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Full Length Research Paper

Kinetic study on leaching of fluorine from green tea

Ma S. C., Wang X. L. and Liang Y. R.*

Zhejiang University Tea Research Institute, 866 Yuhangtang Road, Hangzhou 310058, PR China.

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Kinetic behaviors of fluorine leaching from tea were studied. The leaching process of fluorine could be divided into initial fast stage and later slow stage. The duration of fast stage 1 depended on leaf particle size and temperature. The higher the temperature and the smaller the leaf particle size, the shorter the duration of initial fast stage. Based on the test results, a two-step infusion method was developed to control fluorine level in tea liquor. When the tea was infused in 50°C water for 20 s (first infusion) and then the residue leaf was re-infused in boiling water for 5 min (second infusion), more than 26% of total fluorine was removed during first infusion, but more than 80% of catechins and caffeine of the teas remained in the second infusions which had a F level 0.70 mg L^{-1} or less. It reflected that the two-step infusion method is an alternative to control excessive fluorine exposure for tea drinkers.

Key words: Green tea, fluorine, kinetics, diffusion coefficients, two-step infusion.

INTRODUCTION

Fluorine (F) is an important element to human health and a moderate F intake is confirmed to be beneficial to alleviation of dental caries (Levi et al., 1983; Ermis et al., 2003). However, excessive accumulation of F in human body can cause diseases such as fluorosis (Fung et al., 1999; Browne et al., 2005; Koblar et al., 2012). Tea (*Camellia sinensis*) is widely consumed across the world owing to its healthy and biological effects (Labbe et al., 2006; Wang et al., 2011). However, tea is a fluorine accumulator (Lu et al., 2004) and F content in mature tea leaves was 1000 times higher than water-soluble F level in the soil on which it is grown (Fung et al., 1999). Tea leaf is the major organ accumulating F and the F in tea leaf is nearly 98% of F accumulated in tea plant (Sha and Zheng, 1994; Xie et al., 2001; Wong et al., 2003). Brick tea is usually processed using mature leaves (Cao et al., 2000), resulting in high level of F in brick tea liquors. It was reported that F level in some brick tea infusions ranged from 4.8 to 7.34 mg L^{-1}, being more than 3 times of that in black tea and green tea (Fung et al., 1999; Wong et al., 2003). Tea drinking is considered to be a source of F intake in human dietary (Sha and Zheng, 1994). However, epidemiological observations showed that fluorosis was related to long-term consumption of brick teas containing high levels of fluorine in some inhabitants in the west of China, Turkey and other parts of the world where tea was traditionally consumed (Gulati et al., 1993; Cao et al., 2003; Sofuoglu and Kavcar, 2008; Yi and Cao, 2008).

The study on characteristics of F diffusion from tea leaf into tea liquor during tea brewing is helpful to assess the F exposure to tea drinkers. Xu and Li (2009) reported that total amount F diffused was higher in tea liquors prepared by repeated brewing than those prepared by continuous infusion. Gao et al. (2009) showed that the main factors affecting the extraction rate of F in tea included the ratio of tea to water, extraction time and extraction temperature. Luo et al. (2002) confirmed that the amount of F extracted from brick tea was closely correlated to the boiling time. Different types of tea usually have different concentrations of F owing to the difference in maturity of tea material, processing method and brewing style (Gulati et al., 1993; Sha and Zheng, 1994; Fung et al., 1999; Ruan and Wong, 2001; Shu et al., 2003; Lu et al., 2004). The kinetics of solute extraction from natural sources such as leaves, flowers or seeds into a solvent phase is via mass transfer, assuming that the diffusion is a rate-

*Corresponding author. E-mail: yrliang@zju.edu.cn. Tel: +86 571 8697 8898. Fax: +86 571 8697 8898.

limiting step and the rate can be approximately predicted by the second-order Fickian equation (Hojnik et al., 2008). Particle size of tea leaf is an important factor influencing diffusion kinetics of solutes (Ye et al., 2007) and few studies on this topic in relation to F extraction of tea are available.

