Comparative Studies on decaffeination of tea and coffee with various solvents

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***Abstract* - The daunting mission of researchers to develop the best methods for decaffeination resulted in hundreds of patents to decaffeinate coffee. Today, mainly the traditional chemical process is used for decaffeination because it does a good job in maintaining the flavor profile of the beans. In present work, a comparative study has been done using the traditional chemical process that is the solid liquid extraction with various extracting solvents. As concluded by the FDA in 1987, caffeine consumption includes risks of cancer, coronary heart disease, osteoporosis, reproductive function, birth defects and behavior of children, therefore caffeine content reduction is essential. The experiment has been performed using 'Wagh Bakri' tea and coffee beans with various extracting solvents at laboratory scale and amount of caffeine has been determined.**

Keywords: caffeine, decaffeination, extracting solvents, solid liquid extraction

I. INTRODUCTION

The status tea and coffee has is because of the active ingredients that make the tea and coffee valuable to humans– caffeine but the scenario is changing in today's world as decaf coffee and tea has become one of the growing segments in the market as the caffeine is converted into items that we enjoy in our everyday life-sodas, cosmetics and pharmaceutical products.

Caffeine is an alkaloid a class of naturally occurring compound containing nitrogen and having the properties of an organic amine base. It is a vasodilator as well as diuretic and is the most powerful xanthine in its ability to increase inertness, put off sleep and to increase ones capacity for thinking. In the midst of all these benefits from caffeine several health concerns have also been raised. Many consumers prefer to avoid coffee partially or altogether due to its stimulant effects and health concerns. The effect it has on health on a daily basis includes muscle pain, lack of concentration, headache, sleepiness, irritability, lethargy, constipation, depression, flu like symptoms, insomnia etc. Caffeine increases the release of acid in the stomach, cancer risk, coronary heart disease, osteoporosis, reproductive function, birth defects and behavior of children. For healthy adults with no medical issues, it is generally agreed upon that 300mg-400mg of caffeine can be consumed daily without any adverse effects.

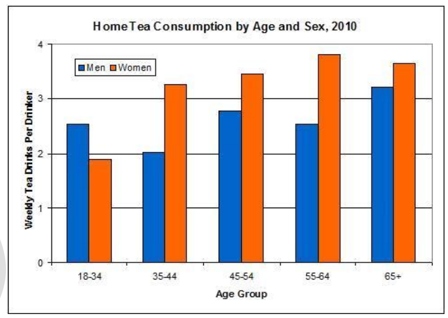

Figure 1: Home tea consumption by age and sex [1]

The decaffeination industry has evolved over the years. The world wide coffee market and the industry that supplies decaffeinated tea are Tetley, Tajmahal, Tulsi green tea (organic india), Lipton, Twinning's, Earl group, chai tea (celestial), Yorkshire tea , typhoo decaf etc. By far the most universal and ancient form of extraction is the brewing of tea or the making of coffee. Every pot of coffee or cup of tea involves solid-liquid extraction, the extraction of organic compounds from solid ground beans or leaves using hot water as the liquid. The lower molecular weight polar molecules such as caffeine dissolve in the hot water and are removed from the high molecular weight water-insoluble cellulose, protein, and lipid materials. Over 200 compounds, some in only trace quantities, are extracted from the solid into a cup of coffee or tea. Decaffeinated coffee is also an excellent example of solid-liquid extraction.

The most popular method of decaffeinating coffee today is Swiss water processing[2] , ethyl acetate processing, methylene chloride processing (direct and indirect method) and supercritical CO_2 processing. Most industries are using the supercritical CO_2 as the extracting solvent. CO_2 provides numerous advantages on one side and few disadvantages that include solubility in polar molecules; it complicates system thermodynamics and increases capital costs.

II. BACKGROUND

Caffeine, 1-3-7 trimethyl xanthine, belongs to a wide class of compounds known as alkaloids as shown in figure 2.The melting point of Caffeine is 238°C. Alkaloids are a diverse group of compounds that are found primarily in plants and contain basic nitrogen atom(s). The basic nature of these compounds makes them exists mostly as salts. Other well-known alkaloids include morphine, strychnine and nicotine, quinine, ephedrine.

Designing an efficient extraction scheme requires analyzing the major components of tea leaves. These include cellulose, proteins and amino acids, pigments and saponins and most important being tannins.

