and porosity analyzer (Micromeritics Instrument Corp., Norcross,