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Adsorption affinity of tea catechins onto polymeric resins: Interpretation from molecular orbital theory

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ABSTRACT

Adsorption of certain tea catechins such as (+) catechin (C), (−) epicatechin (EC), (+) gallocatechin (GC), (−) epigallocatechin (EGC), (+) catechin gallate (CG), (−) epicatechin gallate (ECG), (+) gallocatechin gallate (GCG), and (−) epigallocatechin gallate (EGCG) have been studied using three types of polymeric resins as adsorbents. Adsorption affinity expressed as the slope of the linear region of the isotherm for a solute is found to be different for different adsorbents, and this difference can be interpreted from the chemical nature of the sorbents. Molecular interactions on polymeric resins have been studied based on molecular orbital theory. Electronic states of adsorbent and adsorbate were calculated using the semiempirical molecular orbital (MO) method from which energy of adsorption in aqueous solution was estimated. The adsorptive interaction on the polymeric resins computed on the basis of frontier orbital theory seems to correlate well with the experimentally measured adsorption affinity and enthalpy.

1. Introduction

Recently, green tea has attracted much attention both in the scientific community and in the public opinion, for its pronounced health benefits towards a variety of disorders ranging from cancer to weight loss [1]. Catechins, the principal bioactive compounds in tea are reported to have anti-tumorgenic [2,3], anti-mutagenic [4], anti-pathogenic [5] and anti-oxidative properties [6]. It is believed that much of the anticancer effects of green tea are mediated by its polyphenolic constituents due to their potent antioxidant properties and are generally considered to reflect their ability to scavenge endogenously generated oxygen radicals or those radicals formed by various xenobiotics, radiations, etc. [7].

The methodology and extraction efficiency of catechins from tea is critical in further studying the functionality of these substances. Though the classical methods of solvent extraction are available for the extraction of tea catechins, adsorption and membrane based separation methods are the most emerging and attractive from the economic viewpoint. In recent years, polymeric adsorbents have been increasingly used as an alternative to activated carbon due to their wide variations in functionality, surface area and porosity [8–10]. Because of the high capacity, satisfactory mechanical strength and feasible regeneration under mild conditions, polymeric resins work as excellent adsorbent for removal of phenol from aqueous phase [11–13]. Huang et al. [14] have used poly(styrene-co-divinylbenzene) resin functionalized with methoxy and phenoxy groups to study the adsorption characteristics of phenols. Adsorption of phenolic compounds have also been studied by Li et al. [15] using Amberlite XAD-4 and its acetylated derivative MX-4. We have been studying membrane and adsorptive separation processes for separation and purification of some useful biomolecules using different polymeric resins and membranes as the major part of our current research program [16–23].

For a specific process application, the understanding of the sorption phenomena play crucial role in the selection of appropriate adsorbent. Adsorptive interaction and adsorption affinity are the fundamental aspects of study for assessing the feasibility of an adsorption process for practical application. Usual experimental protocol to quantify these is to determine the adsorption equilibria and enthalpy of adsorption; however, theoretical interpretation is highly essential for surface modification and/or molecular design of adsorbents with high selectivity and capacity at the same time, providing favorable adsorption isotherms. In this paper, we present both theoretical and experimental results for adsorption of certain catechins onto three commercially available structurally dissimilar polymeric sorbents in order to gain mechanistic insight into adsorption of these catechins onto polymeric resins.

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Nomenclature

C	concentration of solute (mmol/l)
C_e	equilibrium liquid-phase concentration (mmol/l)
C_0	initial solute concentration (mmol/l)
C^*	MO coefficient
ΔC	change in solute concentration (mmol/l)
E	stabilization energy (kJ/mol)
E^*	energy level of MO (kJ/mol)
ΔE	perturbation energy by HOMO–LUMO interaction (kJ/mol)
ΔG^0	standard free energy of adsorption (kJ/mol)
ΔH^0	standard enthalpy of adsorption (kJ/mol)
q	amount adsorbed (mmol/g)
R	universal gas law constant (kJ g/mol K)
ΔS^0	standard entropy of adsorption (kJ/mol)
T	absolute temperature (K)
V	solution volume (l)
W	weight of adsorbent (g)
$\Delta\beta$	inter orbital interaction integral (kJ/mol)
Ψ	term signifying solute activity coefficient

2. Materials and methods

2.1. Materials

The catechins used in this study namely (+) catechin(C), (−) epicatechin (EC), (+) gallocatechin (GC), (−) epigallocatechin (EGC), (+) catechin gallate (CG), (−) epicatechin gallate (ECG), (+) gallocatechin gallate (GCG), and (−) epigallocatechin gallate (EGCG) were obtained from Sigma Chemical Co., USA. The other reagents used as buffer (potassium dihydrogen phosphate and dipotassium hydrogen phosphate) were supplied by Qualigens, India (Mumbai) and were of analytical grade. The polymeric resins Amberlite XAD-4, Dianion HP-2MG and Amberlite XAD-7 were also obtained from Sigma Chemical Co., USA. The chemical and physical properties of these resins are shown in Table 1. The adsorbents were washed with distilled water and dried overnight before use.

