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Selective decaffeination of tea extracts by montmorillonite

Takashi Shiono*, Kenichiro Yamamoto, Yuko Yotsumoto, Junichiro Kawai, Nanami Imada, Jumpei Hioki, Hiroyuki Naganuma, Takahiro Eguchi, Makoto Kurihara, Aruto Yoshida, Keiji Deuchi

Research Laboratories for Beverage Technologies, Research & Development Division, Kirin Company, Ltd., 1-17-1, Namamugi, Tsurumi-ku, Yokohama, Kanagawa 230-8628, Japan

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A B S T R A C T

We evaluated the decaffeination of green tea extract via montmorillonite (MMT) to develop a selective and versatile decaffeination technology. MMT is a clay mineral used worldwide in the food industry. MMT adsorbed caffeine with no significant binding to catechins, whereas activated carbon (AC) bound caffeine and catechins simultaneously. This suggests that MMT has a higher selectivity for caffeine adsorption than AC. The taste of the extract decaffeinated by MMT was not significantly altered. MMT stably adsorbed caffeine at 5–35 °C and pH 6–8; however, prolonged incubation caused an undesired elution of Fe ions, which decreases the lightness of green tea beverages. MMT exhibited similar caffeine adsorption properties with various types of tea extracts and a simple caffeine solution. Overall, our findings suggest that MMT is a useful adsorbent for the decaffeination of a range of tea beverages.

1. Introduction

Tea is one of the most widely consumed beverages in the world. It is prepared by pouring hot water over cured leaves of *Camellia sinensis* L. The major types of tea depend upon the manufacturing process, but generally include green tea, oolong tea, and black tea. Related tea products include tea leaves, packaged beverages and instant tea. The production volume of these tea products worldwide was 5 million tons in 2013 (Chang, 2015).

Tea contains polyphenols, including catechins, theaflavins, and/or thearubigin; these polyphenols have attracted attention in recent years because of their positive effects on health (Khokhar and Magnusdottir, 2002; Perva-Uzunalić et al., 2006). Tea polyphenols exhibit numerous health benefits, such as anti-oxidative (Yanagimoto et al., 2003), anti-microbial (Hamilton-Miller, 1995), anti-allergic (Suzuki et al., 2000; Yoshino et al., 2010), hypoglycemic (Matsumoto et al., 1993; Toyoda-Ono et al., 2007) and anti-obesity effects (Ueda and Ashida, 2012; Uchiyama et al., 2011).

Caffeine is an important compound that accounts for about 2%–5% of constituents in the tea leaf (Naik and Nagalakshmi, 1997). It has a bitter taste and exerts both positive and negative physiological effects. For example, positive effects of caffeine include improvement of drowsiness, cognitive decline, and fatigue; these effects are facilitated via stimulation of the central nervous system (Lorist and Tops, 2003; Arab et al., 2013). Some of negative effects of caffeine include sleep disorder (Hindmarch et al., 2000), elevation of blood pressure (Nurminen et al., 1999) and risk of fetal growth disorder (Fernandes et al., 1998). These effects of caffeine vary among individuals according to differences in their caffeine metabolic rate, which can be affected by age, pregnancy, and smoking habits (Von Borstel, 1983). Therefore, limited tea intake might be recommended, depending on the situation.

* Corresponding author.
E-mail address: Takashi_Shiono@kirin.co.jp (T. Shiono).

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Abbreviations

MMT	montmorillonite
AC	activated carbon
EGC	epigallocatechin
EC	epicatechin
EGCg	epigallocatechin gallate
ECg	epicatechin gallate

Alternatively, consumers may choose decaffeinated tea. To date, two approaches have been used for the decaffeination of tea: one is caffeine removal from tea leaves during the processing of the raw materials; and the other is caffeine elimination after tea extraction. The former approach extracts caffeine using hot water (Vuong et al., 2013) or supercritical carbon dioxide (Huang et al., 2007; Park et al., 2007; Tang et al., 2010). In some countries, organic solvents such as ethyl acetate, dichloromethane, and dimethyl ether are also used (Kanda et al., 2013). The latter approach eliminates caffeine from tea extract using an adsorbent such as activated carbon (AC), lignocellulose, poly(acrylamide-co-ethylene glycol dimethylacrylate), or porous polymeric resin (Sakanaka, 2003; Ye et al., 2007; Ye et al., 2009; Lu et al., 2010; Sevillano et al., 2014). None of the above methods are completely satisfactory for consumers because, in addition to caffeine, they reduce other substances such as catechins in tea (Lee et al., 2007, 2009).