The present study aims at investigating the F release characteristics from tea samples with various particle sizes under different extraction conditions including temperature and extraction time.

MATERIALS AND METHODS

Green tea prepared with leaves (*Camellia sinensis* cv. Taicha) was grounded and shifted to three levels of particle sizes, that is, mean size 0.380 mm (ranging from 0.270 to 0.550 mm), 0.160 mm (ranging from 0.150 to 0.180 mm), and 0.113 mm (ranging from 0.109 to 0.120 mm).

Chemicals used in the tests were of analytical-reagent grade except where stated otherwise. Deionized water used was prepared using an EASY pure II UV Ultrapure Water System (Barnstead International, Iowa, USA).

Experimental procedure for kinetic study

Tea sample (2 g) was placed in a flask containing 100 ml deionized water. The samples were extracted under conditions of various temperatures and extraction durations in a thermostated water-bath (Pudong Rongfeng Scientific Instrument Co., Ltd. Shanghai, China) respectively. There were three temperature levels (50°C or Kelvin scale temperature 323.15K, 70°C or 343.15K and 90°C or 363.15K) and 10 levels of extraction durations (20, 40, 60, 90, 120, 150, 300, 480, 600 and 900 s). When the extraction was finished, tea infusion was filtered through a Double-Ring No.102 filter paper (Xinhua paper Ltd. Co., Hangzhou, China) and stored at 4°C for F analysis. The test was carried out in duplicate.

Determination of F concentration

50 ml of the aforementioned filtrate was mixed with 50 ml TISAB buffer (1:1 mixture of 3 M sodium acetate and 0.75 M sodium citrate, v/v) and F concentration in the tea samples were determined according to the method described by Lu et al. (2004) using a pair of combination fluoride ion selective electrode (F-ISE, PF-1, Yueci Electronics Technologies Co. Ltd., China). Calibration curve was prepared using NaF solutions with different F levels. The detection sensitivity of the electrode was 0.02 μg ml^{-1}.

Diffusion kinetic study

Parameters of diffusion were calculated using Fick's second laws (Crank, 1975; Hojnik et al., 2008; Ziaedini et al., 2010) as Equation (1):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial r^2} \tag{1}$$

where R is the size of tea particle, D is the diffusion coefficient and C is the concentration of F in solution. The equation (1) can also be expressed as:

$$\frac{C - C_0}{C_i - C_0} = 1 + \left[\frac{2R}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\frac{\pi n r}{R} * \exp\left\{-\frac{Dn^2\pi^2 t}{R^2}\right\}\right] \tag{2}$$

By integrating the C over the R, the amount of mass transfer at any time [M(*t*)] can be calculated. Then the mass transferred at time *t* relative to the total amount transferred after infinite time M_∞ is expressed as:

$$\frac{M(t)}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left\{-\frac{Dn^2\pi^2 t}{R^2}\right\} \tag{3}$$

when the extraction is considered as fast steady state mass transfer stage and slow unsteady state mass transfer stage, Equation (2) can be expressed as:

$$\frac{C_\infty - C}{C_\infty} = \frac{6}{\pi^2}\left[f_1\exp\left\{-\frac{\pi^2 D_1 t}{R^2}\right\} + f_2\exp\left\{-\frac{\pi^2 D_2 t}{R^2}\right\}\right] \tag{4}$$

where D_1 and D_2 are diffusion coefficients at stages 1 and 2 and f_1 and f_2 are the fractions of the solute at stages 1 and 2 respectively. The parameter D_2 is obtained from the slope and the parameter f_2 from the intercept of the curve where $\ln[c_\infty/(c_\infty\text{-}c)]$ is plotted as function of time *t*.