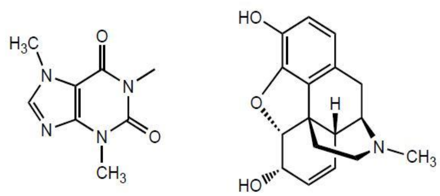

Figure 2: Chemical Structure of Caffeine

Tannins

Tannins are polyphenolic compounds (having OH on aromatic ring) with molecular weights of 50-20,000. Tea tannins are soluble in water and therefore extracted from the leaf and responsible for the typical bitter taste of tea. Tea tannins belong to a subgroup named hydrolysable tannins.

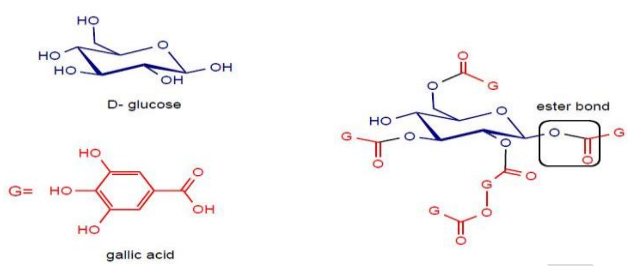

Figure 3: Structure of Tannin

III. Materials and Methods

The experiments have been performed using tea and coffee beans with various extracting solvents and amount of caffeine extracted have been determined. Choosing extraction conditions for isolation of a product from its natural source depend on both the properties of the compound and the composition of the source. Caffeine is soluble in both water and organic solvents. It is possible to extract caffeine from leaves or coffee beans by solid-liquid extraction to hot water.

We can maximize our efficiency by using a few simple techniques.

- Adding NaCl to the caffeine in water solution: The water will be more attracted to the very polar NaCl and less attracted to caffeine thus "salting out" the caffeine from water solution.
- Adding $Ca(OH)_2$ or $CaCO_3$ to a caffeine in water solution: This makes the solution basic so puts caffeine in its least polar form and so more readily solvated in organic solvents and less attracted to water. Basic $Ca(OH)_2$ reacts with tannic acids to form insoluble tannin salts which precipitate and so can be removed from the solution before the caffeine is extracted.

An emulsion is a suspension of tiny droplets of one solvent mixed in the other. Emulsions are common in extraction because proper mixing is essential. One method of removing is to add brine or salt solution into the mixture. If further difficulty is there some drying agent is put into the organic mixture to drain out all the water.

One another problem in liquid-liquid extraction is that no two solvents are completely immiscible with each other. After separating the two solvents, residual water will remain in the solvent or organic layer. This will remain and stick to the solid product when we remove the more volatile solvent. Therefore, chemists remove the water from the organic layer by adding an insoluble inorganic solid to the solution which will absorb the water, thus "drying" it.

The selectivity of various solvents is done on the basis of solubility of caffeine in the solvents and after the extraction process the selectivity of the solvents is carried out to see which one is better and from which the crystal forms of pure caffeine can be obtained through reduced sublimation.

The organic extract will primarily contain caffeine with small amounts of impurities. This solution is washed with 10% NaOH to remove impurities. Caffeine is also water soluble, but by keeping the washing solution basic it minimizes the caffeine lost, while maximizing the removal of impurities. Extractions are most effective when repeated several times with small volumes of solvent rather than once with a large volume.

IV. Experimental Procedure

A. *Batch Run 1 for chloroform*

- 10 gm of tea (Wagh Bakri) is taken for the analysis. In it 4.8 gm of $CaCO_3$ is added so that the tannin can be removed after the filtering of the solution.
- 100 ml distilled water is added to make a solution and is heated for 15 min with continuous stirring.
- The tea solution is boiled because caffeine is more soluble in hot water. The temperature of solution is brought to 45 ^{0}C after heating and then is sent for vacuum filtration with the help of Buchner funnel and Whatmann filter paper and is cooled down to 18 ^{0}C with the help of ice chips.
- 250 ml separating funnel is taken and is washed with water and acetone. The 15 ml of extracting solvent is added to it and then the cooled and filtered tea is added.
- The caffeine is highly soluble in chloroform, Dicholromethylene and because of that the caffeine dissolves in it.
- The extraction process is repeated with fresh solvent

each time of 15 ml. the lowest layers from the separating funnel are collected.

Figure 4: Separate layers of aqueous and organic layers

- 25ml of 10%NaOH is taken and is put into the separating funnel with the extracts obtained to wash away the impurities present in the sample. The resulting solution will is yellowish green in color. After this drying agent anhydrous $MgSO_4$ is added so as to dry the extract obtained.