Montmorillonite (MMT) is a layered clay mineral belonging to the smectite group and a main component of naturally mined bentonite. In the food industry, it is used as a processing aid for the clarification of wine and juice, as well as the bleaching of oils (González-Pradas et al., 1993; Tajchakavit et al., 2001; Yildirim, 2011). MMT particles comprise approximately 1 nm thick plate crystals; they are composed of a basic three-layer structure of silica tetrahedral sheets of $Si_4O_6(OH)_4$ that sandwich a central alumina octahedral sheet of $Al(OH)_6$ (Bergaya et al., 2006). The Al in the alumina central layer partially undergoes isomorphous substitution with Mg and Fe, causing the plate crystal to carry a negative charge; therefore, positively charged ions are present between the layers for replenishment. MMT swells with water and has a capacity for cation exchange; it is capable of adsorbing organic cationic substances, e.g., methylene blue and alkylammonium ions, as well as inorganic cations such as Cs^+ and Rb^+ (Hurel et al., 2009; Sarma et al., 2011; Okada et al., 2014). In addition, MMT adsorbs non-ionic organic compounds such as 3-aminotriazole and benzimidazole fungicides (Russell et al., 1968; Aharonson and Kafkafi, 1975). Last year, we reported that MMT and saponite, both belonging to the smectite group, adsorbed caffeine in aqueous solutions. Furthermore, caffeine adsorption was improved by modifying MMT with benzylammonium (Okada et al., 2015). Similarly, Marçal et al. reported that saponite that had been organically modified with 3-aminopropyltriethoxysilane adsorbed caffeine (Marçal et al., 2015). To date, however, there has been no research involving a detailed examination of the caffeine adsorption properties of these adsorbents in tea extracts.

In this study, we evaluated the utility of MMT for caffeine adsorption in various tea beverages with the aim of developing a selective and versatile decaffeination technology.

2. Materials and methods

2.1. Materials and reagents

Adsorbents MMT (MIZULITE) and AC (FP-3) were obtained from Mizusawa Industrial Chemicals, Ltd. (Tokyo, Japan) and Osaka Gas Chemicals, Co., Ltd. (Osaka, Japan), respectively. Caffeine and catechins (epigallocatechin, EGC; epicatechin, EC; epigallocatechin gallate, EGCg; epicatechin gallate, ECg) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and Funakoshi, Co. Ltd. (Tokyo, Japan), respectively. Various tea leaves, green tea (Sencha in Shizuoka, Japan), oolong tea (Tie-Guan-Yin in China and Taiwan, Dong-Ding-Oolong in China), and black tea (Dimbula in Sri Lanka and Darjeeling in India) were purchased from specialized tea shops in Japan.

2.2. Adsorption test of caffeine and catechins

The adsorption test of caffeine and catechins was carried out with green tea extract, which was prepared as follows: 100 g of tea leaves was added to 1000 mL of hot water at 80 °C and extracted for 8 min. Either 160–2000 mg of MMT or 32–200 mg of AC was added to 40 mL of the diluted green tea extract, whose final caffeine concentration was 3.6 mmol/L. After incubation at 25 °C for 120 min, the suspension was centrifuged at 1920×*g* for 10 min, and the resulting supernatant was filtered through a membrane filter (0.2 μm, PTFE). The concentrations of caffeine and catechins (EGC, EC, EGCg and ECg) were measured by HPLC (LC-2000Plus, JASCO, Corp., Tokyo, Japan). The HPLC conditions were: CAPCELL PAK C18 UG120 (4.6 mm I.D. x 150 mm, 3 μm, Shiseido Co., Ltd., Tokyo, Japan), column temperature 40 °C, flow rate 0.9 mL/min, mobile phase A = water/acetonitrile/phosphoric acid (1000/25/1.0, v), mobile phase B = water/methanol/acetonitrile/phosphoric acid (600/300/15/0.6, v), mobile phase C = methanol/acetonitrile/phosphoric acid (800/200/1.0, v), step gradient: 0–3 min = 94% A and 6% B, 3–8 min = from 94% A and 6% B to 50% A and 50% B, 8–22 min = from 50% A and 50% B to 0% A and 100% B, 22–24 min = from 100% B to 0% B and 100% C, after 5 min = 100% C, detector UV (caffeine, 275 nm; catechins, 230 nm). The taste quality of green tea extracts before and after decaffeination by MMT or AC was compared by five tea experts; these experts were qualified either as Japanese Tea Instructors or had been trained in sensory evaluation for more than two years.

For the adsorption test of a simple caffeine solution, 160–2000 mg of MMT or 16–800 mg of AC was added to 40 mL of a 3.6 mmol/L caffeine solution, and the residual caffeine concentration was measured by HPLC as described above.

2.3. Kinetics of caffeine adsorption

Either 800 mg of MMT or 120 mg of AC was added to 40 mL of the caffeine solution (5.2 mmol/L of caffeine) or green tea extract (5.2 mmol/L of caffeine) and incubated from 2 to 240 min at 25 °C. The residual caffeine concentration was measured by HPLC as described above. The amount of caffeine adsorbed per weight of adsorbent at "*t*" (min) contact time (Q_t, mmol/g) was calculated by the equation:

$$Q_t = V \times (C_0 - C_t)/M \quad (1)$$

where V (L) is the volume of green tea extract; C_0 (mmol/L) is the initial caffeine concentration in green tea extract before adsorption; C_t (mmol/L) is the caffeine concentration in green tea extract at "*t*" contact time; and M (g) is the dry weight of adsorbent.

Subsequently, we tested whether the caffeine adsorption process coincides with a pseudo-first order kinetic model or a pseudo-second order kinetic model. The linear form of the pseudo-first order model (Dang et al., 2009) is given by the equation: