

## Decaffeination of coffee bean waste by solid-liquid extraction

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**Abstract**—Many residues of plants are hydrolyzed to prepare polysaccharides and monosaccharide by bio-methods. Coffee bean waste is emerging as a new feed for producing these carbohydrates, but the appearance of caffeine in coffee bean waste prevents the enzymatic or bacterial hydrolysis. In this case, several solvents were used to remove the caffeine from the coffee waste as well as optimizing the conditions. Ethanol/water (50/50, v/v) at 80 °C was found to be the best condition for caffeine removal.

Key words: Caffeine, Coffee Waste, Solid-liquid Extraction

### INTRODUCTION

Coffee waste is emerging as a new feed for producing polysaccharides and monosaccharide by enzymatic or bacterial hydrolysis. Although the caffeine in coffee waste is lower than that in coffee beans, a large amount of caffeine still remains. Caffeine is a kind of xanthine alkaloid which can be found in various plants, such as coffee, tea and cacao. It is a central nervous system and metabolic stimulant [1], and used medically to reduce physical fatigue and restore mental alertness. The toxic [2] and anti-bacterial [3] properties of caffeine are harmful for some animals and bacteria. In this case, the caffeine should be removed before the enzymatic or bacterial hydrolysis of coffee waste.

Extraction of caffeine from coffee or tea, to produce decaffeinated products, is an important industrial process that can be done by a number of methods, such as solid-liquid [4,5] and supercritical carbon dioxide extraction [6]. For the reason of cost, solid-liquid extraction has been preferred. Solid-liquid extraction allows soluble components to be removed from solids using solvents. Insoluble material can be separated by gravity or vacuum filtration. A sequence of solvents, of varied polarity, can be used to separate complex mixtures into groups. Chloroform, trichloroethylene and dichloromethane have been used as the solvents for decaffeination over the years [7,8], but for reasons of safety, environmental impact and flavor, they have been superseded by others.

By previous considerations, the aim of this study was to find the best condition to remove caffeine from coffee waste. Different solvents were used to extract the residue of coffee with different time and temperature. Dipping, heating and ultrasonic methods were also involved. After optimizing the solvents and methods, the solid/liquid ratio was investigated.

### MATERIALS AND METHODS

#### 1. Materials

Caffeine was purchased from Sigma (St. Louis, MO, USA). Meth-

anol, ethanol, acetonitrile, n-hexane and dichloromethane were obtained from Pure Chemical Co., Ltd. (Ansan, Korea). Distilled water was filtered using a vacuum pump (Division of Millipore, Waters, USA) and a filter (HA-0.45, Division of Millipore, Waters, USA) before use. All other solvents used in the experiment were HPLC or analytical grade. All the samples were filtered by using a filter (MFS-25, 0.2 µm TF, WHATMAN, U.S.A.) before injection into the HPLC system.

#### 2. HPLC Analysis

The HPLC system is comprised of an M930 solvent delivery pump (Young Lin Co. Korea), UV detector (M 720 Absorbance Detector, Young-In Scientific Co., Korea) and integrated data system (Autochromin. Ver. 1.42, Young Lin Co., Korea). Injection valves with 20 µL sample loops were used. The HPLC analysis was performed with a commercial C<sub>18</sub> column (4.6×150 mm, 5 µm) purchased from RStech Co. (Daejeon, Korea). The mobile phase was methanol/water (30/70, v/v) [9]. The flow-rate was set at 0.5 mL/min, the UV wavelength at 274 nm, and the injection volume at 5 µL.

#### 3. Extraction of Caffeine from Coffee Bean Waste

The stock standard solution was prepared by transferring approximately 1 mg of caffeine standard accurately weighed to a 5 mL volumetric flask, and adding about 1mL of methanol to the flask. The standard stock solution was stored and further diluted to different working standard solutions at 4 °C in a refrigerator in darkness.

The coffee bean waste was oven dried, sliced, and crushed into powder for the extraction experiments. Selection of a solvent affects the efficiency of extraction. Water, methanol, ethanol, acetonitrile, n-hexane and dichloromethane were selected as extraction solvents. Different methods of extraction were also investigated, such as dipping, heating and ultrasonic extraction methods.

To obtain the total concentration of caffeine in coffee bean waste, the feed was extracted several times with optimal condition until no caffeine was detected by HPLC. The sum of extracted amount of caffeine in each extract was assigned as the total concentration of caffeine in coffee bean waste.