Two-step infusion of tea

As the aforementioned study showed that the diffusion of F from tea leaf into liquor could be divided into initial fast stage 1 and later slow stage 2, an experiment with two-step infusion method was used to test the extraction rate of F, catechins and caffeine from different kinds of green teas. Green tea bag (mean particle size 1.25 mm), first grade of roasted green tea (mean size 2.0 mm) and fourth grade of roasted green tea (mean size 3.2 mm) were used in the test. Tea sample (3 g) was infused in a tea pot with 150 ml warm water (50°C) for 20 s, poured out the liquor and then the residue leaf was re-infused with 150 ml boiling water for 5 min. The two liquors were centrifuged at 5000 g for 10 min when cooled to room temperature, and they were defined as first infusion and second infusion respectively. The test was carried out in duplicate.

RESULTS AND DISCUSSION

Extraction kinetics

Figures 1 to 3 show that the F extraction could be divided into initial fast stage 1 and later slow stage 2. The duration of fast stage 1 depended on leaf particle size and temperature. The higher the temperature and the smaller the leaf particle size, the shorter the duration of stage 1, and vice versa. Diffusion coefficient data shows the same trend (Table 1). In the extraction at 50°C, the fast stage 1 for the sample with a mean size 0.113 mm lasted 20 s, but lasted 100 and 160 s for samples with mean sizes 0.160 and 0.380 mm, respectively (Figures 1 to 3). It showed the same tendency at 70 and 90°C (Figures 2 and 3). For the sample with mean particle size 0.160 mm, the durations of fast stage 1 were 140, 80 and

