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Resin selection for the separation of caffeine from green tea catechins

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ABSTRACT

This work focuses on the rapid selection of a resin from a defined set of macroporous polymeric resins for the decaffeination of catechins from green tea. High-throughput experimentation and design of experiments are used in order to retrieve as much information as possible from a small set of experiments on the interaction of components with the resins. A multicomponent Langmuir isotherm model is used to describe the adsorption and parameters are regressed with high accuracy. These parameters are subsequently used for the definition of criteria to calculate a weighted resin score. The optimal resin is Diaion 20HP with a score of 90.50%, mainly due to its good selectivity for caffeine over catechin (3).

Keywords: Green tea; Catechins; Caffeine; Macroporous polymeric resins; High throughput experimentation; Resin selection

1. Introduction

Tea is a highly popular beverage, especially in countries like China or India. The beverage is an infusion of the leaves of the plant *Camelia sinensis*. Different types of teas are made by different processing (Cabrera et al., 2006), with green and black tea the most widespread types. The main difference between them is the level of oxidation of the leaves of the plant before the brewing. This oxidation is kept to a minimum in green tea in order to maintain the high concentration of antioxidants in the plant.

An interesting group of antioxidants that can be found in green tea is called catechins (Fig. 1). Catechins belong to a group of polyphenols called flavanols and can be found in green tea in percentages from 30 to 42% (dw) (Graham, 1992). Even though they are mostly known for their presence in tea, catechins can be found in small quantities in such diverse food sources as coconuts, cocoa, peach or vinegar.

Catechins have been related to several health benefits throughout literature. In a recent review (Johnson et al., 2012) the state of the art of clinical evidence on green tea catechins is shown and there seems to be enough evidence to conclude the positive effects of green tea in breast and ovarian cancer. As well, it helps lowering the cholesterol level and it stimulates daily energy expenditure. Liu et al. (2005) reported that both black and green tea are able to inhibit the entrance of HIV1 into cells.

Besides polyphenols, green tea contains other components such as proteins, amino acids, sugars and caffeine. Caffeine is mainly known for its presence in coffee beans and it acts as a stimulant drug. Caffeine has proven to cause several conditions related to the central nervous system such as insomnia (Karacan et al., 1976), irritability (Darragh et al., 1981) and heart palpitations (Greden, 1974) when consumed in large quantities. Due to these effects in the human body it is desirable to decaffeinate both tea beverage and tea extracts.

Decaffeination is a well-known industrial process mostly used by the coffee industry. The most known methodologies involve supercritical CO_2 extraction (supercritical fluid

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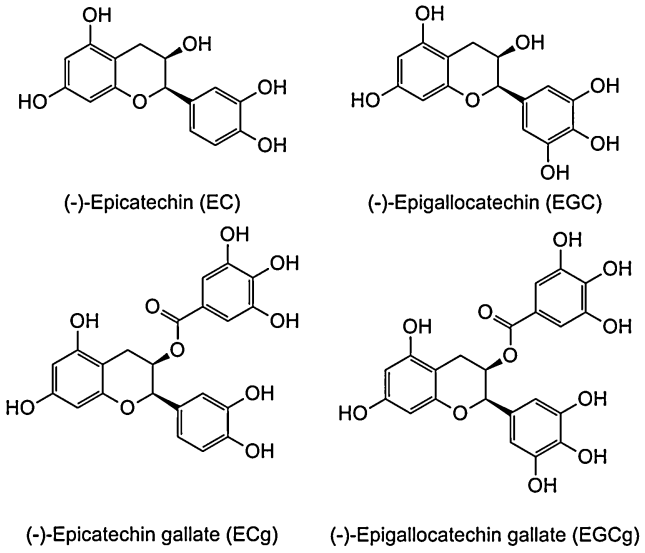

Fig. 1 – Main components of the family of catechins.