### RESULTS AND DISCUSSION

The factors that may influence the extraction were investigated,

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**Table 1. The factors that influence the decaffeination of coffee bean waste**

Variables	Range
Solvent	Water, Methanol, Ethanol, Acetonitrile, n-Hexane, Dichloromethane
Methods	Dipping, heating, ultrasonic
Time (min)	30, 60, 180, 360
Temperature (°C)	20, 40, 60, 80
Solvent/water ratio (v/v)	0/100, 25/75, 50/50, 75/25, 100/0
Solid/solvent ratio (g/mL)	1 : 5, 1 : 10, 1 : 20, 1 : 40, 1 : 60

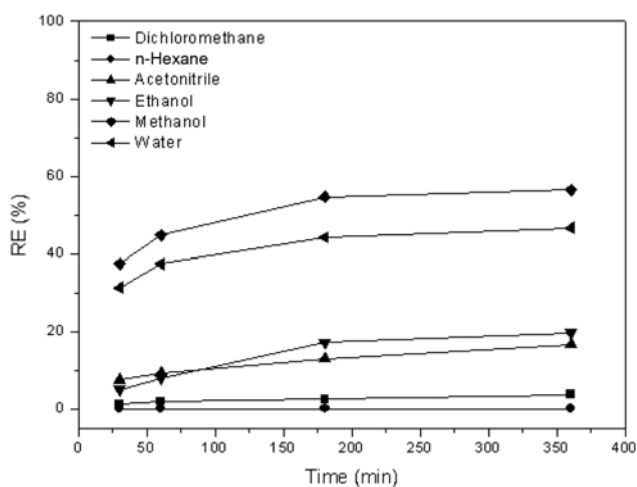
such as different solvents, temperature, methods of extraction and solid/liquid ratio and so on (Table 1). The removal efficiency of caffeine (RE) is calculated by the following equation:

$$RE(\%) = \frac{A}{A_0} \times 100$$

Where, A (mg/mL) is the concentration of caffeine in extraction solution,  $A_0$  (mg/mL) is the total concentration of caffeine in coffee bean waste. The experimental results were as follows.

### 1. Effect of Different Solvents

The effect of solvents was investigated by using water, methanol, ethanol, acetonitrile, n-hexane and dichloromethane. 20.0 mL of solvent was used to extract 1.0 g coffee bean waste during a period

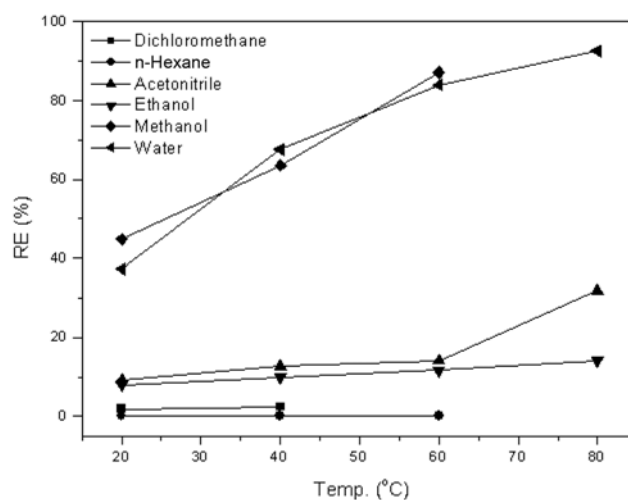


**Fig. 1. Effect of different extraction solvents on decaffeination with different times (temp.=20 °C, solid/solvent ratio=1/20 (g/mL)).**

of 30-360 min under room temperature. Fig. 1 shows that the caffeine in coffee bean waste could be efficiently extracted by polar solvents and the highest RE was obtained with methanol. And there was no obvious increase of RE after 180 min.

### 2. Effect of Different Extraction Methods

The different extraction methods such as dipping extraction and ultrasonic extraction were investigated by extracting 1.0 g of coffee bean waste extracted with 20.0 mL of solvents. In dipping and ultrasonic extraction, the powder was mixed with the solvent for different times. In Table 2, it is seen that the RE increased with the time increasing. Comparing the results of the two methods, it was found that the RE via the ultrasonic method was higher. However, different from the dipping method, water showed a higher RE than



**Fig. 2. Effect of different extraction temperatures on the decaffeination (time=60 min, solid/solvent ratio=1/20 (g/mL)).**

