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Time-dependent extraction kinetics of infused components of different Indian black tea types using UV spectroscopy

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Abstract: Time-dependent aqueous extraction of six tea types was carried out with leaf–water–ratio of 0.5 g/100 ml, temperature of extraction 90°C and time of extraction ranging from 1 to 10 min. UV–vis spectroscopic analysis in the range varying from 220 to 900 nm of the aqueous tea extracts showed a prominent peak at 273 nm in the ultraviolet region which can be associated with n → π* electronic transition of caffeine molecules. Parabolic diffusion, Power law, hyperbolic, Weibull’s and Elovich’s models were fitted to represent the aqueous soluble component extraction behaviour for time-dependent extraction of aqueous extractables. Parabolic diffusion model, Power law and Elovich’s model were a close fit to the experimental data for all the selected tea types with correlation coefficients (R²) ranging 0.8029–0.9953, whereas hyperbolic and Weibull’s models showed poor fitness to represent the extraction behaviour of fanning and AO leaf, LD, fanning and dust, respectively, with R² < 0.8, for time-dependent aqueous soluble component extraction.

Subjects: Environment & Agriculture; Food Science & Technology; Mathematics & Statistics

Keywords: parabolic diffusion model; power law model; hyperbolic model; Weibull’s model; Elovich’s model

1. Introduction

Tea is a non-alcoholic beverage consisting of infusions of the processed and dried leaves of the tea plant, *Camellia sinensis* (L). It is prepared from the young, tender leaves of tea plant which undergo
different unit operations to give various types of teas as black, green and oolong depending on the extent of fermentation. The distribution of bioactive components, especially polyphenols, varies in differently fermented teas, with green tea having the highest concentration of polyphenols such as catechins and black tea having the highest concentration of oxidized polyphenols such as theaflavins and thearubigins. The tea polyphenols and presence of other volatile and non volatile components are responsible for its various health benefits (Ahmad et al., 2013, 2014; Ahmad, Baba, Gani, et al., 2015; Ahmad, Baba, Wani, et al., 2015; Shah et al., 2015). The tea preparation methods (e.g. leaf to water ratio (LWR), duration of infusion, temperature of extraction/infusion and amount of agitation used) vary worldwide among countries and among individuals within countries as revealed by worldwide consumer observations and questionnaire studies. In Western countries, black tea is drunk which is made by infusing tea leaves with or without a bag in boiling water in a pot or in a cup. It is infused for less than 3 min and the beverage is consumed hot, either with or without added milk and/or sugar. In the Indian sub-continent and some Middle Eastern countries, the tea beverage is prepared by boiling black tea leaves in a pan for several minutes prior to consumption together with water, milk and sugar. The varied product and preparation differences on the in-cup composition of tea infusion are of importance because the quality and health properties of the tea beverage are associated with the chemical components extracted from the leaf during brewing. A number of epidemiological and intervention studies have revealed a relationship between tea consumption and reduced risk of cardiovascular disease and cancer (Astill, Birch, Dacombe, Humphrey, & Martin, 2001). Some of the factors affecting the rate of infusion of tea solubles into aqueous solution have been widely studied. Natarajan et al. (1962) studied the influence of different variables such as nature of raw material, the purity and temperature of the water, the infusion time and the water-to-leaf ratio on the brewing behaviour of tea. The rate of extraction of the soluble constituents has been found to increase with decreased particle size, increased brewing temperature and increased water-to-leaf ratio. Spiro and Siddique (1981) and Spiro and Jago (1982) used simple kinetic models to explain the observed rates of extraction of individual tea constituents into aqueous solution. The extracted tea constituents were measured as a function of time, when tea is infused in water at a constant elevated temperature. The concentration of tea soluble was found to increase in the liquor with increase in brew time. The rate of increase in concentration of tea soluble with increased brewing time gradually falls off to equilibrium. The diffusion of the solute through the leaf matrix to the surface was determined to be the rate-determining step in the loose leaf infusion. Price and Spiro (1985) reported the effect of leaf size, origin and manufacture on the rate of infusion of caffeine and theaflavin. With decreased leaf size rate constants increased. Spiro, Jaganyi, and Broom (1992) and Price and Spitzer (1994) compared the rates of caffeine infusion from green and black teas and found that the rate of infusion of caffeine was greater from green tea than from a similarly sized black tea, confirming a possible effect of manufacturing method upon infusion characteristics.

