Available online at www.sciencedirect.com
ScienceDirect
Reactive & Functional Polymers 68 (2008) 768–774
REACTIVE & FUNCTIONAL POLYMERS
www.elsevier.com/locate/react

Selective adsorption of tea polyphenols from aqueous solution of the mixture with caffeine on macroporous crosslinked poly(*N*-vinyl-2-pyrrolidinone)

Ruiying Zhao, Yu Yan, Mingxian Li, Husheng Yan *

Key Laboratory of Functional Polymer Materials, Ministry of Education, Institute of Polymer Chemistry, Nankai University, Tianjin 300071, China

Received 29 June 2007; received in revised form 13 November 2007; accepted 23 November 2007
Available online 3 December 2007

Abstract

A macroporous polymeric adsorbent with moderate hydrophobic matrix and hydrogen-bonding moieties was prepared by free radical suspension copolymerization of *N*-vinyl-2-pyrrolidinone, ethylene glycol dimethacrylate and triallyl isocyanurate. SEM image and N_2 adsorption–desorption isotherm measurements of the resulting resin, defined as PVP–DEGMA–TAIC, show that the average pore diameter and specific surface area are ~400 nm and 114 m^2/g, respectively. The adsorption behavior of tea polyphenols and caffeine on PVP–DEGMA–TAIC resin indicates that the adsorption of tea polyphenols is driven by combined action of hydrophobic interaction and hydrogen bonding, while the adsorption of caffeine is driven by only hydrophobic interaction. The adsorption from an aqueous solution of a mixture of tea polyphenols and caffeine (initial weight concentration ratio was ~5/1) on PVP–DEGMA–TAIC shows that the adsorption capacities for tea polyphenols and caffeine were 98 mg/g and 1–2 mg/g with removal percentages of 93% and 8%, respectively. The product eluted with ethanol contains ~98% tea polyphenols and ~2% caffeine. These results indicate that selective adsorption of polyphenols from the mixture with caffeine on PVP–DEGMA–TAIC resin was excellent.

Keywords: Polymeric adsorbent; Adsorption; Tea polyphenols; Caffeine; Poly(*N*-vinyl pyrrolidinone) resin

1. Introduction

Tea, originated in China, is one of the most popular nonalcoholic beverages in the world. The main bioactive components in tea are catechins (polyphenols) and alkaloids. Catechins, which constitute up to 30% of dry green tea leaves [1], possess various biological, physiological, and pharmaceutical effects, such as antioxidative, anticancerous, and antibacterial effects [2–6]. The main catechin compounds in green tea include (−)-epigallocatechin gallate (EGCG), (−)-epigallocatechin (EGC), (−)-epicatechin gallate (ECG), (−)-epicatechin (EC), (+)-gallocatechin gallate (GCG), (+)-gallocatechin (GC), and (+)-catechin (C). These compounds are believed to have physiological effects by scavenging free radicals, which are generated by metabolic pathways within body tissue or introduced by external sources such as foods, drugs, and environmental

* Corresponding author. Fax: +86 22 23503510.
E-mail address: yanhs@nankai.edu.cn (H. Yan).

1381-5148/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.reactfunctpolym.2007.11.016

pollutants [7–9]. Tea leaves contain 2–4.5% alkaloids, mainly caffeine [10], which stimulates respiration and the central nervous system and has been clinically used as a central stimulant and an adjunct in numerous analgesic preparations [11].