**Table 2. Effects of different extraction methods (temp.=20 °C, solid/solvent ratio=1/20 (g/mL))**

Solvent	RE (%)					
	Dipping			Ultrasonic		
	30 min	60 min	180 min	30 min	60 min	180 min
Water	31.3	37.4	44.2	69.9	85.3	86.5
Methanol	37.4	44.8	54.6	58.9	71.2	79.1
Ethanol	4.9	8.0	17.2	11.7	14.7	25.8
Acetonitrile	7.4	9.2	12.9	14.1	16.0	44.8
n-Hexane	0.0	0.0	0.0	0.0	0.0	0.0
Dichloromethane	1.2	1.8	2.5	1.8	3.1	3.7

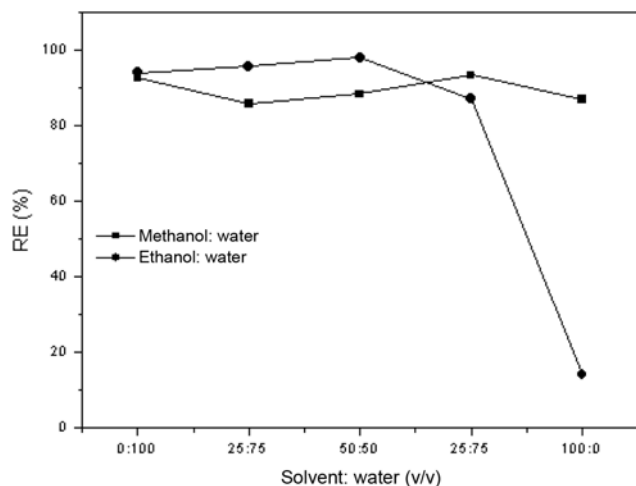


Fig. 3. The effect of organic solvent concentration in water on the decaffeination (time=60 min, solid/solvent ratio=1/20 (g/mL), temp.=80 °C).

that of methanol in ultrasonic extraction.

### 3. Effect of Extraction Temperature

Different dipping temperatures ranging from 20 °C to 80 °C were evaluated while the dipping time was fixed at 60 min. The results are shown in Fig. 2. The RE increased with an increase of temperature increasing from 20 °C to 80 °C. Comparing the results with those obtained via the dipping method, the RE from coffee bean waste via 60 min dipping and ultrasonic under room temperature were lower than those for 60 min dipping under 80 °C. Heating was found to be an efficient method for extraction of caffeine.

### 4. Effect of Component of Extraction Solution

Water was mixed with methanol and ethanol under 80 °C, respectively, to investigate the effect of the component of extraction solution. The results are shown in Fig. 3. The concentrations of extracted caffeine in coffee bean waste were greatly influenced by the organic solvents concentration in water. The concentration of caffeine increased with increasing organic solvent concentration firstly. Then the concentration of caffeine decreased with further increase in organic solvent concentration. The reason may be related to solvent polarity and the solubility of caffeine. The polarities of water and methanol are similar, so the mixture of water/methanol cannot adjust the polarity effectively. In comparison with the polarities of water and methanol, the polarity of ethanol is much lower than water and methanol. In this case, adjustment of the ratio of ethanol/water can obtain the suitable polarity for extraction of caffeine. Comparing the efficient of the mixed solution and different solvents, 50% ethanol concentration in water was used in the following experiments.

The decaffeination of coffee bean waste at room temperature by 50% ethanol was also investigated. In Fig. 4, the RE increased with the time increasing. The equilibrium concentration was arrived at after 24 h extraction. It shows an economic method to remove caffeine from coffee bean waste.

### 5. Effect of Solid/Solvent Ratio

Fig. 5 shows that the extraction of caffeine increased with increasing solid/solvent ratio. When the solid/solvent ratio increased from 1 : 5 to 1 : 60 (g/mL), the RE increased. It is obvious that the solid/solvent ratio is useful for improving extraction yields. The dissolu-

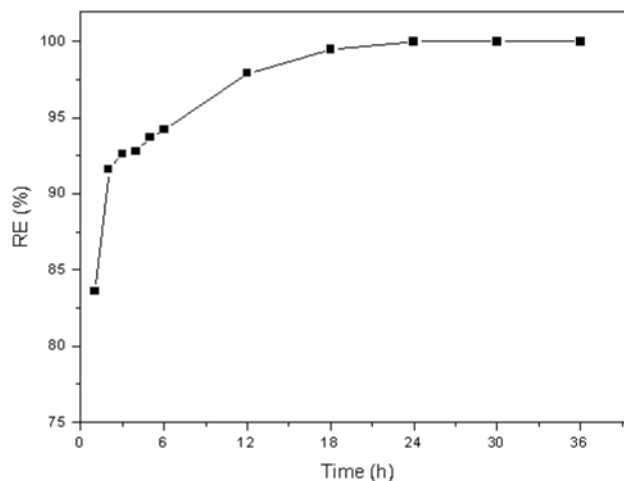


Fig. 4. Decaffeination of coffee bean waste at room temperature by 50% ethanol (solid/solvent ratio=1/20 (g/mL)).