The refreshing and soothing properties of tea are due to the hundreds of bioactive compounds such as polyphenols and caffeine, which are water soluble and are readily transferred to the hot brew. Efficient brewing shall contribute to the maximum release of desirable components and lesser release of undesirables, complemented with an attractive colour. In the present study, the time-dependent aqueous extraction behaviour of different tea types has been observed using some solid–liquid extraction models.

2. Materials and methods

Three black tea types (Assam Orthodox Leaf Grade, Assam Orthodox FBOP Grade and Assam Orthodox Dust Grade) used in this study were procured from the Poobong Tea Co. Ltd. Assam, India. Other three samples (Lipton Darjeeling, red label and fannings) were procured from the local market of Sungrur, Punjab, India (Figure 1).

2.1. Parameters for aqueous extraction

Time-dependent aqueous extraction was carried out for the selected tea types with LWR of 0.5 g/100 ml, temperature of extraction as 90°C and extraction time ranging from 1 to 5 min and finally at 10 min interval.
2.2. **UV–vis spectral analysis of the aqueous tea extract**

UV–vis spectroscopic analysis in the range varying from 220 to 900 nm of the aqueous tea extracts showed a prominent peak at 273 nm in the ultraviolet region without any distinct peak in visible region (Figure 2). Based on these findings, the subsequent experimentations were concentrated in ultraviolet spectroscopic analysis. Available empirical kinetic models were used to describe the behaviour of time-dependent extraction of the aqueous extractable tea components in terms of extraction yield at 273 nm.

2.3. **Extraction models and model fitting**

Available empirical models representing the extraction kinetics of present process in case of tea component extraction are represented (Table 1). Fitting of these models and validation of extraction behaviour for active aqueous components of tea have been assessed. The considered models have also been used elsewhere in representing the extraction behaviour (Kitanović, Milenović, & Veljković, 2008; Cheung, Siu, & Wu, 2013).

2.4. **Adequacy and validation of model fitting**

The regression model adequacy was assessed using statistical parameters such as coefficient of multiple determinations ($R^2$) together with statistical significance indexes, $F$ and $p$ values (Peck & Devore, 2012).

3. **Results and discussion**

When electromagnetic radiation of the correct frequency is absorbed by a compound, an electron transition occurs from bonding molecular orbitals ($\sigma$ or $\pi$) or non-bonding orbitals ($n$) to antibonding
molecular orbitals ($\sigma^*$ or $\pi^*$) (Figure 3). UV–vis spectroscopic analysis of the aqueous tea extracts showed a prominent peak at 273 nm in the ultraviolet region. This region can be associated with $n \rightarrow \pi^*$ electronic transition of caffeine molecules. The absorption band around 275 nm is related to the C=O chromophore absorption of caffeine (Souto et al., 2010). This transition kinetics of aqueous extractables of tea is associated with electron excitation from loan-pair orbital localized on the oxygen to the $\pi^*$ orbital of the carbonyl group of caffeine (Swarbrick, 2006).

Figure 4 shows the change in the extraction yield (in terms of OD) with time for the six different tea types. In case of dust and fannings, a higher initial yield is observed which may be due to their finer particle size and an increased surface area which may enhance the extraction efficiency of water. AO Leaf and LD showed a comparatively lower initial yield than dust and fannings, which may be due to twisted and folded leaf structures which take some time to hydrate and allow water penetration. FBOP showed the lowest initial extraction yield, which may be due to its lowest bulk density compared to other types, which makes it float on the water surface until its leaves get hydrated and swollen.

