



Equilibrium adsorption of caffeic, chlorogenic and rosmarinic acids on cationic cross-linked starch with quaternary ammonium groups



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ABSTRACT

In the present study, the equilibrium adsorption of caffeic acid (CA) and its derivatives, namely, chlorogenic (CGA) and rosmarinic (RA) acids on cationic cross-linked starch (CCS) with degree of substitution of quaternary ammonium groups of 0.42 have been investigated in relation to the structure and acidity of phenolic acids. The Langmuir, Freundlich and Dubinin-Radushkevich adsorption models have been used to describe the equilibrium adsorption of CA, CGA and RA from their initial solutions and solutions having the equimolar amount of NaOH at different temperatures. In the case of adsorption from the initial solutions of acids the values of adsorption parameters were closely related to the dissociation constants of investigated acids. According to the increasing effectiveness of adsorption, phenolic acids could be arranged in the following order: CA < CGA < RA, i.e. in the range contrary to increasing value of pK_a. At temperature of 30 °C the maximum Langmuir sorption capacity was 0.76, 1.11 and 2.68 mmol/g for CA, CGA and RA, respectively. The addition of equimolar amounts of NaOH to the acids solutions changed their sorption properties which became mostly related to the acids structure.

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1. Introduction

Starch is a low-cost natural renewable polymer that can be modified easily by chemical reactions. Cross-linking of starch with epichlorohydrin (EPCH) in the heterogeneous reaction is the most commonly used method in polysaccharide chemistry [1]. When during cross-linking with EPCH ammonium hydroxide was added to the reaction mixture starch derivatives having tertiary amino groups were obtained and could be used to adsorb the anionic compounds [2]. Cross-linking of starch with aliphatic or aromatic diisocyanates in homogeneous reactions produced the starch-based adsorbents capable to adsorb the aromatic harmful compounds from industrial wastewater [3,4]. Reaction of starch with 2,3-epoxypropyltrimethylammonium chloride (EPTMAC) is commonly used method to obtain the cationic starch derivatives with quaternary ammonium groups [5,6]. Haack and co-workers [5] investigated the reactions of starch with EPTMAC both under homogeneous and heterogeneous (water suspension) conditions. In both cases the degree of substitution (DS) depended on the molar ratio of reagents, and varied between 0.38 and 1.05 in the case of heterogeneous reaction and between 0.37 and 0.57 in the case of

homogeneous reaction with the same reaction efficiency from 40% to 76%. In our previous work [6] the cationic (CS) or cross-linked cationic (CCS) starches with preserved microgranular structure, the degree of substitution from 0.2 to 0.85 and reaction efficiency from 82% to 93%, were obtained during etherification of starch or cross-linked starch in a mixture containing EPTMAC, “free” water and 0.04–0.08 mol/AGU sodium hydroxide under heterogeneous conditions. Due to strong basic quaternary ammonium groups both CS and CCS could adsorb anionic compounds [7]. The equilibrium adsorption investigation showed that CCS is more suitable than CS for anionic dye adsorption from a dye solutions. CCS adsorbed the anionic dyes in a few minutes and acted in the wide range of pHs [7]. CCS with preserved structure of microgranules were also used to adsorb hexavalent chromium [8] and anionic species of iodine [9].

Among the major groups of bioactive compounds, phenolic acids are one of the diverse classes of phenolic compounds synthesized by plants and constitute approximately 30% of the dietary phenolics present in plants in free and bounded forms [10]. The interest in phenolic acids arises from their protective role against oxidative damage diseases [11]. The hydroxycinnamic acids have been found to have significantly higher antioxidant activities than the hydroxybenzoic acids [12]. The higher antioxidant capacity of hydroxycinnamic acid derivatives is linked to the presence of the propenoic side chain, instead of the carboxylic groups of benzoic

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acid derivatives; the conjugated double bond in the side chain could have stabilizing effect by resonance on the phenoxyl radical, thus enhancing the antioxidant activity of the aromatic ring [12]. The combination of two acid phenols also can increase the antioxidant activity. For example, rosmarinic acid which is an ester of caffeic acid and 3,4-dihydroxyphenyllactic acid, has a better antioxidant efficiency than caffeic acid. In contrary, the chlorogenic acid which is an ester of caffeic and quinic acids was less effective than caffeic acid [13]. Chlorogenic acid (CGA) is one of the most common naturally occurring phenolic compounds [14]. Meanwhile, rosmarinic acid (RA) is a second of most frequently occurring caffeic acid esters in the plant kingdom [15].

The presence of unsaturated bonds in the molecules of CGA, RA and CA makes them vulnerable to heat, oxygen, light and moisture [16] and influences instability during storage especially at higher temperatures [17]. So, the effectiveness of phenolic compounds depends on preserving the stability, bioactivity and bioavailability of active ingredients. Different methods are used to protect bioactive phenolic compounds from oxidative damage: encapsulation techniques include extrusion, liposome entrapment, fluidized bed coating, spray drying, spray cooling/chilling, coacervation, centrifugal suspension separation, lyophilization, co-crystallization and emulsion formation [18]; formation of the inclusion complexes [19] or nanoparticles [20,21]. Due to its simple design, adsorption is one of the most commonly used processes in the recovery, concentration and purification of high added value bioactive phenolic compounds [22]. Chitosan and cross-linked chitosan were used to study the equilibrium adsorption of aliphatic carboxylic acids [23]. Also, the synthetic polymeric adsorbents with functional amine groups were used for the adsorption of gallic acid [24]. The Langmuir, Freundlich, Dubinin-Radushkevich and Temkin adsorption models were used to describe the adsorption of phenolic compounds on investigated adsorbents [23,24].