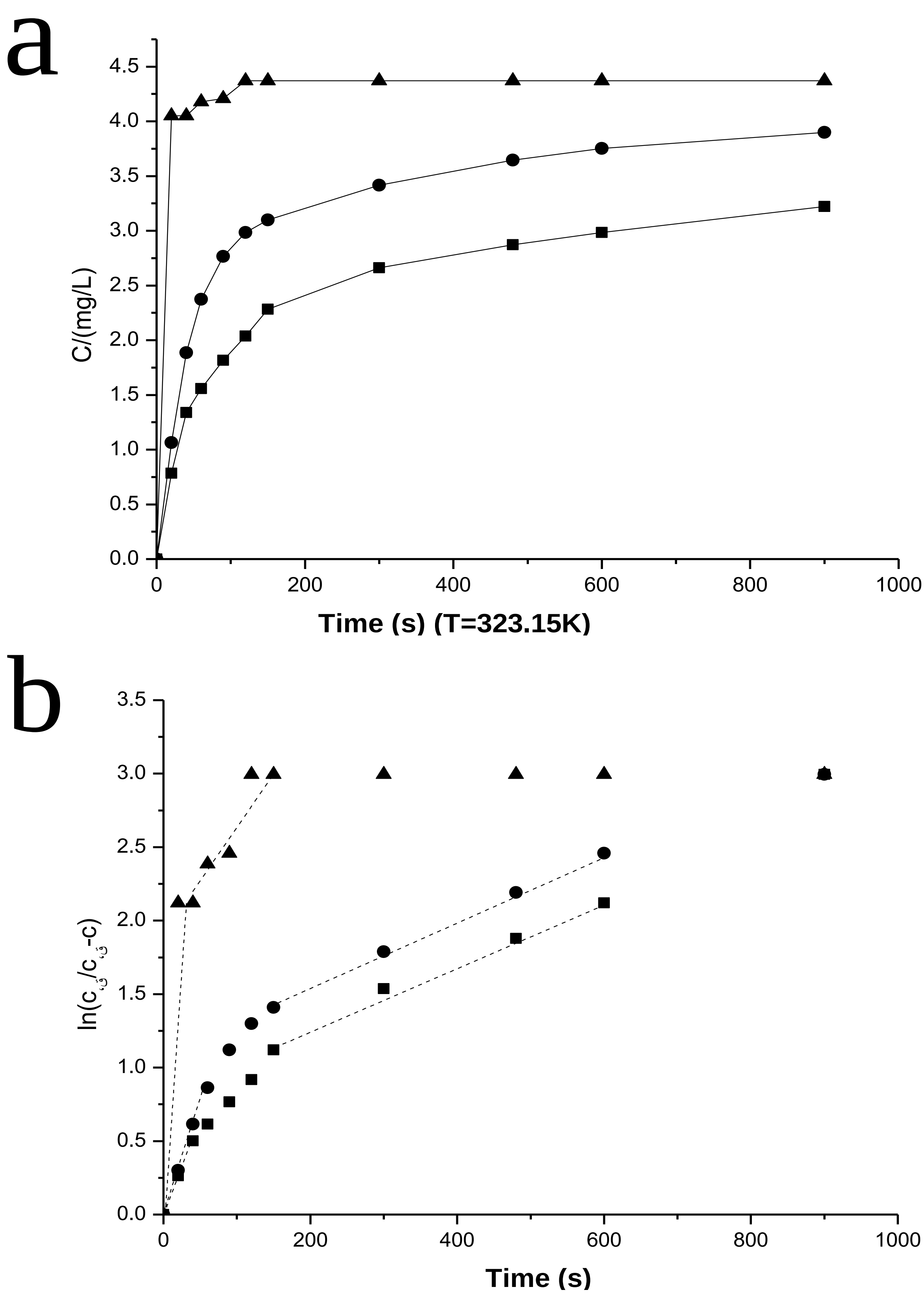

Figure 1. Kinetics of F extraction at 50°C. a: Changes in F concentration with extraction time; b: Functional relationship of $\ln[c_\infty/(c_\infty\text{-}c)]$ with time. Particle mean size: ▲, 0.113 mm; ●, 0.160 mm; ■, 0.380 mm.