Table 2 shows the coefficient of multiple linear regression fit of the experimental data to different kinetic models for the different tea types and the corresponding model parameters. Parabolic diffusion model showed good fitness to represent the extraction behaviour for all the selected tea types.
with $R^2$ ranging from 0.9277 to 0.9930. It characterizes a two-stage extraction process, an initial washing stage (to an initial yield $A_0$) followed by a slow stage (with yield increasing linearly with $t^{1/2}$). The tea suspended in water usually aggregated into soft and loose flocks which was more accessible to the water. Figure 5 shows the plot of extraction yield versus time for the selected tea types with parabolic diffusion model. The Power law also satisfactorily represented the extraction behaviour of the selected tea types with $R^2$ ranging from 0.9208 to 0.9923. This model is the most applicable for extraction of a substance from a non-swelling device (Sinclair & Peppas, 1984) with a diffusion exponent $n < 1$ for extraction of plant materials (Kitanović et al., 2008). As observed during the experiments, tea leaves/grains appeared well dispersed in water, suggesting a higher degree of dispersion in the aqueous phase.

Table 2. Correlation coefficients ($R^2$) and model constants for various kinetic models fitted by linear regression to the aqueous extraction experimental data (extraction yield $q$ vs. time)

| Model          | AO   | LD   | FBOP | RL   | FAN   | DUST  |
|----------------|------|------|------|------|-------|-------|
| Parabolic diffusion | $R^2$ | 0.9740 | 0.9930 | 0.9634 | 0.9462 | 0.9277 | 0.9300 |
| $A_0$          | 0.0092 | 0.0286 | $-$0.0828 | 0.0967 | 0.3174 | 0.4407 |
| $A_1$          | 0.3143 | 0.3057 | 0.3553 | 0.3057 | 0.2250 | 0.1911 |
| Power law      | $R^2$ | 0.9674 | 0.9923 | 0.9747 | 0.9670 | 0.9208 | 0.9969 |
| $B$            | 0.3310 | 0.3378 | 0.2708 | 0.3685 | 0.5275 | 0.6040 |
| $n$            | 0.4717 | 0.4744 | 0.5976 | 0.4767 | 0.2794 | 0.2344 |
| Hyperbolic     | $R^2$ | 0.8854 | 0.9421 | 0.9684 | 0.9953 | 0.7787 | 0.9185 |
| $C_2$          | 2.0592 | 1.9987 | 2.4492 | 1.7089 | 0.8958 | 0.7127 |
| $C_1$          | 0.5180 | 0.4956 | 0.3340 | 0.4686 | 1.1780 | 1.3850 |
| Weibull's      | $R^2$ | 0.7286 | 0.7461 | 0.8029 | 0.8155 | 0.7176 | 0.7517 |
| $D$            | $-$0.1967 | $-$0.2034 | $-$0.1537 | $-$0.2340 | $-$0.3872 | $-$0.4954 |
| $m$            | 1.6484 | 1.6506 | 1.8118 | 1.6723 | 1.4188 | 1.3582 |
| Elavich’s      | $R^2$ | 0.9181 | 0.9591 | 0.9493 | 0.9911 | 0.9040 | 0.9706 |
| $E_0$          | 0.2733 | 0.2859 | 0.2072 | 0.3356 | 0.5024 | 0.5905 |
| $E_1$          | 0.2883 | 0.2888 | 0.3332 | 0.2956 | 0.2099 | 0.1844 |
rigidity and similarity to a non-swelling device. Figure 6 shows the plot of extraction yield vs. time for the selected tea types with linearized Power law model. The hyperbolic model showed good fitness to represent the extraction behaviour of the selected tea types except fanning with $R^2$ ranging from 0.8854 to 0.9953. This model represents an extraction kinetic behaviour that is first order, with the yield increasing linearly with time in the initial stage and zero order in the very late stage, with the yield reaching maximum. All the tea types, except fannings, showed the same extraction behaviour, which shows a little deviation from this extraction behaviour (Figure 4). This deviated extraction behaviour of fannings makes hyperbolic model unsuitable for it with the $R^2$ of <0.8. Figure 7 shows the plot of extraction yield vs. time for the selected tea types except fanning with linearized

Figure 5. Plot of parabolic diffusion model for six selected tea types.

Figure 6. Plot of Power law model for six selected tea types.