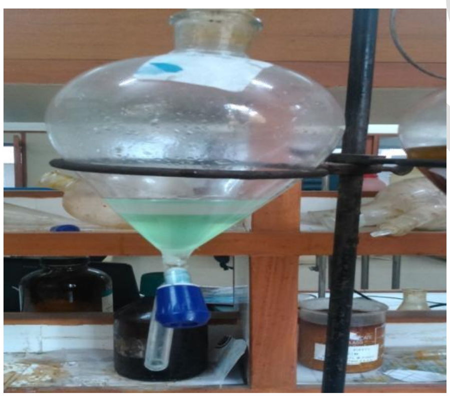

Figure 5: Extraction of caffeine by chloroform

B. Batch Run 2 for 1-Propanol

- 10 gm of tea (Wagh Bakri) is taken for the analysis. In it 26 gm of NaCl and 1gm of Na_2CO_3 is added so that the tannin can be removed after the filtering of the solution. 75 ml distilled water is added to make a solution and is heated for 15 min with continuous stirring.
- The tea solution is boiled because caffeine is more soluble in hot water. The temperature of solution is brought to 45^0C after heating and then is sent for vacuum filtration with the help of Buchner funnel and Whatmann filter paper and is cooled down to 18^0C with the help of ice chips.

Figure 6: Vacuum filtration

- 250 ml separating funnel is taken and is washed with water and acetone. The 15 ml of extracting solvent is added to it and then the cooled and filtered tea is added.
  The caffeine is highly soluble in 1-Propanol and because of that the caffeine dissolves in it.The extraction process is repeated with fresh solvent each time of 15 ml. the lowest layers from the separating funnel are collected and further.
- 25ml of 10%NaOH is taken and is put into the separating funnel with the extracts obtained to wash away the impurities present in the sample. After this drying agent anhydrous $MgSO_4$ is added so as to dry the extract obtained.

B. Batch Run 3 for Dichloromethane

- Coffee beans are taken and are soaked in water for about 10 hours as is done to make a strong cup of coffee.
- After 10 hours the water has soaked enough so around 20ml of coffee soaked water is taken in a separating funnel with 20ml of dichloromethane.
- The extraction procedure is repeated 3 times by taking fresh solvent each time. The combined extracts obtained are taken and are further analyzed.
- Water and dichloromethane is slightly soluble in each other. So, after separating the solvents, residual water will remain the organic layer.[4]
- Mainly anhydrous sodium sulfite is used for the removal of water from organic layer. Anhydrous sodium sulfite is an insoluble inorganic solid which will absorb water, thus drying it.
- The same procedure is repeated for various amount of solvent and a comparative study is done to check the variation in the amount of caffeine obtained on changing the volume of the extracting solvent.
- column cross-sectional area [m^3/m^2h]
- Easy operation and maintenance because no moving parts are involved
- For corrosive media are almost unlimited options for the material selection available, from stainless steel to high-alloyed metal, from polypropylene to

PTFE, technical ceramics or pure carbon.

- A simple operation also at high pressure or temperatures

V. Results and Discussion

The analysis of caffeine content was done using titration method and distribution coefficient is calculated for different solvents used. It is likely that some impurities were present in the extract, as it is likely that tea does contain some other compounds were eluted by the water and were soluble in the extracting solvent hence the variations in result are likely to occur.

$$K_d = \frac{\text{[Solubility of organic (g/100ml)}}{\text{[Solubility of water (g/100ml)]}}$$

Chloroform

Amount of caffeine in chloroform solvent=4.01mg

Amount of caffeine in water=70mg

Amount of solvent taken=15ml

Amount of distilled water taken=100ml
Using above equation, we get

Kd =0.3812

The constant K , is essentially the ratio of the concentrations of the solute in the two different phases once the system reaches equilibrium.

Table 1: Analysis of caffeine

S.No	**System**	**Caffeine Content (mg/L)**	**Kd**
1.	Tea + Chloroform	4.01	0.3819
2.	Tea + 1-Propanol	1.44	0.102
3.	Coffee Beans Dichloromethane	2.31	0.181

VI. Conclusion

The experiment of extraction was carried out successfully with the help of various extracting solvents in batch process and further an idea has been proposed about designing of a packed bed for continuous operation which will be carried out in the future. It is a comparative study where the distribution coefficients of the solvents are found out by proper analysis of caffeine content. The various factors essential for an extracting solvents have been mentioned and the criteria on the basis of which they are selected are explained. The analysis of batch experiments has been done and an attempt for designing of a semi-batch or a continuous type of column for extraction is proposed for 99.9% extraction of caffeine. The idea of a packed column for the adsorption of caffeine to get directly decaffeinated products has also been proposed. Perhaps in the future a substance will be developed with the positive effects of Caffeine, but without the addictive qualities or possible side effects of this substance.

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