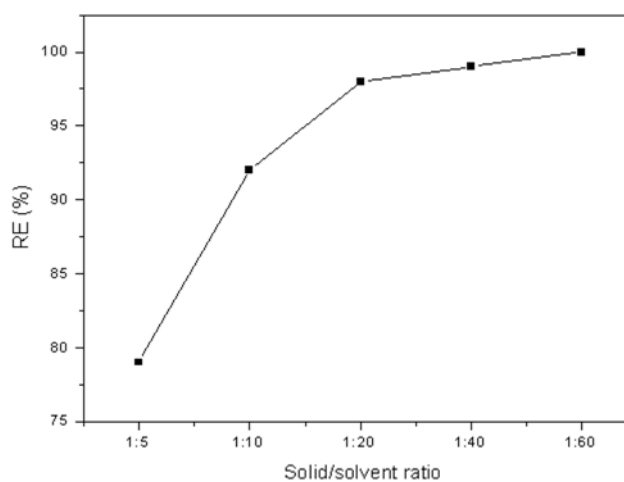
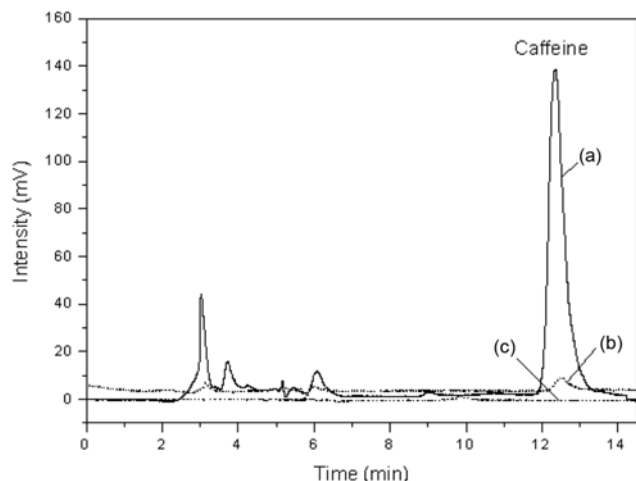


Fig. 5. The effect of solid/solvent ratio on the decaffeination (ethanol/water=50/50 (v/v); temp.: 80 °C; time: 60 min).

tion of bioactive components into the solvent is a physical process. When the amount of solvent increases, the chance of bioactive components coming into contact with the solvent goes up, which leads to higher leaching-out rates. The solid/solvent ratio of 1 : 20 (g/mL) was sufficient to reach the high extraction efficiency.

### 6. Determination of Caffeine by HPLC

The decaffeination of coffee bean waste was dipping under 80 °C with a solid/solvent (g/mL) ratio of 1 : 20 for 60 min. After filtration, the residue of coffee bean waste was extracted twice at the same condition. The chromatograms of these three extraction solution are shown in Fig. 6. Most of the caffeine in coffee bean waste was removed at the first time extraction and RE was 98%. The total extracted amount of caffeine after three extractions was 3.26 mg/g. A calibration curve was constructed using the areas of the chromatographic peaks measured at seven increasing concentrations, ranging from  $2 \times 10^{-3}$  to 0.2 mg/mL. The measurement at each concentration point was repeated three times and good linearity was obtained throughout the concentration range. The linear correlation equation was  $y=69182.14x-219.5$  ( $r^2=0.98$ ) for caffeine.



**Fig. 6.** Chromatogram of extraction solution of caffeine from coffee bean waste (ethanol/water=50/50 (v/v); solid/solvent ratio=1/20 (g/mL); temp.: 80 °C; time: 60 min). (a) first time extraction, (b) second time extraction, (c) third time extraction.

### CONCLUSIONS

Solid/liquid extraction is a convenient method used to remove caffeine from coffee bean waste. By investigation of the extraction

method, solvent, temperature and solid/solvent ratio, the use of water/ethanol (50/50, v/v) with a solid/solvent ratio of 1 : 20 (g/mL) and an extraction time of 60 min under a temperature of 80 °C is the optimum condition for the decaffeination of coffee bean waste. The total extracted amount of caffeine was 3.26 mg/g. The method of extraction can be applied as a highly efficient, shorter extraction time method for caffeine removal. Instead of 80 °C in optimal condition, the use of room temperature is a low energy consumption extraction method for decaffeination.

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