Figure 7. Plot of hyperbolic model for five selected tea types.
The Weibull’s model could only represent the extraction behaviour of FBOP and RL with $R^2$ of 0.8029 and 0.8155, respectively, although this model is successfully applied in nuclide release from paraffin waste (Kitanović et al., 2008). Figure 8 shows the plot of extraction yield vs. time for FBOP and RL with linearized Weibull’s model. The Elovich’s model also showed good fitness to represent the extraction behaviour of all the selected tea types with large $R^2$ values ranging from 0.9040 to 0.9911. This model is a logarithmic relation fitted to the leaching curves and derived by

![Figure 8. Plot of Weibull’s model for two selected tea types.](image)

![Figure 9. Plot of Elovich’s model for six selected tea types.](image)

Table 3. Statistical significance indexes ($F$ and relative $p$-values) for the linear regression fit of various kinetic models to the aqueous component extraction of tea experimental data (corresponding to Table 2)

| Model       | Index | AO          | LD          | FBOP        | RL           | FAN           | DUST          |
|-------------|-------|-------------|-------------|-------------|--------------|----------------|----------------|
| Parabolic   | $F$   | 149.5518    | 570.108     | 105.1793    | 70.28942     | 51.29544       | 53.177         |
|             | $p$ value | 0.000257   | 1.82E-05    | 0.00051     | 0.001107     | 0.002012       | 0.00188        |
| Power law   | $F$   | 118.8559    | 518.6283    | 154.2254    | 117.1932     | 46.49162       | 127.3663       |
|             | $p$ value | 0.000402   | 2.2E-05     | 0.000242    | 0.000413     | 0.002419       | 0.000351       |
| Hyperbolic  | $F$   | 30.89165    | 65.09724    | 122.7656    | 846.6488     | 14.07321       | 45.07641       |
|             | $p$ value | 0.00013    | 0.001282    | 0.000377    | 8.3E-06      | 0.019922       | 0.002562       |
| Weibull’s   | $F$   | 10.7385     | 11.75341    | 16.29146    | 17.67465     | 10.16361       | 12.10717       |
|             | $p$ value | 0.030588   | 0.026576    | 0.015652    | 0.01365      | 0.033278       | 0.025363       |
| Elovich’s   | $F$   | 44.83496    | 93.77892    | 74.86142    | 446.6156     | 37.65551       | 131.9459       |
|             | $p$ value | 0.002588   | 0.000636    | 0.000982    | 2.96E-05     | 0.003575       | 0.000328       |
assuming that leaching rate decreases exponentially with increasing extraction yield. Figure 9 shows the plot of extraction yield vs. time for the selected tea types with Elovich’s model. A kinetic model showing a close fit to the experimental data with a large coefficient of multiple regression ($R^2$) value also had a large $F$ and small $p$ value from regression, indicating the statistical significance of the model fit (Tables 2 and 3).

4. Conclusion
The absorption peak observed at 273 nm of the tea extracts owes to $n \rightarrow \pi^*$ electronic transition of caffeine molecules. Extraction behaviour as represented through parabolic diffusion model, Power law and Elovich’s models was a close fit to the experimental data for all the selected tea types except for hyperbolic and Weibull’s models which showed poor fit to represent the extraction behaviour of fanning and AO leaf, LD, fanning and dust, respectively.

Nomenclature

| Term       | Definition                                                                 |
|------------|-----------------------------------------------------------------------------|
| AO leaf    | Assam orthodox leaf grade                                                  |
| LD         | Lipton Darjeeling                                                           |
| FAN        | fannings                                                                    |
| FBOP       | flowery broken orange pekoe                                                  |
| RL         | red label                                                                   |
| $\bar{q}$  | extraction yield (=absorbance of extractable substances extracted at 273 nm/absorbance of maximum extractables extracted at 273 nm) |
| $A_0$      | initial yield                                                               |
| $A_1$      | diffusion coefficient                                                       |
| $B$        | rate constant                                                                |
| $n$        | diffusion exponent (kinetic order)                                           |
| $C_1$      | extraction rate at the very beginning (min$^{-1}$)                           |
| $C_2$      | constant related to maximum extraction yield (capacity constant)            |
| $D$        | scale parameter of the Weibull equation (min m)                             |
| $m$        | shape factor of the Weibull equation                                         |
| $E_0$      | initial yield                                                               |
| $E_1$      | initial extraction rate                                                     |
| UV         | ultraviolet                                                                 |

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