CCS with strong basic quaternary ammonium groups could be also used as adsorbent of bioactive phenolic acids. The adsorption of phenolic acids is closely related with ionization of their carboxylic group, and, consequently, to pH value of solution. For this reason, the usage of CCS has an advantage, because the effectiveness of CCS as adsorbent is independent from pH value of adsorbate solution [7]. However, our attempt to find literature data on bioactive phenolic acids adsorption onto cationic starches from solution was unsuccessful. Therefore, the purpose of present investigation was to evaluate the equilibrium adsorption of CA and its derivatives – CGA and RA onto CCS at different temperatures in order to find novel sorbents for delivery of bioactive compounds. The Langmuir, Freundlich and Dubinin-Radushkevich adsorption models have been used to assess the adsorption data, and also the thermodynamic characteristics have been determined.

2. Experimental

2.1. Materials

The native potato starch (BEROXFOOD Natural Ingredients, Germany) was dried at 104 °C temperature before use. 2,3-Epoxypropyltrimethylammonium chloride (70%), epichlorohydrin, rosmarinic, caffeic and chlorogenic acids were purchased from Sigma-Aldrich and used without further purification. Other reagents used were of analytical grade and were used as received.

2.2. Preparation of cationic cross-linked starch

The molecular mass of the anhydroglucoside unit (AGU) was assumed as a mole of starch. CCS was prepared by two-step modification reaction according to [6]. Briefly, in the first step

starch was cross-linked with 0.1 mol/AGU of epichlorohydrin in the presence of sodium hydroxide at room temperature for 24 h, washed with cold water, dried and then cationized with 2,3-epoxypropyltrimethylammonium chloride (EPTMAC) in the presence of sodium hydroxide as catalyst (the molar ratio AGU: EPTMAC: NaOH: H₂O was 1: 0.45: 0.04: 4) at 45 °C for 24 h. After the reaction CCS was washed with water–isopropanol mixture and dried. The number of cationic groups in CCS was expressed as the degree of substitution (DS), which was calculated from the nitrogen content estimated by the Kjeldahl method after purification by Soxhlet extraction with methanol for 16 h. The DS of synthesized CCS used in the adsorption experiments was 0.42.

2.3. Equilibrium adsorption studies

0.1 g of CCS was placed into an Erlenmeyer flask, and 100 ml of CA, CGA or RA solution or the solution of respective phenolic acid having the equimolar amount of NaOH of a certain concentration were added. The pH values of initial solutions of CA, CGA and RA were in the intervals 3.20 ± 0.1 , 3.15 ± 0.05 and 2.95 ± 0.05 , respectively. Meanwhile, the pH values of CA, CGA and RA solutions containing the equimolar amounts of NaOH were determined to be 6.7 ± 0.1 , 6.8 ± 0.1 and 6.5 ± 0.1 , respectively. The flask was stoppered and shaken for 60 min at temperature of 30 °C, 40 °C and 60 °C and fixed shaking intensity in a thermostating bath with the temperature control of ± 1 °C (Memmert GmbH, Germany). Then the mixture was filtered through a paper filter, and the residual concentration of phenolic acid in the filtrate solution was estimated. The amount of the adsorbed phenolic acid q_e (g/g) was calculated according to the equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{W} \quad (1)$$

where C_0 is the initial concentration (g/L) of phenolic acid, C_e is the concentration (g/L) at the equilibrium in the supernatant solution, V is the volume of the solution (L), and W is the weight of CCS (dry material, g).

To determine the concentration of CA, CGA or RA in the supernatant, the solution was diluted with distilled water and the UV absorbance at λ_{\max} of the sample was measured by using a UV/VIS spectrophotometer (Jenway 6715, Great Britain). λ_{\max} was 316 nm, 325 nm and 326 nm for CA, CGA and RA, respectively. The concentration of phenolic acids was determined from the calibration curves.

2.4. FT-IR analysis

FT-IR spectra of microgranules of CCS and CCS with adsorbed acids (CCS-CA, CCS-CGA and CCS-RA) were recorded by using a Perkin-Elmer Frontier spectrophotometer with a single reflectance horizontal ATR (Attenuated Total Reflectance) cell equipped with a diamond crystal. The data were recorded in the spectral range from 655 to 2000 cm^{-1} by accumulating 5 scans with a resolution of 4 cm^{-1} . To obtain the CCS-CA, CCS-CGA and CCS-RA microgranules, adsorption mixture (see Section 2.3) was filtered through a glass filter, washed twice with distilled water and dried at temperature of 104 °C.

3. Results and discussion

3.1. FT-IR analysis of CCS with adsorbed phenolic acids

The microgranules of the cationic cross-linked starch (CCS) with the strong basic quaternary ammonium groups (Scheme 1a) were used for the adsorption of bioactive phenolic acids due to electrostatic interactions between cationic groups of starch and carboxylic

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