Tea polyphenols and caffeine are often isolated from tea leaves by organic solvent extraction [12–16]. Separation of tea polyphenols and caffeine are usually carried out by partition with water/chloroform. Organic solvent extraction method has the shortcomings of high cost, environmental pollution and high toxicity of some of these organic solvents. Polymeric adsorbents have been used to isolate and purify natural polyphenols from plant extract [17–22]. In previous paper [23], we found that a macroporous poly(styrene-divinylbenzene) (PS-DVB) resin adsorbs both tea polyphenols and caffeine with moderate capacities. PS-DVB resins functionalized with hydrogen-bonding moieties adsorb more tea polyphenols and less caffeine, indicating the adsorption of tea polyphenols may be driven by hydrophobic interaction and hydrogen bonding while the adsorption of caffeine may be driven by only hydrophobic interaction. However, the adsorption capacities for caffeine on these resins are still moderate because of the hydrophobic PS-DVB matrix and it is difficult to selectively adsorb tea polyphenols from the mixture with caffeine in aqueous solution [23]. Recently, we are focusing on the design of highly selective polymeric adsorbents by mimicking the multiple weak interactions and their synergistic effect of biospecific affinity [24–28]. Based on the Second Law of Thermodynamics, when two or more weak interactions contribute simultaneously to the adsorption, they act synergistically and the total adsorption energy is greater than the sum of each energy of these interactions when they act individually, which was also proved experimentally [26,27]. In this paper, a polymeric adsorbent with hydrogen-bonding moieties and less hydrophobic matrix was synthesized. This polymeric adsorbent adsorbed little caffeine due to its relative low hydrophobic matrix. But it can still strongly adsorb tea polyphenols driven by multiple weak interactions (hydrophobic interaction and hydrogen bonding).

2. Experimental

2.1. Materials

Triallyl isocyanurate (TAIC), ethylene glycol dimethacrylate (EGDMA), Poly(vinyl alcohol) (PVA, average polymerization degree 1700, hydrolization degree 88%) and ADS-5 (a macroporous PS-DVB resin, specific surface area is ∼600 m^2/g) were provided by Hecheng Co. Ltd (Tianjin, China). *N*-vinyl-2-pyrrolidinone (VP) was purchased from Fluka. Toluene was purchased from Tianjin Sixth Chemical Co. (Tianjin, China). *n*-Butanol was purchased from Jinhua Yongsheng Co. Ltd (Tianjin, China). Green tea polyphenols (polyphenols ⩾ 98%, catechins ⩾ 90%, EGCG ⩾ 70%) was purchased from Changzhou Zhongxin Green Leafage Products Co., Ltd (Changzhou, China). Caffeine was purchased from Shanghai Second Chemical Co. (Shanghai China).

2.2. Synthesis of macroporous crosslinked poly(N-vinyl-2-pyrrolidinone) resin

Macroporous copolymer of *N*-vinyl-2-pyrrolidinone, ethylene glycol dimethacrylate and triallyl isocyanurate (PVP–DEGMA–TAIC) was prepared by free radical suspension copolymerization. An organic phase which was composed of 10 g of VP, 10 g of EGDMA, 10 g of TAIC, 0.2 g AIBN, 10 g of toluene and 10 g of *n*-butanol was suspended in an aqueous phase (200 ml) containing 10% NaCl and 1% PVA. The mixture was stirred and heated to 75 °C, and kept at this temperature for 5 h. The suspension was then warmed to 80 °C and kept for 3 h. The resulting resin were washed thoroughly with water to remove PVA and followed by extraction in a Soxhlet extractor with acetone to remove the porogen toluene and *n*-butanol. Yield, 25.8 g (86%). The resin in the range of 40–60 mesh size was used for the following experiment. The specific surface area of the resin was determined using Autosorb-1 (Quantachrome) to be 114 m^2/g. Elemental analysis, found: C 55.7%, H 7.46%, N 7.89%; calculated: C 62.1%, H 7.05%, N 9.38%.

2.3. Adsorption of green tea polyphenols or caffeine by PVP–DEGMA–TAIC resin

The adsorption was measured by batch method. A resin sample (∼0.05 g) was added into an Erlenmeyer flask containing 25 ml of aqueous solution of green tea polyphenols or caffeine with certain initial concentration. The flask was sealed and shaken for 24 h at 25 °C. The equilibrium concentration of tea polyphenols or caffeine of the supernatant was determined by UV spectrophotometry at 280 nm.