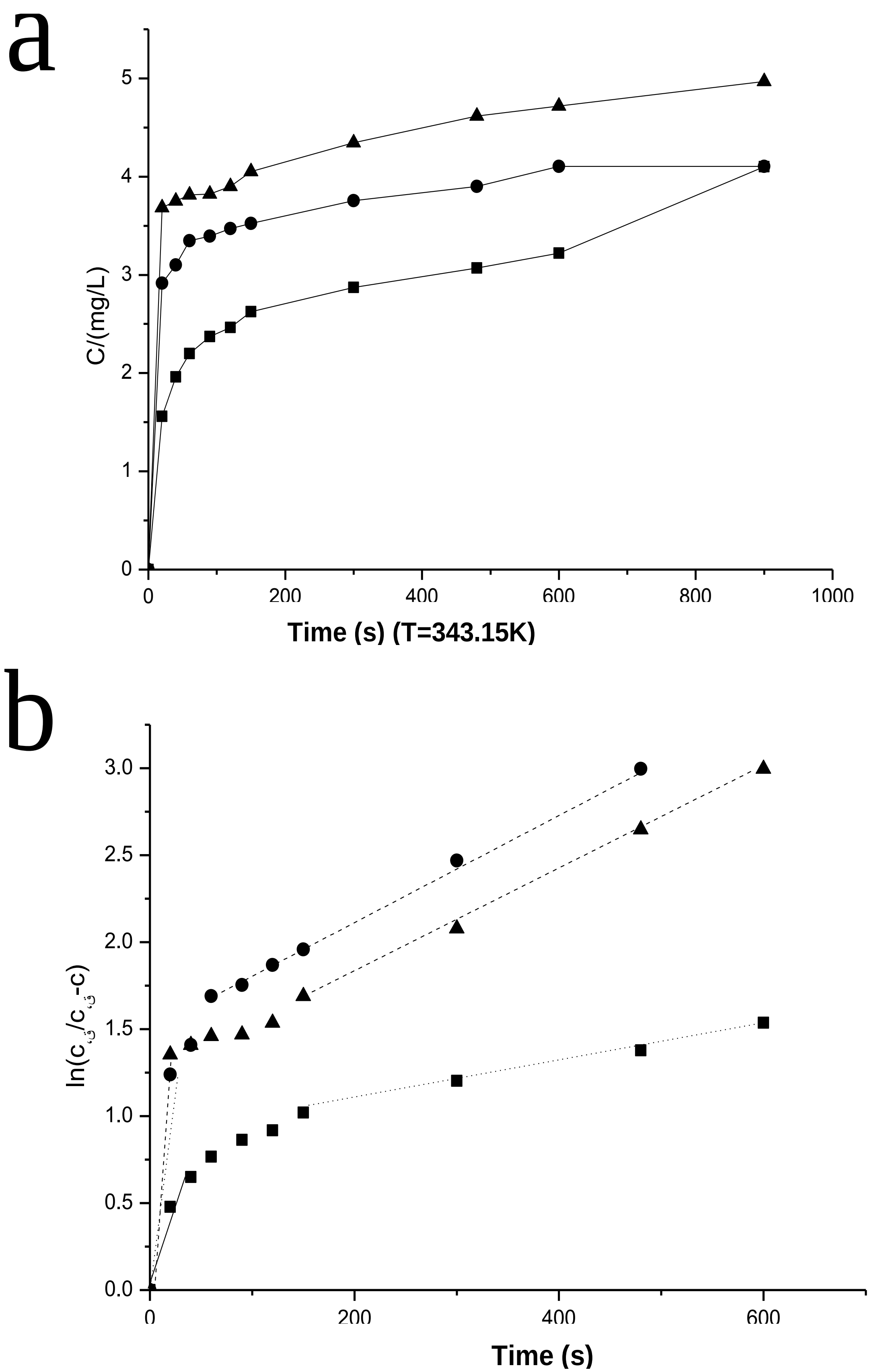

Figure 2. Kinetics of F extraction at 70°C. a: Changes in F concentration with extraction time; b: Functional relationship of $\ln[c_\infty/(c_\infty - c)]$ with time. Particle mean size: ▲, 0.113 mm; ●, 0.160 mm; ■, 0.380 mm.