Equilibrium isotherms for the catechins were obtained at pH 7. The pH of solutions were measured in a pH meter and maintained at 7 by using phosphate buffer reagents of appropriate dosages. The initial concentrations of the catechins were taken between 5 and 10 mM at 25 ± 0.5 °C for 3–4 h, i.e. in the range of which linearity of the adsorption isotherm was obtained. Preliminary runs showed that the adsorption equilibrium adsorption was achieved after 3–4 h of contact time for all tested resins. After attainment of equilibrium, the aqueous phase was analyzed for solute concentrations by a UV–Vis spectrophotometer (Shimadzu 160A) calibrated at appropriate wavelength (280 nm) using a calibration curve of the respective catechin standards. The UV analysis was carried out in duplicate and the reproducibility was found to be ±2%. For estimation of adsorption enthalpy from adsorption affinity, equilibrium experiments were conducted at two other temperatures 40 and 55 °C. The adsorbents used were Amberlite XAD-4, XAD-7 and Dianion HP-2MG. The amounts of catechins per gram of adsorbent q (mmol/g) was calculated as $q = V(C - C_e)/W$, where C and C_e are the initial and equilibrium solute concentrations (mmol/l), V is the solution volume (l) and W is the weight of the adsorbent (g). All the experiments were carried out in triplicate and the reproducibility was found to be ±2%.

The numerical values of the adsorption affinity (q/C_e) can be determined by two techniques; (1) individual values of q/C_e can be averaged and (2) the slope of the best-fit line for the isotherms can be evaluated. For adsorption equilibrium studies low concentrations of catechins were used to limit the adsorption to the linear region of the isotherm where all of the isotherms could be extrapolated to the origin. The adsorption affinities (q/C_e) were determined from the slopes of individual isotherms in the linear region and the values are identical to the averaged values of individual adsorption affinities.

2.2. Adsorptive interaction in aqueous solutions

2.2.1. Molecular orbital (MO) calculation

Molecular orbital provides information on the basis of electronic states of adsorbents in an adsorption system, which will exploit to sorbent–solute interactions. In order to calculate electronic states of adsorbents by MO (molecular orbital) method, it is necessary to provide a structural (molecular) model of the adsorbents as discussed by previous workers and we have extended successfully the model for calculation of β-lactum antibiotics and some other biomolecules on polymeric resins [10]. Recently, the MO theory has been exploited to correlate Freundlich isotherm parameter for adsorption of phenols, 4-chlorophenols, and 3-nitrophenols on Amberlite XAD-2000 [24]. Mardis et al. [25] have calculated standard free energy of binding using quantum mechanical calculations to elucidate the mechanism of selectivity of oxygenated aromatic compounds onto acrylic ester sorbent XAD-7. Like our earlier work [10,16], we use a styrene-divinylbenzene (SDVB) polymer as the cluster model of synthetic adsorbent XAD-4 as shown in Fig. 1(a). Fig. 1(b) gives the cluster model of synthetic adsorbent XAD-7, which is an aliphatic carboxylic acid polymer. We use a methacrylate polymer as the cluster of synthetic adsorbent HP-2MG as shown in Fig. 1(c). Tamon et al. [26] have used cluster models to study the adsorptive interaction of organic compounds on activated carbon and synthetic adsorbents. The cluster size is very important in the MO calculation. If the cluster size is small, the size seriously influences the electronic state of adsorbent surface. So, we have calculated the electronic state of the cluster models adopting the minimum cluster size to get the more appreciable influence on the energy level.

The electronic state of adsorbents and adsorbates can be determined by semiempirical molecular orbital calculations. Though several semiempirical MO methods such as Austin model (AM1), complete neglect of differential overlap (CNDO), modified intermediate neglect of differential overlap (MINDO), modified neglect of differential overlap (MNDO), parameterized model number 3 (PM3), and parameterized model number 5 (PM5) can be used for calculation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, the basis of which may be understood from the solute–solvent model (Fig. 2). However, in our case we have used PM5 as it gives satisfactory results because all the parameters for most of the atoms are available in PM5. All these methods are semiempirical and used for the quantum calculation of molecular electronic structure in computational chemistry and based on the neglect of differential diatomic overlap integral approximation. The interaction energy between adsorbate and adsorbent is calculated on the basis of the frontier orbital theory (FOT) proposed by Fukui et al. [27]. According to FOT, two body interactions such as adsorbent–adsorbate, adsorbent–solvent, are regarded as the mixing of HOMO and LUMO. The HOMO energy is a measure of how hard it is to remove an electron from a neutral molecule and the LUMO energy is a measure of how hard it is to add an electron to the neutral molecule. Fig. 2 shows the concept of MO mixing. In this figure, molecule A is electron donating, and molecule B is electron attracting. Considering the charge transfer from atom r of molecule A to s of molecule B the energy level of HOMO of molecule A changes to the more stable level by orbital mixing. On the other hand, the energy level of LUMO of molecule B attains a more unstable level. The energy dif-