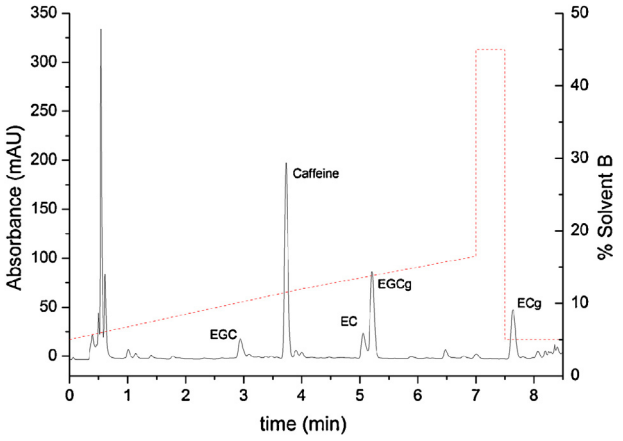

Fig. 2 – UPLC Chromatogram of a green tea sample (solid black line, left axis) and profile of solvent B during the analysis (red dash line, right axis). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

extraction or scFE) (Sun et al., 2010) or extraction with organic solvents (liquid–liquid extraction or LLE) like chloroform, dichloromethane (Kazi, 1984), etc. While for the coffee case, the only interest is to reduce the amount of caffeine in either the coffee or the coffee bean, the challenge for tea is different since catechins and caffeine behave in a similar manner. Because of this feature, during the extraction of caffeine, catechins are extracted as well, which decreases the yield of the process. Furthermore scFE and LLE require either the use of costly supercritical equipment for the operation or organic solvents (harmful in some cases).

Solid phase extraction offers some advantages with respect to the discussed methods above. These advantages are mainly the non-toxicity and the ease of recovery (when compared to LLE) and a more economic process (in comparison with scFE). Some work has been done toward the use of macroporous resins for the adsorption of polyphenols and decaffeination, but a thorough study is lacking for the commercially available food-grade resins.

This work focuses on fast resin selection based on the information given by interaction parameters regressed from a small set of experiments. Adsorption behavior of catechins and caffeine is measured on different commercially available food-grade macroporous resins. Isotherms are shown for the different main components and modeled with a multicomponent isotherm model. The regressed parameters are later used for the calculation of selectivity and capacity and based on that, a resin selection is performed.

2. Materials and methods

2.1. Materials

Freeze-dried green tea extract was obtained from UNILEVER. Epicatechin, Epigallocatechin, Epicatechin gallate and Epigallocatechin gallate (EC, EGC, ECg and EGCg respectively) were obtained from Nacalai USA, Inc. with a purity of 98% or higher. Caffeine was purchased from Merck. Methanol, formic acid and acetonitrile (purchased from Sigma–Aldrich) and mili-Q water are used as solvents.

2.2. Characterization of the green tea

A good characterization of the main components is important in order to quantify the different influences in the adsorption. However, in high throughput experimentation analytics tend to be the bottleneck of the experimental process and it is crucial to analyze the key components of the system accurately and in the shortest time possible.

EC, EGC, ECg, EGCg and caffeine were analyzed by UHPLC (Ultimate 3000, Thermo Scientific, USA) based on the protocol described by Zhao et al. (2011) in a C18 column (Acquity UPLC HSS column, 1.8 μm, 2.1 mm × 100 mm Waters, Milford, USA). Mobile phase A (0.1% formic acid in milli-Q water) and mobile phase B (0.1% formic acid in acetonitrile) were run through the column with a constant flow of 0.7 ml/min with the following profile of solvent B: 0 min – 5%, 7 min – 16.5%, 7 min – 45%, 7.5 min – 45%, 7.5 min – 5% and 8.5 min – 5%. Most of the peaks showed baseline separation at a wavelength of 270 nm. An example is shown in Fig. 2.

In Fig. 2 it can be seen that the peaks of EC and EGCg are not fully resolved. Because of this, a deconvolution of the peaks was performed by fitting them to two Gaussian curves.

The concentration of the target components of green tea is as follows (in % dry weight) EC: 1.71, EGC: 7.23, ECg: 3.81, EGCg: 13.29 and Caffeine: 7.29.

2.3. Resins

Seven different food-grade macroporous resins were used. From the AMBERLITE™ XAD™ series, the resins selected were 761, FPX66, 4, 16, 1180N and 7HP while from DIAION™, the resin selected was HP20. FPX66 was purchased from Dow Chemicals while the rest were purchased from Sigma–Aldrich.

2.4. Isotherm characterization

In order to design a process, both kinetics and thermodynamic equilibrium are important. Since diffusion coefficients can be predicted quite precisely with several models in literature (Einstein, 1905; Nakanishi and Furusawa, 1978; Tyn and Calus, 1975; Wilke and Chang, 1955), the main experimental challenge lies in measuring adsorption equilibria, or isotherms, as they cannot be easily predicted a priori. Because