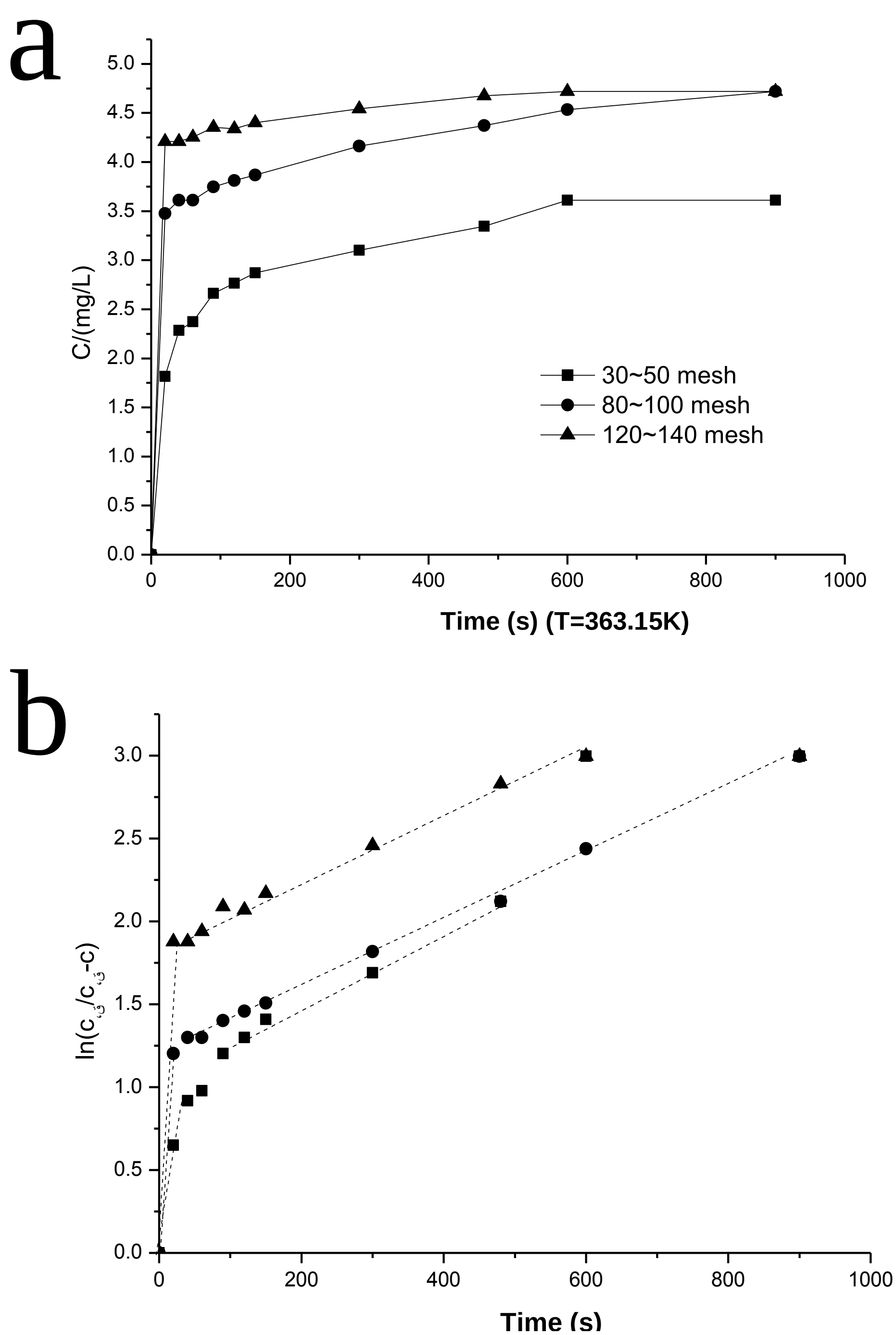

Figure 3. Kinetics of F extraction at 90°C. (a) Changes in F concentration with extraction time; (b) Functional relationship of $\ln[c_\infty/(c_\infty-c)]$ with time. Particle mean size: ▲, 0.113 mm; ●, 0.160 mm; ■, 0.380 mm.

Table 1. Diffusion coefficients.

Mean particle size (mm)	D_1 ($cm^{-2}\ s^{-1}$)			D_2 ($cm^{-2}\ s^{-1}$)		
	50°C	**70°C**	**90°C**	**50°C**	**70°C**	**90°C**
0.380	7.77×10^{-7}	2.58×10^{-6}	3.22×10^{-6}	3.58×10^{-7}	1.64×10^{-7}	3.25×10^{-7}
0.160	4.42×10^{-7}	1.42×10^{-6}	1.65×10^{-6}	5.47×10^{-8}	8.27×10^{-8}	5.19×10^{-8}
0.113	8.22×10^{-7}	5.56×10^{-7}	9.35×10^{-7}	7.06×10^{-8}	3.76×10^{-8}	2.51×10^{-8}

Table 2. Effect of two-step infusion on F concentration of tea liquors (mg L^{-1})[1].

Tea sample	First infusion	Second infusion	Total
Green tea bag	0.25±0.01 (26.32%)	0.70±0.06 73.68%)	0.95±0.08
First grade	0.19±0.01 (26.76%)	0.52±0.03 (73.24%)	0.71±0.04
Fourth grade	0.18±0.00 (29.51%)	0.43±0.01 (70.49%)	0.61±0.01

[1]: Data in the brackets are the percentage among total F extracted in the sample.

Table 3. Effect of two-step infusion on chemical composition of tea liquors (mg L^{-1}).

Sample	Infusion	GC	EGC	C	EC	EGCG	GCG	ECG	CG	Total catechins	Caffeine	Total catechins (%)	Total caffeine (%)
Green tea bag	1st infusion	0.01±0.00	0.13±0.01	0.01±0.00	0.02±0.00	0.16±0.02	Trace	0.03±0.01	Trace	0.36±0.03	0.08±0.01	15.53	15.01
	2nd infusion	0.05±0.00	0.54±0.01	0.03±0.00	0.10±0.00	1.04±0.01	Trace	0.17±0.01	Trace	1.93±0.02	0.45±0.02	84.46	84.99
First grade	1st infusion	0.01±0.00	0.10±0.01	0.01±0.00	0.02±0.00	0.13±0.00	Trace	0.02±0.00	Trace	0.29±0.02	0.07±0.01	16.73	14.94
	2nd infusion	0.04±0.00	0.4±0.01	0.02±0.00	0.08±0.00	0.76±0.01	0.02±0.01	0.13±0.00	Trace	1.44±0.08	0.37±0.02	83.27	85.06
Fourth grade	1st infusion	0.01±0.00	0.10±0.00	0.01±0.00	0.02±0.00	0.13±0.01	Trace	0.02±0.00	Trace	0.29±0.02	0.06±0.01	19.64	17.11
	2nd infusion	0.03±0.00	0.33±0.01	0.02±0.00	0.06±0.00	0.62±0.01	0.01±0.00	0.10±0.01	0.01±0.00	1.17±0.03	0.31±0.01	80.36	82.89

20 s at temperatures 50, 70 and 90°C, respectively (Figures 1 to 3). It can be understood as temperature increases, the kinetic energy of the particles increases, resulting in an increase in the speed of solute molecules and the rate of diffusion. As the size of the particle increases, the diffusion path increases which in turn leads to a longer diffusion time.

However, it is observed that there was no significant difference in the duration of the fast stage 1 for tea sample with the smallest particle size (0.113 mm) between the three tested temperatures (Figures 1 to 3), suggesting that particle size is a more important factor influencing the diffusion rate of F than temperature. Gao et al. (2009) reported that extraction temperature and extraction time were important factors affecting F extractability from tea leaf. When tea leaf was extracted at temperatures ranging from 70 to 100°C, the extracted F was linearly correlated to extraction temperature from 70 to 85°C and then increased slowly from 85 to 100°C. If the tea was extracted using boiling water, the amount of extracted F increased with time from 5 to 23 min, and then stabilized. Luo et al. (2002) showed that F extractability of brick tea was affected by the ratio of tea to water and less F was extracted at a higher ratio of tea to water. There has no report on the F extraction from tea at low temperature as 50°C.

Effect of two-step infusion on chemical composition of tea liquors

When the tea sample was infused in 50°C water for 20 s and then the residue leaf was infused in boiling water for 5 min, more than 26% of total fluorine was removed during first infusion in the three kinds of teas (Table 2), resulting in a lower F level in the second infusions. Table 3 shows that more than 80% of catechins and caffeine of the teas remained in the second infusions. These results suggested that the removal of fluorine was more than the removal of catechins and caffeine during the first infusion. An excessive intake of fluorine is harmful to health. The recommended concentration of fluorine in drinking water is 1.5 mg L^{-1} (WHO, 2004) and acceptable fluorine concentrations are between 0.5 and 1.5 mg L^{-1} (Hichour et al., 1999; Mohan et al., 2012). On January 7, 2011, the U.S. Department of Health and Human Services Agency (HHS) announced a proposal recommending that water systems practicing fluoridation adjust their fluoride content to 0.7 mg L^{-1}, as opposed to the previous temperature-dependent optimal levels ranging from 0.7 to 1.2 mg L^{-1} (HHS, 2011). Its purpose is based on the reason that the proposed concentration provides a better balance of protection from dental caries while limiting the risk of dental fluorosis. It was reported that the risk of dental fluorosis at 1 mg L^{-1} fluoride in drinking water was extremely low, particularly in relation to the impact of fluoride on dental caries, but when the level of fluoride is above 1.5 mg L^{-1} in drinking water, dental fluorosis can occur (DenBesten and Li, 2011). Though total fluorine concentration in samples of green tea bag and first grade green tea were above 0.70 mg L^{-1}, the tea liquors of second infusions prepared by the two-step infusion method had fluorine level 0.70 mg L^{-1} or less (Table 3). It is considered that the two-step infusion method is an alternative to control excessive fluorine exposure for tea drinkers.

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